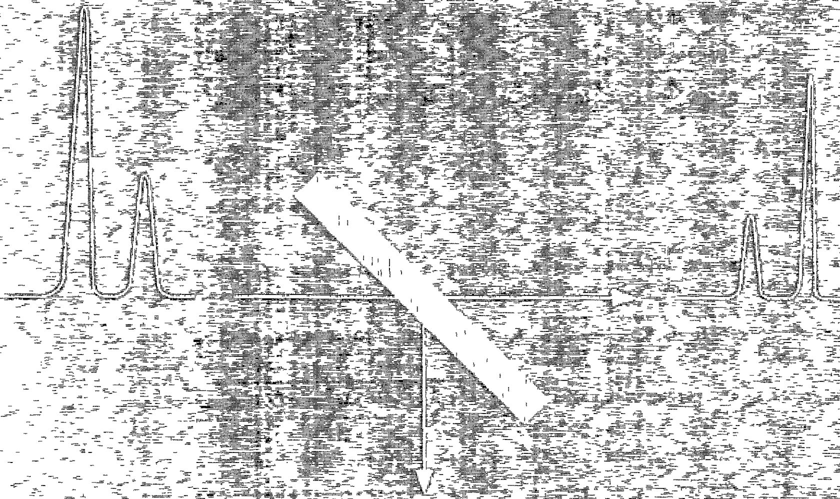
POLYOXADIAZOLE AND POLYTRIAZOLE GAS SEPARATION MEMBRANES

Synthesis and Properties



Edwin Hensema

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POLYOXADIAZOLE AND POLYTRIAZOLE GAS SEPARATION MEMBRANES

Synthesis and Properties

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
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Edwin René Hensema

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CONTENTS

Chapter 1 Gas separation using membranes An introduction

Chapter 2 Two reaction routes for the preparation of aromatic polyoxadiazoles and polytriazoles Syntheses and properties

Publications

Parts of chapter 1 have been published in:

- E.R. Hensema and C.A. Smolders, "Latest developments in membrane technology for gas and vapour separation", *in* E.F. Vansant and R. Dewolfs (Eds.) "Gas separation technology, Process Technology Proceedings 8", Elsevier, Amsterdam, 1988.

- E.R. Hensema, B. Gebben, M.H.V. Mulder and C.A. Smolders, Polyoxadiazoles and polytriazoles as new heat and solvent resistant membrane materials, Bull. Soc. Chim. Belg., Vol. 100 (2), 129-136, 1991.

- E.R. Hensema en C.A. Smolders, Gasscheiding met membranen (I) *en* (II), I^2-Procestechnologie, Vol. 7(5), 9-12 *en* 13-16, 1991.

Parts of chapters 2, 3, 4, and 5 have been published by means of various posters which have appeared in the issues 4 and 5 of the magazine "Membraantechnologie". The chapters will also be submitted for publication in various journals.

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Gas separation using membranes. An introduction.

E.R. Hensema, M.H.V. Mulder and C.A. Smolders

SUMMARY

Gas separation using membranes is utilised with increasing interest. This separation technology has distinct advantages over conventional separation technologies like ab- and adsorption processes and cryogenic distillation. The technology is relatively young and membrane systems are still being improved and they become more and more competitive in comparison with conventional techniques.

Present materials research is dedicated to the development of asymmetric and composite membranes with improved flux at sufficient selectivities, and to the development of "tailor-made" polymers as gas separation membrane materials. In this thesis two families of "tailor-made" polymers are studied in order to elucidate the relation between the macromolecular structure and the resulting physical properties on one hand and the gas separation properties on the other.

HISTORY

In 1830 Mitchell discovered that balloons of natural rubber filled with hydrogen gas which had ascended in his lecture room in the Philadelphia Medical Institute would descend after a period of time, varying from an hour to two days[1]. According to Mitchell there were a number of possibilities; either the gas reacted with the rubber, or it permeated through the dense wall of rubber balloon or the gas escaped at the ligature. To gain a better understanding he took a wide mouthed bottle and filled it with hydrogen gas. Over the aperture he had firmly tied a thin sheet of rubber, see figure 1. After a few hours the cover had sagged into the cavity of the bottle and finally the cover did burst. The rubber sheet had not gained any weight. The experiment was repeated under a glass bell-shaped jar holding atmospheric air. Mitchell found that the gas mixture under the bell-jar had become an explosive one, while the covered bottle only contained pure or nearly pure hydrogen.

Mitchell concluded that the permeation through the membrane, which was able to let the rubber cover burst, was caused by some inherent power of a considerable magnitude.

A year later Mitchell presented the rates of escape of ten gases from natural rubber balloons and showed that there was a range of a hundred-fold between carbon monoxide and ammonia. He also noticed that the rapidly permeating gases were absorbed by the rubber to a considerable amount[2].

In 1866 the Scotchman Graham reported on the transport of gases through natural rubber and he postulated a simple form of the solution/diffusion mechanism of transport[3]. He described the permeation of gases as a sequence of three steps; first the gas dissolves in the membrane, permeates through the membrane and desorbs at the other interface of the membrane. In the same article he demonstrated that oxygen enriched air will permeate into a vacuum evacuated rubber bag which is exposed to air. The permeate was sufficiently enriched to relight a glowing splint.

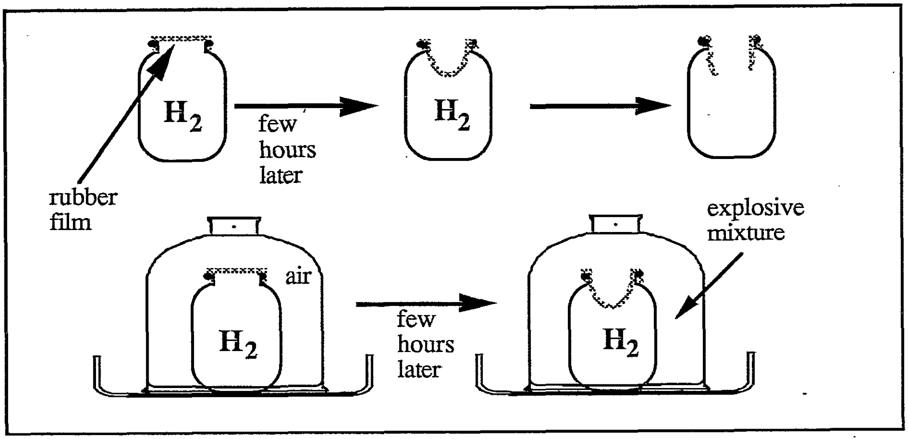

Fig. 1. Mitchell's permeation experiments.

In the early forties of this century gas separation with membranes was used to enrich uranium.

In 1960 Loeb and Sourirajan described the preparation of asymmetric phase inversion membranes with a very thin, dense, selective skin layer which is supported by a thicker highly-porous, non-selective layer of the same material. This meant for the development of gas separation membranes that membranes with a high selectivity *and* a high flux might become possible.

Then, two decades later, in 1979 Monsanto presented the Prism™ module system for the recovery of hydrogen from purge streams in the ammonia synthesis, making use of a plugged type of asymmetric membrane which shows some defects before coating.

During this last decade, both the number of companies supplying membrane systems for the separation of gas mixtures and the number of gas mixtures to be separated has increased because of the development and introduction of improved membranes. The interest in this "new" method of separating gases is still growing and the expectations for the future are high. Tomorrow's membrane systems will have higher fluxes and higher selectivities which makes gas separation by membranes more competitive towards the more mature now existing separation techniques.

Besides polymer membranes, ceramic membranes are more and more investigated because of their applicability in harsh environments. The reader is referred to the literature for detailed discussions on these membrane materials[4].

PRESENT MEMBRANE SYSTEMS AND THEIR APPLICATIONS

In the fall of 1979 Monsanto introduced the Prism™ system for the recovery of hydrogen from process streams in the ammonia synthesis. Due to the abrupt rise in energy costs in the 1970's the appeal for cryogenic, thermal and absorption methods decreased. Although energy prices have stabilised, cost reduction is still one of the driving forces behind the interest in membrane technology for gas separations. In table 1 the different gas mixtures separated by today's membrane systems are shown.

Table 1. Gas mixtures separated with membrane systems and their applications[5].

Gas mixture	Application	Gas mixture	Application
H_2/N_2	Hydrogen recovery from purge streams in ammonia plants	O_2/N_2	Oxygen enriched air Nitrogen enriched air
H_2/CO	Hydrogen ratio adjustment in synthesis gas	He/N_2 He/Hydrocarbons	Helium recovery Helium separation
H_2/Hydrocarbons	Hydrogen recovery from hydrogenation processes	Hydrocarbons/air	Hydrocarbon recovery Pollution control
CO_2/Hydrocarbons	Acid gas treatment Landfill gas upgrading	H_2O/Air H_2S/Hydrocarbons	Air dehumidification Sour gas treatment
H_2O/Hydrocarbons	Natural gas dehydration		

Membranes used for gas separation are mostly made of polymers like cellulose derivatives, polysulphones, polyamides and polyimides. The membrane modules consist mostly of hollow fibre membranes or spiral-wound flat sheet membranes. The hollow fibre modules have the advantage of having a much larger surface to volume ratio.

Monsanto used polysulphone as a membrane material which has a fairly high gas selectivity and because asymmetric hollow fibre membranes can relatively easily be prepared from this polymer. The skin of asymmetric membranes should be as thin as possible, however pinholes have to be avoided because they will dramatically reduce the selectivity. For this reason Monsanto coated its asymmetric polysulphone membranes with the highly permeable silicon rubber to plug the defects.

Advantages of membrane systems over the more conventional techniques include the low capital investment, ease of operation, low energy consumption and good weight and space efficiency[5].

The economics of gas separation by membranes are governed by the performance of the membranes. Important parameters are selectivity, permeability and lifetime of the membranes. Spillman has recently discussed the economics of membrane gas separation in an excellent article[5]. Gas separation by membranes is a relatively young technique and membranes are still being improved. For example air separation membranes are now a factor 2 to 4 more efficient than they were in 1985 due to an increased performance in both permeability and selectivity[5]. This means that present data on economics for the various separations may again be outdated after a short period of time.

Below the present commercial applications of gas separation membranes are discussed briefly.

Hydrogen

Monsanto's Prism™ systems were originally designed for the recovery of hydrogen from purge gas streams in the ammonia synthesis. This hydrogen previously had been either flared or burned for fuel because conventional separation was considered to be too expensive. Monsanto demonstrated that membranes provided a cost-effective separation that resulted in energy savings.

Another growing application is the recovery of hydrogen from refinery and petrochemical process streams. The demand for hydrogen in these industries is growing because of the increasing levels of sulphur in the crude oil which requires more hydrodesulphurisation and because of the increasingly heavier feedstocks which require more hydrocracking.

Another petrochemical application is the hydrogen/carbon monoxide ratio adjustment of synthesis gas.

Nitrogen

Nitrogen production via membranes is growing rapidly for applications requiring inert gas blanketing. Commercial membrane systems have selectivities ranging from 3.5 to 5.5 (O_2/N_2) and are able to produce nitrogen of more than 99% purity. In applications were size and weight or low maintenance are important the range of applicability of membranes is extended like in the case of off-shore applications or at ships for the storage of flammable liquids, fruits, vegetables flowers, etc.

Oxygen

Oxygen can also be produced using membrane technology, but since today's membranes have a selectivity ranging from 3.5 to 5.5 (O_2/N_2) oxygen can not be produced economically above 40-50% with the commercial membrane systems. Oxygen enriched air can be used for some medical applications, enhanced combustion (fuel saving), sewage treatment and oxidation processes in the manufacture of chemicals.

Carbon dioxide

Carbon dioxide, water and hydrogen sulphide are present in natural gas and should be removed in order to meet pipeline quality specification. Enhanced Oil Recovery (EOR) is another application where carbon dioxide has to be separated from hydrocarbon gases. Membranes offer an interesting alternative to the more mature techniques like amine absorption especially when high concentrations of carbon dioxide are present like for example with landfill gas. Membranes have clear advantages like a lower capital investment and lower maintenance costs. The applicability of membrane systems for EOR can however be limited due to the plasticising effect of carbon dioxide at high partial pressures (e.g. cellulose derivatives are very susceptible for this phenomenon). This results in a permeability increase through the membrane of all the gases present, which means a reduced selectivity. Besides the loss in selectivity, membrane mechanical stability may also suffer under high partial carbon dioxide pressures.
Related membrane processes are air dehydration and organic vapour separation from air, not to be discussed here.

Expectations

Sales on membrane systems will grow at the expense of the more mature techniques like cryogenics. The best possibilities for membrane systems are nitrogen enrichment by separation oxygen from air and separation of hydrogen in the petrochemical industry.

Sales on gas separation systems using membranes is still modest compared with the other membrane technologies but the expectations for the near future are high due to high research efforts both in industry and at universities.

THEORY

Most of the membranes used in gas separation are made of polymers. Transport of gases through polymer films is believed to occur in three successive steps[3]:

1. sorption of the penetrant in the polymer film
2. diffusion of the penetrant through the polymer film
3. desorption at the permeate side.

This means that permeation depends on the diffusivity, solubility and on the concentration gradient of the penetrant in the membrane. Since homogeneous polymer membranes are studied in this thesis only gas transport through non-porous films will be considered.

The transport of low molecular weight species in polymer membranes is mostly described by Fick's first law:

$$J = -D\frac{dc}{dx} \tag{1}$$

When a linear relation between the gas pressure and the gas concentration at the membrane surface is assumed:

$$c = Sp \tag{2}$$

Substitution of equation (2) in (1) and subsequent integration over the membrane thickness, assuming that the diffusion coefficient and solubility coefficient are independent of the pressure, yields equation (3):

$$J = D\,S\,\Delta p/\delta \tag{3}$$

where δ is the membrane thickness. The permeability coefficient is defined as:

$$P = D.S \tag{4}$$

The influence of both diffusivity and solubility on the permeability of simple gases in natural rubber is nicely illustrated in figure 2 and 3. Solubility mostly increases with increasing molecular weight while diffusivity is decreased.

Frisch and Stern[7] have excellently reviewed the most relevant models describing gas transport in rubbery and glassy polymers.

Rubbers

Molecular models

Diffusion in rubbers is described by *molecular* and *free volume* models. The *molecular* models assume that the microcavities present in a rubber matrix are of different sizes and are continuously formed and destroyed as a result of thermal random motions of the polymer segments. The diffusing gas molecules are dissolved in the polymer matrix and are localised in holes of a suitable size and may migrate to another hole upon opening up of a chain segment.

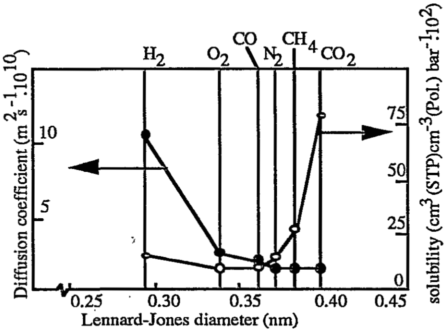

Fig. 2. Diffusion Coefficient and Solubility of different gases in natural rubber as a function of the molecular diameter of the diffusing particle[6].

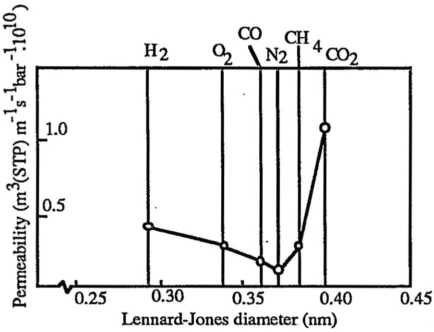

Fig. 3. Permeability of different gases in natural rubber as a function of the molecular diameter of the diffusing particle[6].

The *molecular models* include: the "jump" model of Meares[8], the "activated zone" theory of Barrer[9], the "energy of activation" model of Brandt[10], the "activated state" model of DiBenedetto and Paul[11] and the model of Pace and Datyner[12], the latter combining the models of Brandt and DiBenedetto and Paul.

Free volume models

In the case of the *free volume models* the rate of diffusion is assumed to be determined by the available polymer free volume and the penetrant size.

- The model of Fujita[13] using the Doolittle equation:

$$D = RTA\ exp[-\frac{B}{V_f}] \tag{5}$$

with A and B depending on the molecular size and shape of the penetrant molecule and V_f being the free volume.

- The model of Vrentas and Duda[14,15]. Vrentas and Duda have introduced additional parameters into Fujita's equation to account for the fact that not all the free volume is available for permeation.

Diffusion in rubbery polymers will not be discussed in detail here since all polymers to be discussed in this thesis are in the glassy state. It should however be kept in mind that a number of theories are applicable for both rubbery and glassy polymer systems.

Glassy polymers

Gas sorption and transport in glassy polymers is traditionally described by the dual mode sorption theory[16]. The free volume theory of an older date and originally developed for rubbers has however gained a lot of interest lately since gas transport in glassy polymers could successfully be described by this theory.

The dual mode sorption theory[16].

This theory postulates the existence of two populations of gas molecules present in the polymer matrix:

- gas molecules dissolved according to Henry's law; the concentration of the molecules C_D is related to the pressure, p

$$C_D = k_D p \tag{6}$$

with k_D the solubility constant.

- gas molecules absorbed in microcavities "frozen" into the polymer matrix; the concentration of these molecules is related to the pressure p by the Langmuir isotherm:

$$C_H = C_H' bp/(1 + bp) \tag{7}$$

with C_H' as the hole saturation constant and b as the hole affinity constant which represents the ratio of rate constants of gas ad- and desorption in the microcavities.

The total concentration of a gas absorbed in a glassy polymer is then represented by:

$$C = C_D + C_H = k_D p + C_H' bp/(1 + bp) \tag{8}$$

Initially it was assumed that gas molecules in the microcavities were totally immobilised and that the permeability could be represented by

$$P = k_D D_D \tag{9}$$

Petropoulos[17] and later Paul and Koros[18] modified the dual mode sorption theory by assuming that the molecules sorbed in the microcavities possessed limited mobility and participated in the permeability:

$$P = k_D D_D\{1 + KF(1+ bp)^{-1}\} \tag{10}$$

with $K = C_H'b/k_D$ as the relative amount of gas sorbed in the two modes, $F = D_H/D_D$ as the diffusivity ratio being a measure of the degree of immobilisation and D_H as the diffusivity of the gas molecules in the holes.

In the dual mode sorption theory it is further assumed that the sorbed gases do not interact with the polymer matrix, in other words, k_D, D_D and D_H are pressure and concentration independent.

Raucher and Sefcik have shown that this assumption is not allowed in all cases and they have proposed another mechanism for the gas sorption and transport in a polymer: the gas-polymer-matrix model in which the diffusivity is a function of penetrant concentration[19].

They used NMR techniques to study the chain motions in polyvinyl chloride at various carbon dioxide concentrations and could observe only one population of gas molecules. They argued that the dual mode sorption theory provides an adequate mathematical description of sorption and transport in glassy polymers but that the physical assumption of the presence of two distinct populations is invalid. In the case of interacting penetrants, like carbon dioxide, the polymer matrix is altered due to the presence of gas molecules having its impact on the gas transport through this matrix which results in a concentration dependent diffusivity.

Wessling et al. recently found by means of a combination of dilation and sorption experiments that carbon dioxide diffusivity is concentration dependent and that the polymer matrix is altered/plasticised due to the presence of carbon dioxide[20].

The free volume theory

This model was originally proposed for rubbers but is now also used to describe the transport of gases in glassy polymers. It correlates diffusivity to the polymer free volume, using the equation of Fujita:

$$D = RTA\, exp[-\frac{B}{V_f}] \tag{5}$$

with $V_f = V - V_0$, V is the specific volume of the polymer which can be obtained by a density measurement and V_0 is the specific occupied volume of the polymer chains, which can be estimated using Bondi's group contribution method[21]. This simple equation relates the diffusion coefficient nicely to the free volume of many polymers. The free volume model employing equation (5) has gained a lot of interest lately. Lee[22] was the first to relate the gas permeability of a number of commercial polymers (glasses and rubbers) to their free volume[1].

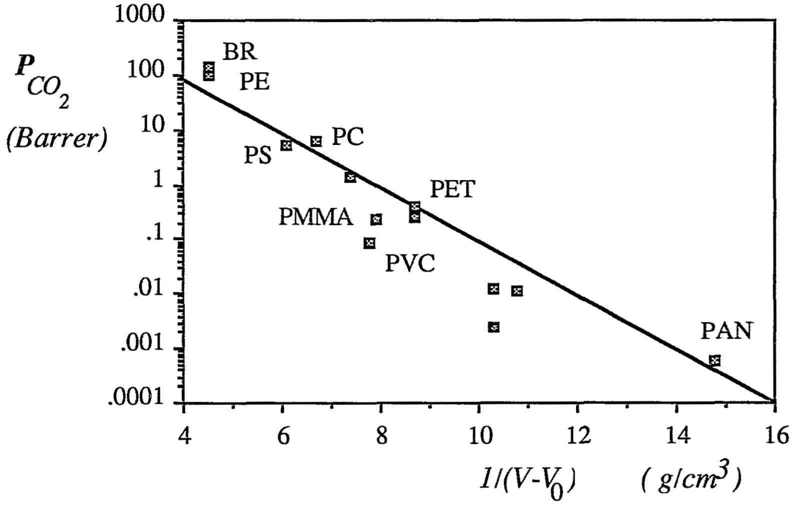

Fig. 4. Carbon dioxide permeability as a function of the reciprocal polymer free volume[22].

More recently this correlation was used by Maeda and Paul[23] to explain the reduction in transport in polysulphone and polyphenylene oxide containing low molecular weight antiplasticisers. The reduction in transport due to the addition of these additives could be explained nicely in terms of a decrease in free volume.

Barbari, Koros and Paul[24] used Fujita's equation to relate the free volume of polymers based on bisphenol-A to the diffusivity. In the same group Muruganandam[25] did this for substituted polycarbonates, whereas Min[26] studied the influence of the tacticity of polymethyl methacrylate using this equation. Schmidhauser and Longley[27] recently studied a large number of polycarbonates also employing the free volume approach of Fujita.

Fujita's equation implies that for a given penetrant a straight line should describe the diffusivity for all polymers for a given gas with A and B as constants. However a wide scattering of data

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[1] $P = S.D = S.A\ exp(-B/V_f)$, so $log\ P = log\ S + log\ A - B/V_f$. A and B are polymer independent and S is assumed to vary only little with respect to D[21].

may be found when more polymers are plotted in one graph, because of specific gas/polymer solubility effects and because of polymer local segmental motions that are not sensitive to free volume.

Duda and Vrentas have introduced a revised version of equation (5) since not all the free volume will be available for permeation[28]:

$$D = D_0 exp\,[-\frac{E}{RT}]\; exp\,[-\frac{\gamma\xi V_2}{V_{FH2}}] \qquad (11)$$

in which D_0 is a constant pre-exponential factor, E is the energy per mole that a molecule needs to overcome attractive forces which holds it to its neighbours, γ is an overlap factor which is introduced because the same free volume is available to more than one molecule, and ξ is the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit. V_{FH2} is the average hole free volume per gram of polymer, component 2, and V_2 is the specific critical hole free volume of polymer required for a jump.

Equation (5) and (11) become identical if:

$$A = D_0\; exp[-E/RT]\; and\, B = \gamma V_1 M_l/M_2 \qquad (12)$$

in which V_1 is the specific critical free volume required for a jump of the penetrant and M_1 and M_2 are the molecular weight of the penetrant and the polymer jumping unit respectively.

In the equation of Vrentas and Duda A and B depend on both polymer and penetrant and not only on the penetrant as in equation (5).

The equation of Vrentas and Duda may better describe the process of permeation but introduces parameters which are not known or easily obtained for the polymers studied in this thesis, viz.; this reduces these parameters to "*correcting*"-parameters. An advantage of the Duda and Vrentas approach is the fact that their model does account for both polymer/gas interaction ánd for the free volume.

The gas transport properties of the polymers studied, the poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles, will be related to their free volume as will be described in chapter 4 and 5 of this thesis.

RESEARCH ON GAS SEPARATION MEMBRANES

Research on gas separation membranes takes place mainly in Western Europe, Japan and the United States. In Japan and the U.S.A. most of the research is carried out in industry itself while in Europe most of the research is done at universities and research institutes.

Materials research topics can be divided into roughly two classes:

- development of new membrane morphologies allowing higher fluxes (e.g. asymmetric membranes, hollow fibre membranes and composite membranes).
- development of new polymer membrane materials with improved selectivities and permeabilities; the search for "tailor-made" polymers.

A totally different concept of membrane separation, not to be discussed here, is facilitated transport. These systems mostly consist of a supported liquid membrane containing a carrier which transports the oxygen from the high to low pressure side of the membrane.

In this study new "tailor-made" poly-1,3,4-oxadiazole and poly-1,2,4-triazole membrane materials are studied and investigated regarding their gas separation properties.

In general new membrane materials are developed with the aim to increase membrane selectivity and permeability. "Tailor-made" polymers are studied to investigate the effect of the molecular structure on the gas separation properties of membranes prepared from these materials. The influence of the intersegmental packing density and the segmental mobility of these macromolecules as well as their sensitivity to plasticisation is studied in order to predict the gas separation properties.

New membrane material research is focussed on the following polymers:

- Poly(1-trimethylsilyl-1-propyn), PTMSP. This is a glassy polymer which has the highest gas permeability of any known glassy or rubbery polymer. The molecular structure of PTMSP, consisting of relatively rigid backbone chains separated by bulky trimethylsilyl groups is responsible for an extremely large free volume[29]. The polymer appears to have an open structure characterised by a 20% available void volume (versus 3 to 6% for other polymers), and a chain to chain distance of at least 4 Å. The gas transport is shown to occur via interconnected microvoids[30]. Langsam et al. have investigated the possibility of increasing the selectivity of PTMSP without loosing too much in permeability by surface fluorination[31]. They were able to increase the selectivity for O_2/N_2 from 1.49 to 5.1.

In the Soviet Union Poly(vinyl-trimethylsilane), PVTMS, also a new highly permeable membrane material, is studied[32].

- Polyimides containing bulky trifluoromethyl groups form a second group of tailor-made membrane materials. This class of materials is studied in almost any company producing gas separation membranes and also at many universities, a.o. the University of Texas[33], and can be considered to be one of the most interesting new classes of polymers.
- Poly-[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles]. These are polymers with excellent selectivities and reasonable permeabilities for CO_2/CH_4 and O_2/N_2 and they were originally studied by Gebben et al.[34]. In the present continued research on this topic, new poly-1,2,4-triazoles and poly-1,3,4-oxadiazoles have been synthesised and their gas separation properties have been determined.

In figure 5 the permeabilities and selectivities of some of these "tailor-made" polymers are compared for the separation of CO_2 and CH_4 with the values for conventional membrane materials. This figure shows that it is possible to shift from the typical trade-off between permeability and selectivity as found for the conventional polymers. The all-aromatic rigid tailor-made polymers have higher permeabilities at comparable selectivities than found for other glassy polymers. The high permeability is often explained in terms of their high free volume due to bulky groups, preventing a more efficient packing.

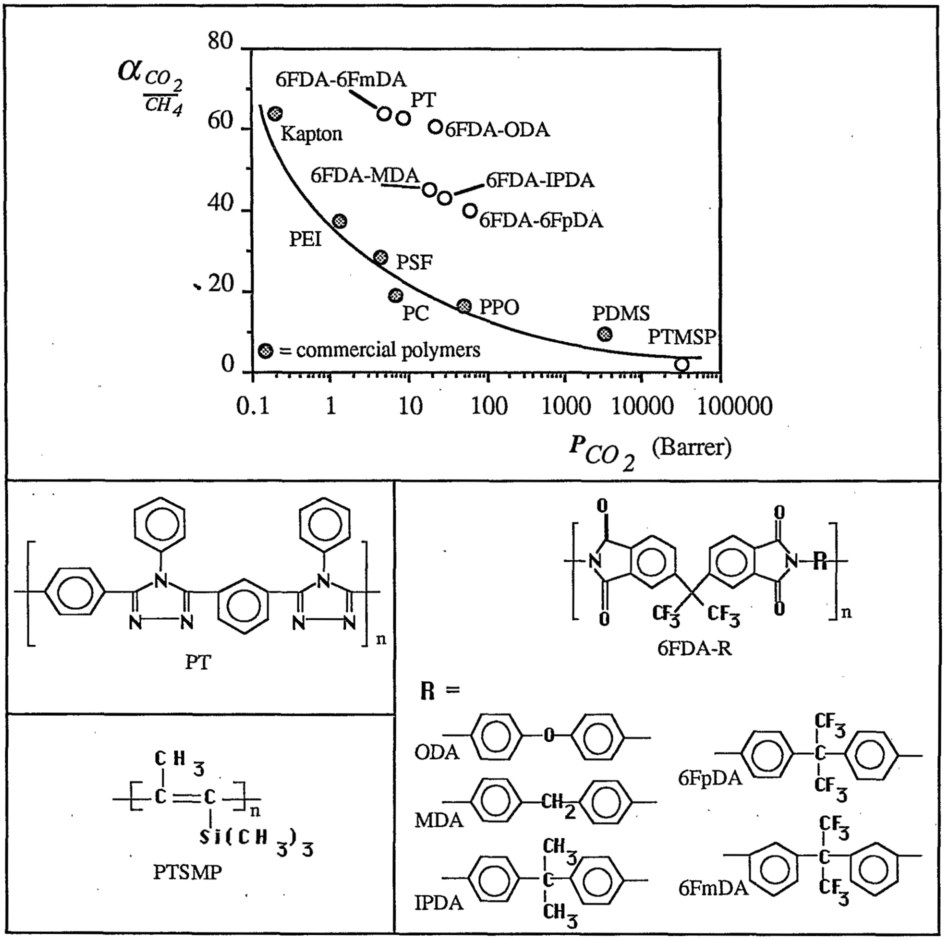


Fig. 5. Gas separation properties of conventional and tailor-made polymers. Permeability and selectivity data were taken from the following sources: Kapton[35], 6FDA-ODA, 6FDA-MDA and 6FDA-IPDA[36], 6FDA-6FpDA and 6FDA-6FmDA[37], PEI[23] (Ultem), PSF[38], PC[39], PPO[40], PDMS[41], PTMSP[31] and PT[34].

The high selectivity is assumed to originate from their rigid, molecular sieve-like structure. Breck[40] has determined the kinetic diameters of a number of gases using molecular sieves, see table 2.

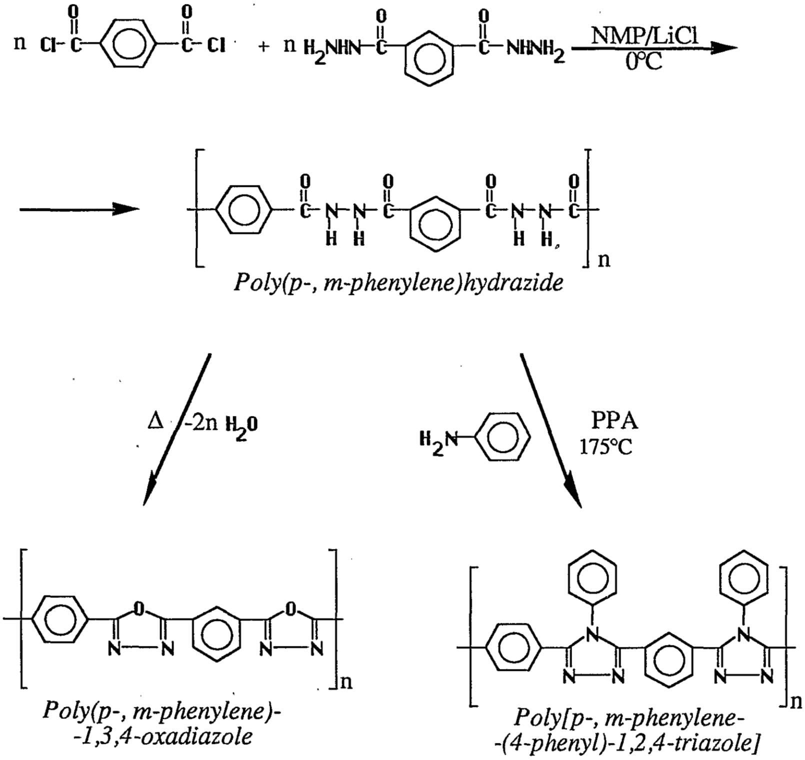
Table 2. Kinetic diameters of simple gases.[42]

gas molecule	kinetic diameter (nm)	gas molecule	kinetic diameter (nm)
He	0.26	O_2	0.346
H_2	0.289	N_2	0.364
CO_2	0.33	CO	0.376
Ar	0.34	CH_4	0.38

The same order as shown in table 2 is also found for the permeation rates of these gases in glassy polymer membranes. This suggests that selectivity is merely based on a sieving mechanism then on specific gas/polymer interactions which is supported by the typical trade-off between selectivity and permeability. A polymer matrix with large voids shows a high permeability but cannot discriminate between permeating gas molecules resulting in a low selectivity. Presently investigated "tailor-made" polyimides and poly-1,2,4-triazoles posses both high permeabilities and selectivities likely to be due to their rigid structure and hindered structure not allowing a dense packing of macromolecules.

SYNTHESIS AND PROPERTIES OF POLY-1,3,4-OXADIAZOLES AND POLY-1,2,4-TRIAZOLES.

In 1984 the Dutch Ministry of Economic Affairs started an Innovative Research Programme on membranes (IOP-Membranen). One of the projects was the development of thermally stable and chemically resistant polymer membranes. The aim was to develop membranes that could be applied under severe conditions like elevated temperatures, in an acidic or a basic environment and which would be resistant towards organic solvents. Two classes of related polymers, the poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles, have been investigated regarding their applicability. Both polymers are stable up to 450-500°C and are only soluble in strong acids like concentrated sulphuric acid. They can be prepared from a tractable precursor polymer, a polyhydrazide[43,44,45], see figure 6. The polyhydrazide can be processed into a desired membrane configuration and converted into a poly-1,3,4-oxadiazole membrane by means of a heat treatment. The kinetics of this cyclodehydration reaction was studied by Gebben et al. using isothermal and non-isothermal gravimetrical analysis[46,47]. Fully converted poly-1,3,4-oxadiazole membranes using this reaction route were however too brittle to be applied. In chapter 2 of this thesis, an alternative route for the preparation of high molecular weight poly-1,3,4-oxadiazoles from which flexible membranes can be prepared, will be discussed.



PPA = PolyPhosphoric Acid

Fig. 6. Synthesis routes of poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles[43,44,45].

The synthesis of poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazole] using poly(*p*-, *m*-phenylene)-hydrazide has extensively been studied by Holsten and Liliquist[46]. Membranes prepared from this polymer appeared to combine excellent gas separation properties[34] with a high thermal stability and a good chemical resistance[48]. These gas separation membranes can be applied for the separation of oxygen/nitrogen and carbon dioxide/methane gas mixtures. Membranes of these polymers may also be applicable in harsh environments caused by elevated temperatures and acidic gases. Because of the excellent gas separation properties this project was continued with the aim to elucidate the relationship between the macromolecular structure of the poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles and their physical properties on one hand and the resulting gas transport properties on the other.

In practice this means that a large variety of poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles have been prepared and homogeneous membranes from these polymers have subsequently been investigated regarding their gas separation properties. In chapter 2 and 3 the synthesis and properties of new poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles are described. The gas transport and separation properties of these polymers are discussed in chapter 4 and 5 of this thesis where it will be shown that the permeability can be expressed as a function of the polymer free volume.

A disadvantage of these polymers is their limited solubility in common solvents hampering asymmetric membrane formation. The solubility of poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles] is markedly increased upon doping with Br_2, I_2 and $FeCl_3$[49]. For example, poly[*m*-phenylene(4-phenyl)-1,2,4-triazole] is only soluble in formic acid and concentrated sulphuric acid but upon doping with $FeCl_3$ it becomes soluble in acetone and nitromethane and flexible films are obtained from these polymer solutions. Besides the increase in solubility Hagiwara et al. noticed an increase in electrical conductivity of the poly-1,2,4-triazoles upon doping. The increased tractability of doped and electroactive poly-1,2,4-triazoles has also been described by Schroeder et al.[50].

The solubilisation of various rigid chain and ladder polymers in aprotic solvents by means of Lewis acids has recently been reported by Jenekhe et al.[52] and Jenekhe and Johnson[53]. Poly(*p*-phenylene)-1,3,4-oxadiazole, known commercially as Oxalon® (Techmaschimport, Moscow), also becomes soluble in these solvent systems[51].

We have increased the solubility of poly-1,3,4-oxadiazoles by a different approach , namely by means of incorporation of polar, bulky and asymmetric groups in the polymer main chain as will be discussed in chapter 3.

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LITERATURE

1. J.K. Mitchell, Am. J. Med., 7, 36-67(1830).
2. J.K. Mitchell, Royal Inst. J., 2, 101 and 307(1831).
3. T. Graham, Phil. Mag., 32, 401-420(1866).
4. R.J.R. Uhlhorn and A.J. Burggraaf, "Gas separation using inorganic membranes", *in* R. Bhave (Ed.), "Inorganic membranes", Nortrand and Reinholdt, New York, 1990.
5. R.W. Spillman, Chem. Eng. Progr., 85, 41-62(1989).
6. R.W. Baker and I. Blume, Chemtech., 16, 232-238(1986).
7. H.L. Frisch and S.A. Stern, Diffusion of small molecules in polymers, *in* CRC Critical Reviews in Solid State and Materials Science, Vol. 11, No. 2, CRC Press, Inc., 1983, 123-187
8. P. Meares, J. Am. Chem. Soc., 76, 3415-3422(1954).
9. R.M. Barrer, J. Phys. Chem., 61, 178-189(1957).
10. W.W. Brandt, J. Phys. Chem., 63, 1080-1084(1959).
11. A.T. DiBenedetto and D.R. Paul, J. Polym. Sci., A, 2, 1001-1015(1964).
12. R.J. Pace and A. Datyner, J. Polym. Sci., Polym. Phys. Ed. 17, 437-451, 453-464 and 465-476(1979).
13. H. Fujita, Fortschr. Hochpolym. Forsch., 3, 1-47(1961).
14. J.S. Vrentas and J.L. Duda, Macromolecules, 9, 785-790(1976).
15. J.S. Vrentas and J.L. Duda, J. Polym. Sci., Polym. Phys. Ed. 15, 403-416, and 417-439(1977).
16. W.R. Vieth, J.M. Howell and J.H. Hsieh, J. Membrane Sci., 1, 177-220(1976).
17. J.H. Petropoulos, J. Polym. Sci., A2, 8, 1797-1801(1970).
18. D.R. Paul and W.J. Koros, J. Polym. Sci., Polym. Phys. Ed., 14, 675-685(1976).
19. M.D. Sefcik and D. Raucher, Gas transport and cooperative main-chain motions in glassy polymers *and* Transport in glassy polymers: gas-polymer-matrix model, *in* Industrial Gas Separations, ACS Symposium Series 223, T.E. Whyte, C.M. Yon and E.H. Wagener (Eds.), Washington, 1983, 89-110 *and* 111-124.
20. M. Wessling, Th. van den Boomgaard and C.A. Smolders, Gas Separation and Purification, to be published.
21. A. Bondi, Physical properties of molecular crystals, liquids and glasses, John Wiley and sons, New York, 1968.
22. W.M. Lee, Pol. Eng. Sci., 20, 65-69(1980).
23. Y. Maeda and D.R. Paul, J. Polym. Sci., Polym. Phys. Ed., 25, 1005-1016(1987).
24. T.A. Barbari, W.J. Koros and D.R. Paul, J. Polym. Sci., Polym. Phys. Ed., 26, 709-727(1988).
25. N. Muruganandam, W.J. Koros and D.R. Paul, J. Polym. Sci., Polym. Phys. Ed., 25, 1999-2026(1987).
26. K.E. Min, W.J. Koros and D.R. Paul, J. Polym. Sci., Polym. Phys. Ed., 26, 1021-1033(1988).
27. J.C. Schmidhauser and K.C. Longley, J. Appl. Polym. Sci., 39, 2083-2096(1990).
28. J.S. Vrentas, J.L. Duda and H.-C. Ling, J. Membrane Sci., 40, 101-107(1989).
29. Y. Ichiraku and S.A. Stern, J. Membrane Sci., 34, 5-18(1987).
30. S.R. Auvil, R. Srinivasan and P.M. Burdan, "Gas transport in Poly[trimethylsilyl propyne]" presented at the International Symposium on Membranes for gas and Vapour Separation, 1989, Suzdal, USSR.
31. M. Langsam, M. Anand and E.J. Karwacki, Gas separation & purification, 2, 162-170(1988).
32. S.G. Durgar'yan, Yu. P. Yampol'skii and N.A. Plate, Russian Chemical Reviews, 57, 549-558(1988).
33. T.H. Kim, W.J. Koros, G.R. Husk and K.C. O'Brien, J. Membrane Sci.,37, 45-62 (1988).
34. B. Gebben, M.H.V. Mulder and C.A. Smolders, J. Membrane Sci., 46, 29-41(1989).
35. R.T. Chern, W.J. Koros, H.B. Hopfenberg and V.T. Stannet, "Material Selection for Membrane-Based Gas separations", *in* D.R. Lloyd (Ed.), "Materials Science of Synthetic Membranes", ACS Symposium Series, Vol. 269, Washington, 1985.
36. T.H. Kim, W.J. Koros, G.R. Husk and K.C. O'Brien, J. Membrane Sci., 37, 45-62(1988).
37. M.R. Coleman and W.J. Koros, J. Membrane Sci., 50, 285-297(1990).

38. A.J. Erb and D.R. Paul, J. Membrane Sci., 8, 11-21(1981).
39. M.W. Hellums, W.J. Koros, G.R. Husk and D.R. Paul, J. Membrane Sci., 46, 93-112(1989).
40. Y. Maeda and D.R. Paul, Polymer, 26, 2055-2063(1985).
41. W.L. Robb, New York Acad. Sci., 146, 119 (1964).
42. D.W. Breck, Zeolite Molecular Sieves, John Wiley and Sons, New York, 1974, p.636.
43. A.H. Frazer, F.T. Wallenberger, J. Polym. Sci., A2, 1147-1156(1964).
44. A.H. Frazer, W. Sweeny, F.T. Wallenberger, J. Polym. Sci., A2, 1157-1169 (1964).
45. J.R. Holsten, M.R. Liliquist, J. Polym. Sci.,A, 3, 3905-3917(1965).
46. B. Gebben, M.H.V. Mulder and C.A. Smolders, J. Polym. Sci., Polym. Chem. Ed., 26, 1743-1757(1988).
47. B. Gebben, M.H.V. Mulder and C.A. Smolders, J. Polym. Sci., Polym. Chem. Ed., 26, 1757-1768 (1988).
48. B. Gebben, M.H.V. Mulder and C.A. Smolders, J. Polym. Sci., Polym. Chem. Ed., 27, 3481-3499(1989).
49. T. Hagiwara, T. Demura and K. Iwata, Nippon Kagaku Kaishi, 3, 356-364(1986); Chem. Abstr. CA 104:217211v.
50. A.H. Schroeder, P. Denisevich, S. Suzuki and V.P. Kurkov, U.S. Pat. 4,519,940(1985).
51. B. Schulz, Institut für Polymerenchemie "Erich Correns", Teltow-Seehof, Germany, private communication.
52. S.A. Jenekhe, P.O. Johnson and A.K. Agrawal, Macromolecules, 22, 3216-3222(1989).
53. S.A. Jenekhe and P.O. Johnson, Macromolecules, 23, 4419-4429(1990).

2

Two reaction routes for the preparation of aromatic polyoxadiazoles and polytriazoles. Syntheses and properties.

E.R. Hensema, J.P. Boom, M.H.V. Mulder and C.A. Smolders

SUMMARY

Two reaction routes for the preparation of aromatic poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles are studied. The preparation routes and their influence on the physical properties, i.e. inherent viscosity, glass transition and degradation temperature and film integrity of the final products are discussed.

Aromatic poly-1,3,4-oxadiazoles are prepared by means of a polycondensation reaction of terephthaloyl chloride and isophthalic dihydrazide yielding a precursor polymer, poly(*p*, *m*-phenylene)hydrazide, which is converted into the corresponding poly-1,3,4-oxadiazole by means of a cyclodehydration reaction. Poly-1,3,4-oxadiazoles are also prepared by means of a polycondensation reaction between terephthalic and isophthalic acid and hydrazine. The latter reaction is more direct and yields poly-1,3,4-oxadiazoles with higher inherent viscosities. Flexible poly-1,3,4-oxadiazole films are obtained only if the inherent viscosities of the polymers used, are higher than 2.7 dl/g. The polymers are investigated regarding their thermal properties by means of DSC and TGA techniques. Thermal stability is found to increase with increasing content of *p*-phenylene groups in the polymer backbone.

Aromatic poly-1,2,4-triazoles are prepared using polyhydrazides with alternating *para*- and *meta*-phenylene groups and poly-1,3,4-oxadiazoles with a random incorporation of *para*- and *meta*-phenylene groups in the main chain as precursor polymers. The glass transition temperatures are found to increase with increasing content of *p*-phenylene groups in the main chain of theses polymers. Cold crystallisation is only observed for the alternating polymer and its occurrence is believed to be directly related to the alternating incorporation of the phenylene groups in the main chain.

INTRODUCTION

Aromatic poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles are chemically resistant and thermally stable polymers since they are only soluble in strong acids and stable up to 450°C[1]. We have studied these polymers as new membrane materials[2,3], with the aim to develop membranes that can be applied under severe operating conditions, such as elevated temperatures and acidic or basic environments. Such membranes also should be highly resistant towards organic solvents. A number of reaction routes are known for the preparation of these poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles[4].

We decided to study the preparation of aromatic poly-1,3,4-oxadiazoles by means of a solid state cyclo-dehydration reaction of an aromatic polyhydrazide[5,6], the latter being used as a tractable precursor polymer. Since poly-1,3,4-oxadiazoles with inferior mechanical properties were obtained[2], a second reaction route was also studied. This route directly yields aromatic poly-1,3,4-oxadiazoles from hydrazine sulphate and terephthalic and isophthalic acid as monomers[7]. Aromatic poly-1,2,4-triazoles were prepared by a reaction of an aromatic polyhydrazide[8] and poly-1,3,4-oxadiazoles[9] with aniline in polyphosphoric acid.

The synthesis routes are represented in figure 1. Polyhydrazides with alternating *para-* and *meta-*phenylene groups in the main chain were prepared using terephthaloyl chloride and isophthaloyl dihydrazide as monomers. Conversion of this precursor polymer yields poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles with alternating *p-* and *m-*phenylene groups, see reaction route A.

Employing mixtures of terephthalic and isophthalic acid in different ratios in combination with hydrazine sulphate results in the direct formation of poly-1,3,4-oxadiazoles were *p-* and *m-*phenylene groups are incorporated randomly, see reaction route B. These poly-1,3,4-oxadiazoles were used as a precursor polymer for the poly-1,2,4-triazole synthesis. They were converted into poly-1,2,4-triazoles, having the same incorporation of *p-* and *m-*phenylene groups in the main chain as the precursor polymer, by means of a reaction with aniline in polyphosphoric acid.

In this paper we wish to report on the synthesis routes used and on the properties of the polymers prepared. The gas separation properties of membranes of these polymers are discussed elsewhere[10].

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EXPERIMENTAL

Materials

All chemicals were supplied by Merck, and were used as received, except NMP which was distilled before use under reduced pressure over CaH_2, lithium chloride which was dried in a vacuum oven at 150℃ and aniline which was distilled under reduced pressure. The colourless distillate was stored under nitrogen in a sealed flask in a refrigerator.
Isophthaloyl dihydrazide was prepared from isophthalic dimethyl ester and hydrated hydrazine hydrate[11].

Poly(*p*-, *m*-phenylene)hydrazide synthesis (I)[5,6]

Isophthaloyl dihydrazide, 74.242 g (0.382 mol.) and 16.21 g LiCl are dissolved in a three necked flask containing 600 ml NMP at 60℃ under dry nitrogen. After dissolution the stirred solution is cooled to 0℃ and 77.619 g (0.382 mol.) terephthaloyl chloride is added in 4 equal portions. Each portion is added when the terephthaloyl chloride of the previous portion has completely dissolved. Total addition lasts approximately 2 hours. The viscous solution is stirred overnight and the polymer is precipitated and washed in hyperfiltrated demineralised water. Subsequently the polymer is washed in ethanol and dried in a vacuum oven at 150℃ during at least 24 hours.

Poly-1,3,4-oxadiazole synthesis (II) using (I) as a precursor polymer[2,5,6]

Alternating poly(*p*-, *m*-phenylene)-1,3,4-oxadiazole is prepared by heating solid poly(*p*-, *m*-phenylene)hydrazide in a nitrogen atmosphere. Various heating cycles have been applied, including: 24 hours at 276℃, 24 hours at 288℃, 24 hours at 285℃, 62 hours at 280℃ followed by 100 hours at 300℃ and a heating cycle of 48 hours at 310℃.

Poly-1,2,4-triazole synthesis (III) using (I) as precursor polymer[8]

In a three necked flask 310 g polyphosphoric acid (PPA) is heated to 150℃ under nitrogen. Aniline, 76.65 g (0.823 mol.), is added dropwise to the stirred solution, meanwhile maintaining the temperature at 150℃. After addition, the temperature is raised to 175℃, and 10 g poly(*p*-, *m*-phenylene)hydrazide is added. The reaction mixture is kept at this temperature during 140 hours. This mixture is poured into hyperfiltrated demineralised water and neutralised with sodium hydroxide under stirring. The product is washed in a 5% sodium hydroxide solution and twice in hyperfiltrated demineralised water. Subsequently the product is extracted with ethanol using a Soxhlet extractor after which it is dried in a vacuum oven at 150°C during 24 hours. The product is dissolved in formic acid and insoluble parts are removed by means of filtration over a 5 µm filter. Homogeneous poly-1,2,4-triazole films are directly prepared from these solutions, as will be discussed below.

One-step synthesis of poly-1,3,4-oxadiazoles (IV)[12]

To 18.75 g (0.14 mol) hydrazine sulphate, in a three necked flask and in a dry nitrogen atmosphere, is added 230 ml chlorosulfonic acid. To this stirred solution is added 30 ml 30% SO_3 fuming sulphuric acid and 140 ml concentrated sulphuric acid followed by the addition of 20 g (0.12 mol) of a mixture of terephthalic and isophthalic acid and 1.2 g benzene sulphonic acid. (Hydrazine is employed in a 20 mol. % excess yielding poly-1,3,4-oxadiazoles with higher inherent viscosities than obtained under equimolar conditions[7].) After addition the temperature is raised to 135°C and stirred at this temperature until the viscosity of the reaction mixture has reached its maximum lasting 2 hours for poly(*p*-phenylene)-1,3,4-oxadiazole and 8 hours for poly(*m*-phenylene)-1,3,4-oxadiazole.

The reaction mixture is cautiously poured into ice water and washed with hyperfiltrated demineralised water during 24 hours. The polymer is dried at 150°C in a vacuum oven during at least 24 hours.

Poly(*p*-phenylene)-1,3,4-oxadiazole was also prepared using only fuming sulphuric acid as a reaction medium[7]. After addition of the reactants the temperature is raised to 90°C and maintained at this temperature for 2 hours. Subsequently the temperature is raised to 130°C and kept at this temperature for another 5 hours. After completion, the reaction mixture is poured into hyperfiltrated demineralised water. Further purification is identical to the procedure described above.

Poly-1,2,4-triazole synthesis (V) using (IV) as a precursor polymer[9]

Random poly(*p*-, *m*-phenylene)-1,3,4-oxadiazoles were used as precursor polymers for the preparation of the corresponding poly-1,2,4-triazoles. The same procedure as described for the preparation of poly-1,2,4-triazoles using polyhydrazide as a precursor polymer is applied, however the reaction temperature is in this case 225°C while a reaction time of 35 hours is required[9]. This procedure, described by D'Yachenko et al., yielded poly-1,2,4-triazoles after reaction times much longer than 35 hours and in yields of only 5 to 10%, as will be discussed below. For this reason the synthesis was altered; first the poly-1,3,4-oxadiazole is dissolved in

PA at 150°C followed by the addition of aniline. The temperature is raised to 225°C and naintained at this temperature. After 35 hours the reaction mixture is poured into hyperfiltrated lemineralised water and the precipitate is purified as described under "Poly-1,2,4-triazole ynthesis (III) using (I) as precursor polymer ".

Preparation of homogeneous films

Poly(p-, m-phenylene)hydrazide films

Homogeneous transparent colourless polyhydrazide films are prepared by casting a 10-15 wt.% polymer solution in DMSO onto a glass plate using a casting knife with a slit height of 0.30 mm, followed by evaporation of the solvent at 80°C under a continuous nitrogen flow. The film is removed from the glass plate and dried at 150°C in a vacuum oven to remove residual solvent. Films are obtained with thicknesses between 20 and 60 μm.

Poly[p-, m-phenylene-(4-phenyl)-1,2,4-triazole] films

Homogeneous poly-1,2,4-triazole films are prepared by casting a 15 wt.% polymer solution in formic acid on a glass plate using casting knives with slit heights of 0.3 and 0.5 mm, followed by evaporation of the solvent in a nitrogen atmosphere at room temperature. After evaporation, the glass plate is immersed into a water bath and the poly-1,2,4-triazole film is easily removed from the glass plate. Transparent yellow films are obtained with thicknesses between 20 and 60 μm.

Poly(p-, m-phenylene)-1,3,4-oxadiazole film

Poly-1,3,4-oxadiazole films are obtained by solid state cyclodehydration of polyhydrazide films, obtained as described above, using different heating cycles and heating times.

Poly-1,3,4-oxadiazole films were also obtained by casting a 4 to 5 wt.% polymer solution in concentrated sulphuric acid onto a glass plate using a casting knife with a slit height of 0.5 mm, followed by immersion in a bath containing a 50 wt.% aqueous sulphuric acid solution. The film is rinsed with demineralised water during 24 hours followed by immersion into an ethanol bath and a hexane bath. The films are dried between polysulphone micro-filtration membranes under slight pressure to prevent curling. The transparent poly-1,3,4-oxadiazole film is removed from the polysulphone membranes with the help of a little water and dried in a vacuum oven at 70°C. The thickness of these films was approximately 50 μm.

Thirdly, poly-1,3,4-oxadiazole films are obtained by casting the sulphuric acid diluted reaction mixture of poly(*p*-phenylene)-1,3,4-oxadiazole acid onto a glass plate. The reaction mixture is diluted with sulphuric acid in order to reduce the viscosity of this casting solution. The solution is cast on a glass plate followed by immersion into a 50 wt.% aqueous sulphuric acid solution. The transparent film is rinsed with demineralised water and dried in a vacuum oven.

Characterisation

Inherent viscosity

The inherent viscosities are determined of 0.5 g polymer solutions in 100 ml solvent at 30℃. For the polyhydrazides DMSO, for the poly-1,2,4-triazoles formic acid and for the poly-1,3,4-oxadiazoles concentrated sulphuric acid, is used as a solvent.

Differential Scanning Calorimetry (DSC)

DSC measurements are performed on a Perkin-Elmer DSC 4 in combination with a System 4 Microprocessor Controller and a Thermal Analysis Data Station (TADS), model 3700. The polymer samples are placed in aluminium sample pans and the temperature is increased with a heating rate of 20℃/min. from 50 to 450℃ under a nitrogen purge gas stream. As glass transition temperature its midpoint is taken, calculated by means of the TADS software.

Thermo-gravimetrical Analysis (TGA)

TGA experiments are carried out on a Perkin-Elmer TGS-2 in combination with a system 4 microprocessor Controller and a Thermal Analysis Data Station, model 3700. Experiments are carried out under a nitrogen purge gas stream from 50 to 600℃. The temperature of the polymer samples is increased with a heating rate of 20℃/min. Weight loss over a certain temperature interval is calculated by means of the TADS software.

Thermo-mechanical measurements

A Myrenne torsion pendulum is used to obtain thermo-mechanical spectra of the poly-1,2,4-triazoles from -175 to 350℃. The temperature of the samples is increased with a heating rate of 1.8℃/min. The applied frequency was 1 Hz. Poly-1,2,4-triazole coated glass fibres are used as samples. For this purpose glass fibres were heated at 450℃ during several hours to remove any coating. Subsequently a bundle of fibres was dip-coated in a poly-1,2,4-triazole solution in formic acid followed by evaporation of the solvent. Residual solvent was removed at 70℃ in a vacuum oven. Samples with dimensions of 55 by 1 by 0.75 mm are obtained.

Wide Angle X-ray diffractograms (WAXS)

WAXS-diffractograms are recorded on a Philips Röntgen diffractometer, PW 1710 using copper diffraction (Cu Kα, λ = 1.5418Å).

RESULTS AND DISCUSSION

Poly-1,3,4-oxadiazoles via polyhydrazides

A number of polyhydrazides were prepared and their IR-spectra are in agreement with the IR-spectrum reported by Frazer et al.[6] The results of the elemental analysis of one of the polyhydrazides: PH-p/m-1 is represented in table 1. The experimental values found are somewhat lower than the theoretical ones. Nonetheless the C/N quotient is close to its theoretical value indicating that the polyhydrazide contains residual impurities.

Polyhydrazides with inherent viscosities up to 1.39 dl/g were obtained, see table 2. From all these polymers flexible transparent films were prepared. Polyhydrazides having higher inherent viscosities are reported when hexamethyl phosporamide, HMPA, is used as a solvent instead of NMP[34]. HMPA was not used since it is very carcinogenic[13].

Films of polyhydrazide PH-p/m-1, see table 1, were converted into poly-1,3,4-oxadiazole films by heating the films during 24 hours at 285°C in a nitrogen atmosphere. The values of elemental analysis of the converted polyhydrazide, POD-p/m-1, are in agreement with the theoretical values, see table 1. The IR-spectrum is similar to the one reported by Frazer et al.[6] where the same characteristic absorption peaks are found (=C-O-C= stretching at 960 cm^{-1} and >C=N-stretching at 1550 cm^{-1}).

Various polyhydrazide films were isothermally converted into poly-1,3,4-oxadiazole films in a nitrogen atmosphere in a furnace at temperatures between 250 and 320°C during 24 to 100 hours. Conversion resulted in all cases in shrunken and embrittled poly-1,3,4-oxadiazole films[2]. The films were brittle in such a manner that they disintegrated upon the slightest force applied upon them. No mechanical properties could be measured.

Embrittlement of converted polyhydrazide films has also been reported by Frazer and Sarasohn[14]. This in contrast to reported flexible converted polyhydrazide fibres prepared by the same group[15,16]. In both cases amorphous polyhydrazides with similar inherent viscosities were applied. Cumbersome conversions of polyhydrazide-related polyamide-hydrazides into poly-1,3,4-oxadiazole-amides resulting in inferior mechanical qualities of the latter, are also reported by Preston et al.[17].

The observed brittleness is likely to be caused by chain shrinkage upon conversion, a low molecular weight or a lack of orientation or a possibly combination of these phenomena.

Macroscopic shrinkage is caused by shrinkage of polyhydrazide macromolecules upon conversion into poly-1,3,4-oxadiazoles. Shrinkage of these macromolecules is caused by the ring closure of the hydrazide groups into the 1,3,4-oxadiazole groups, see figure 2. X-ray analysis showed that upon ringclosure the carbon-carbon distance in hydrazide segment decreases with 30%[17,18]. This means for the presently investigated poly(*p*-, *m*-phenylene)-hydrazide a size reduction of approx. 16% per monomeric unit upon conversion. If this would have been a freely jointed chain, its end-to-end distance would also have decreased with 16% since the end-to-end distance is proportional to the unit length. A polyhydrazide film does however not consist of freely jointed chains. The glassy poly(*p*-, *m*-phenylene)hydrazide matrix consists of entangled polymers stiffening and shrinking upon cyclodehydration into the corresponding poly-1,3,4-oxadiazole which results in stress build-up in the polymer matrix contributing to the embrittlement of the film.

Table 1. Elemental analysis of poly(*p*-, *m*-phenylene)hydrazide and poly(*p*-, *m*-phenylene)-1,3,4-oxadiazoles.

Polymer	p/m-ratio	η_{inh}† (dl/g)	C (wt.%)	N (wt.%)	H (wt.%)	C/N
PH-p/m-1	alternating	0.82*	56.05	16.02	3.58	3.50
POD-p/m-1	alternating		65.39	19.21	2.77	3.40
POD-0/100-1	0/100	1.5	66.15	19.58	2.92	3.38
POD-25/75-1	25/75	1.9	66.06	19.20	2.94	3.44
POD-25/75-2	25/75	1.2	62.70	18.43	2.76	3.44
POD-33/67-1	33/67	2.0	66.30	19.72	2.88	3.36
POD-50/50-1	50/50	2.7	64.55	18.78	2.85	3.44
POD-50/50-2	50/50	1.6	63.33	18.04	2.47	3.51
POD-50/50-3	50/50	4.2	64.22	18.43	2.91	3.48
POD-67/33-1	67/33	2.5	64.72	19.02	2.80	3.40
POD-75/25-1	75/25	2.0	66.06	19.23	2.85	3.44
POD-75/25-2	75/25	1.4	63.74	18.54	2.86	3.44
POD-75/25-3	75/25	2.9	64.51	19.11	2.80	3.38
POD-100/0-1	100/0	0.9	63.42	19.08	2.92	3.32
POD-100/0-2	100/0	2.2	59.20	16.60	2.89	3.56
Theoretical values	PH		59.26	17.28	3.73	3.43
	POD		66.67	19.44	2.80	3.43

† Inherent viscosity determined in concentrated sulphuric acid.

* Inherent viscosity determined in DMSO.

Table 2. Inherent viscosities of poly(*p*-, *m*-phenylene)hydrazides, as-prepared, before and after thermal conversion[2].

Polyhydrazide	Conversion cycles		Polyoxadiazole
η_{inh}(dl/g)*	Time (hr)	T (℃)	η_{inh} (dl/g)†
0.69	24	276	0.30
0.69	24	288	0.33
1.07	62/100	280/300	0.55
1.17	62/100	280/300	0.64
1.39	48	310	0.86

* Inherent viscosity determined in DMSO.

† Inherent viscosity determined in concentrated sulphuric acid.

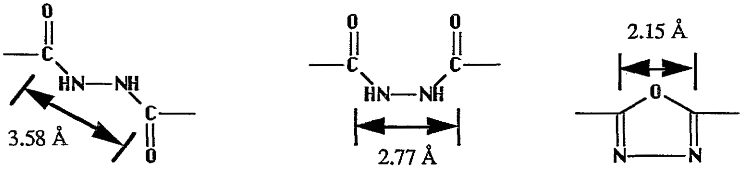

Fig. 2. Decrease in intramolecular carbon-carbon distance due to cyclodehydration.

Polyhydrazide films were observed to undergo a dimensional decrease of approximately 12%, during a thermal conversion of 48 hours at 300℃, slightly deviating from the calculated 16%, obviously due to hindered shrinkage in the solid state.

Conversion of oriented poly(*p*-, *m*-phenylene)hydrazide fibres yielded poly-1,3,4-oxadiazole fibres with superior mechanical properties[20]. We speculate that this orientation results in a controlled contraction of the polyhydrazide fibre upon cyclodehydration and thus minimising stress build-up, this in contrast to the non-oriented polyhydrazide film.

The observed brittleness can however not be explained in terms of stress build-up alone, since dissolving converted polyhydrazide in sulphuric acid, and thus eliminating stresses, followed by casting of this polymer solution onto a glass plate and immersion into a 50 wt.% aqueous sulphuric acid bath did not yield a flexible film. From this experiment it can be concluded that another factor is responsible for the observed brittleness. Besides stress build-up, mechanical behaviour of the converted films is of course determined by the molecular weight of the poly-1,3,4-oxadiazole formed in situ which is obviously too low since no flexible film is obtained after the above described immersion casting process. A similar strong dependence between intrinsic viscosity and the mechanical properties of converted poly(*p*-, *m*-phenylene)hydrazide fibres is also reported by Frazer and Reed[20]. Polyhydrazide films are flexible because of strong intermolecular forces due to hydrogen bonding between hydrazide groups in the polyhydrazide macromolecules. During a heating cycle these strongly interacting and flexible hydrazide groups are converted into rigid and less interacting 1,3,4-oxadiazole groups. A certain minimal intermolecular adherence between the macromolecules is required to attain flexibility of the final product. It is therefore believed that higher molecular weight poly-1,3,4-oxadiazoles are needed to overcome this decline in macromolecular interactions and thus maintaining flexibility of films and fibres. Low molecular weight of the final poly-1,3,4-oxadiazole can be due to the fact that the molecular weight of the initial polyhydrazide is too low or may be caused by a decrease in molecular weight due to chain rupture during conversion. These two phenomena may of course also occur simultaneously.

The inherent viscosities of poly-1,3,4-oxadiazoles obtained applying different polyhydrazides and heating cycles are represented in table 2. Poly-1,3,4-oxadiazoles with inherent viscosities varying between 0.30 to 0.86 dl/g were obtained[2]. It is shown that there exists a proportional relation between the inherent viscosities of polyhydrazides and poly-1,3,4-oxadiazoles. The inherent viscosity is obviously only a function of the inherent viscosity of the precursor polymer and is not influenced by the temperature or the duration of the thermal conversion. One would expect a decreasing inherent viscosity with conversion time and applied temperature in the case of degradation.

It can thus be concluded that flexible poly-1,3,4-oxadiazole films can only be obtained if polyhydrazides with higher inherent viscosities are used as a precursor polymer. However, stress build-up and chain shrinkage may then still have a deteriorating effect on the mechanical properties of poly-1,3,4-oxadiazole films.

One-step synthesis of poly-1,3,4-oxadiazoles.

Poly-1,3,4-oxadiazoles with higher inherent viscosities are easily prepared by a one-step synthesis using dicarboxylic acids and hydrazine as monomers. High molecular weight poly(*p*-phenylene)-1,3,4-oxadiazoles were prepared using the reaction originally reported by Iwakura et al.[7]. Poly(*p*-phenylene)-1,3,4-oxadiazoles having inherent viscosities from 2.9 to 3.2 dl/g. were obtained. Flexible yellow films were obtained by casting the sulphuric acid diluted reaction mixture onto a glass plate followed by immersion into a 50 wt.% aqueous sulphuric acid bath. Since low molecular weight poly-1,3,4-oxadiazoles were obtained when mixtures of terephthalic and isophthalic acid were used, another reaction procedure was chosen where instead of fuming sulphuric acid, a mixture of chlorosulphonic acid and 100% sulphuric acid was employed[12]. Less coloured products with moderate inherent viscosities were obtained, in all cases containing less than 0.7 wt.% sulphur. Poly-1,3,4-oxadiazoles with various ratios *para-* and *meta*-phenylene groups using mixtures of terephthalic and isophthalic acid, were obtained in nearly quantitative yield.

Elemental analysis indicates that the desired products were obtained, see table 1. The values found are somewhat lower than the theoretical values indicating some residual impurities. The quotient C/N is in good agreement with the theoretical value. Iwakura removes residual impurities by boiling the products in water during 5 hours prior to elemental analysis[7]. In our case further purification was however omitted since these polymers are used as precursor for the poly-1,2,4-triazole synthesis.

Infrared spectra of poly-1,3,4-oxadiazoles prepared by cyclodehydration of polyhydrazides and directly by a reaction of dicarboxylic acids with hydrazine sulphate are identical and are in agreement with the spectra given by Frazer et al.[6] and Iwakura et al.[7]

No or negligible sulphonation has taken place since only minor quantities of sulphur are found in the final product, in all cases lower than 0.25 wt.% except for POD-25/75-2 and POD–100/0–1 both containing 0.7 wt.% sulphur. Another argument against sulphonation is the fact that no enhancement in solubility is observed, a phenomenon often encountered upon sulphonation. The poly-1,3,4-oxadiazoles prepared are only soluble in concentrated sulphuric acid and in polyphosphoric acid. During polymerisation sulphonation must compete with the polycondensation reaction. Since only minor quantities of sulphur are found, the latter reaction takes place preferentially over the sulphonation reaction. Sulphonation might then additionally take place when the polycondensation reaction is complete. However, aryl substituted 1,3,4-oxadiazoles are considered as chemically resistant materials, for example 2,5-diphenyl-1,3,4-oxadiazole is not effected by concentrated HNO_3 or by a treatment with fuming H_2SO_4 at 100°C for 4 hours[21]. It is therefore believed that residual sulphur is not bound to the polymer by means of a sulphonation reaction but that it is present in an unbound state and is due to incomplete purification.

The polycondensation reaction is assumed to take place in two steps; first a condensation reaction between hydrazine and dicarboxylic acid followed by cyclodehydration of the hydrazide group into the 1,3,4-oxadiazole group[22], see figure 3.

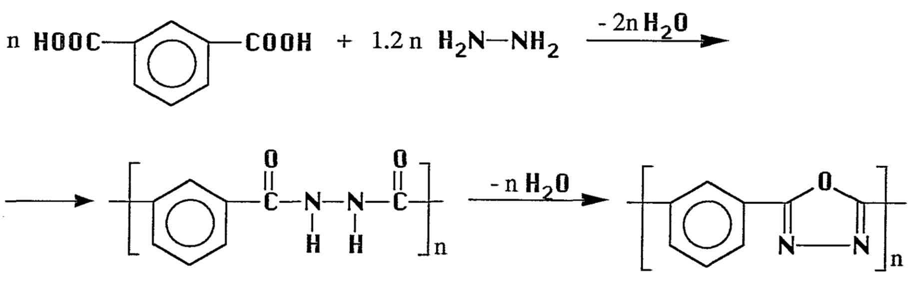

Fig. 3. Two step reaction mechanism for the formation of random poly(*p*-, *m*-phenylene)-1,3,4-oxadiazoles using hydrazine sulphate and isophthalic acid as monomers.

In case of an incomplete reaction, unclosed hydrazide groups are present in the final product and a carbonyl peak at 1720 cm^{-1} is observed in the IR-spectrum. The percentage unclosed rings in the final product can be determined by means of thermo-gravimetrical analysis. A TGA curve of POD-75/25-3 is represented in figure 4. Three distinct phases of weight loss can be observed[14]: at approximately 100°C the loss of absorbed water, between 250 and 400°C a weight loss can be observed due to the loss of water caused by cyclodehydration of unclosed hydrazide groups into 1,3,4-oxadiazole groups. A maximal weight loss is observed here in the theoretical case when no ring has yet been closed at all. Such a thermogram is obtained for a poly(*p*-, *m*-phenylene)hydrazide where a maximal weight loss of 11.1% is recorded. From the actual weight loss curve the percentage unclosed rings can be calculated. A weight loss of 1.0% was observed for POD-100/0-1 and POD-100/0-2 while for POD-25/75-2 a weight loss of 0.6% was recorded indicating the presence of 8 and 5% unclosed hydrazide groups, respectively. In all other cases weight losses of less than 0.4% were observed until degradation. At temperatures above 450°C a weight loss is observed due to loss of volatiles indicating final degradation of the polymer.

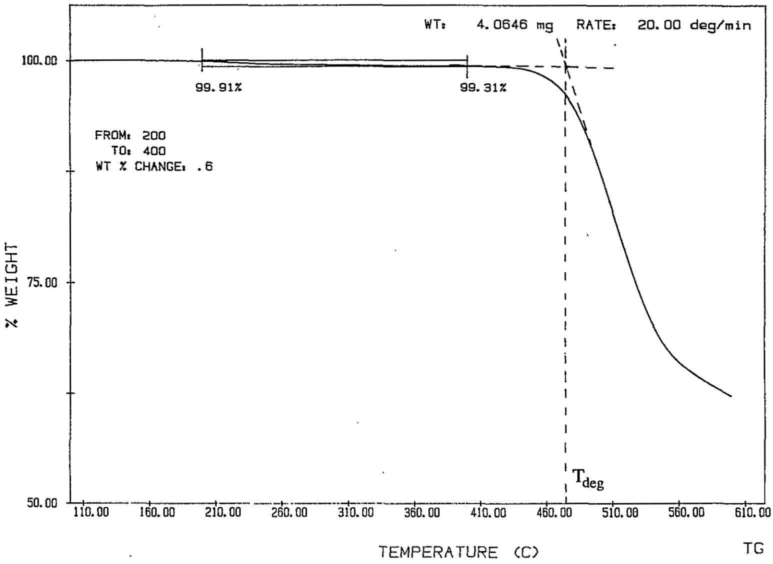

Fig. 4. Thermo-gravimetrical weight loss curve POD-25/75-1 recorded at a heating rate of 20°C/min.

The degradation temperature T_{deg} is defined as the point intersection of the tangents, see figure 4. In figure 5, the degradation temperatures of the poly(*p*-, *m*-phenylene)-1,3,4-oxadiazoles are plotted versus the content *p*-phenylene groups in the main chain. Increasing the content *p*–phenylene results in a more thermally stable product likely to be due to resonance stabilisation of the *p*-phenylene ring. These findings are in agreement with the results of Varma et al.[23] who studied the thermal stability of poly(*p*-, phenylene)-1,3,4-oxadiazole and poly(*m*-phenylene)-1,3,4-oxadiazole.

No glass transition temperature was observed for the poly(*p*-, *m*-phenylene)-1,3,4-oxadiazoles using DSC-techniques since these polymers undergo degradation before the glass transition is reached[24].

Flexible films could be prepared from poly(*p*-phenylene)-1,3,4-oxadiazoles prepared in fuming sulphuric acid with inherent viscosities of 2.8, 2.9, 3.0 and 3.2 dl/g, from POD-75/25-2 (η_{inh} = 2.9 dl/g), from POD-50/50-1 (η_{inh} = 2.7 dl/g) and from POD-50/50-3 (η_{inh} = 4.2 dl/g). All other films disintegrated upon handling. Flexible poly-1,3,4-oxadiazole films were investigated regarding their gas separation properties[10]. Flexibility did not seem to depend on the ratio *p*/*m*-phenylene groups in the main chain but merely on the inherent viscosity. A similar result is observed by Imai in the case of fibres; he only obtained tough filaments for random poly(*p*-, *m*-phenylene)-1,3,4-oxadiazoles containing 75% *p*- and 25% *m*-phenylene groups if the inherent viscosity was 1.7 dl/g or higher[25].

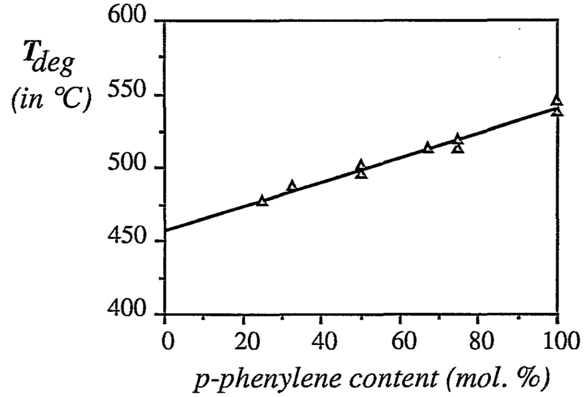

Fig. 5. Degradation temperatures (T_{deg}) of random poly(*p*-, *m*-phenylene)-1,3,4-oxadiazoles as a function of the amount of *p*-phenylene groups in the main chain.

In figure 6(A), an X-ray diffractogram of alternating poly(*p*-, *m*-phenylene)hydrazide powder is shown, indicating a completely amorphous product. On conversion a moderately oriented poly(*p*-, *m*-phenylene)-1,3,4-oxadiazole is obtained, figure 5 (B). X-ray diffractograms of POD-0/100-1, POD-50/50-3 and POD-100/0-1, figure 5 (C), (D) and (E) respectively, are similar to the alternating polymer and it is shown that POD-100/0-1, despite its more regular molecular structure, has almost no increased ordering as indicated by the identical WAXS-diffractogram.

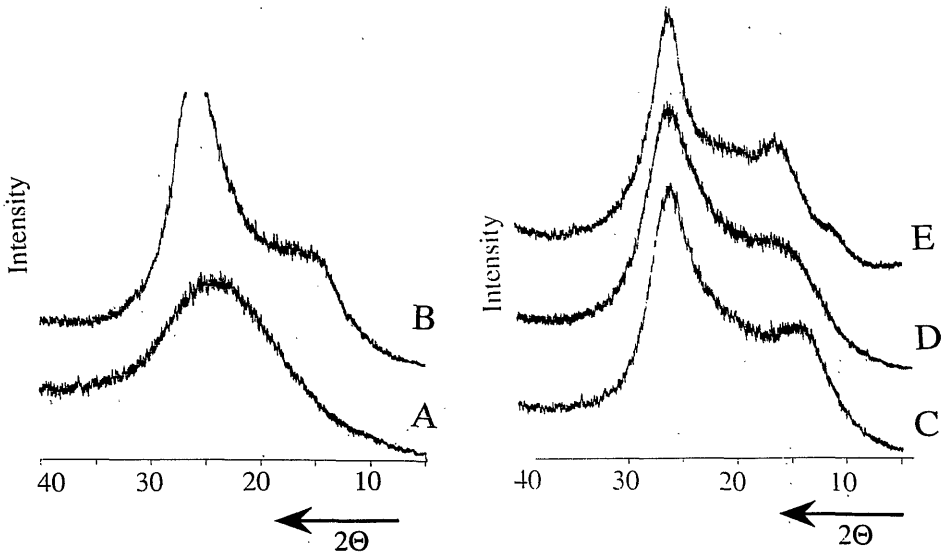

Fig. 6. WAXS-diffractograms of powdered samples of alternating poly(*p*-, *m*-phenylene)-hydrazide[2] (A) and poly(*p*-, *m*-phenylene)-1,3,4-oxadiazole[2] (B) and random poly(*p*-, *m*-phenylene)-1,3,4-oxadiazoles, POD-0/100-1, POD-50/50-3 and POD-100/0-1 (C), (D) and (E) respectively.

Poly-1,2,4-triazole via polyhydrazide

The conversion reaction of poly(*p*-, *m*-phenylene)hydrazide into poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole] was first investigated by Holsten and Lilyquist[8]. They determined the ideal reaction conditions. Poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles] with the highest inherent viscosities were obtained if the reaction was carried out at 175°C during 140 hours. Shorter reaction times are possible when higher reaction temperatures are employed resulting however in polymers with decreased inherent viscosities.

The elemental analysis of poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole] PT-p/m-1 is given in table 3. The experimental values found are somewhat lower than the theoretical ones. The carbonyl absorption peak in the IR-spectrum present in the precursor polymer has completely disappeared while an absorption peak at 700 cm^{-1} due to the phenyl group has appeared in the spectrum of the poly-1,2,4-triazole. The infrared spectrum is in agreement with the one of Korshak[26].

A DSC-thermogram of PT-p/m-1 is represented in figure 7. PT-p/m-1 has a glass transition temperature of 264℃. The exothermic peak at 319℃ was identified as cold crystallisation[27]. WAXS experiments indicated that films of alternating poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole] are completely amorphous[27].

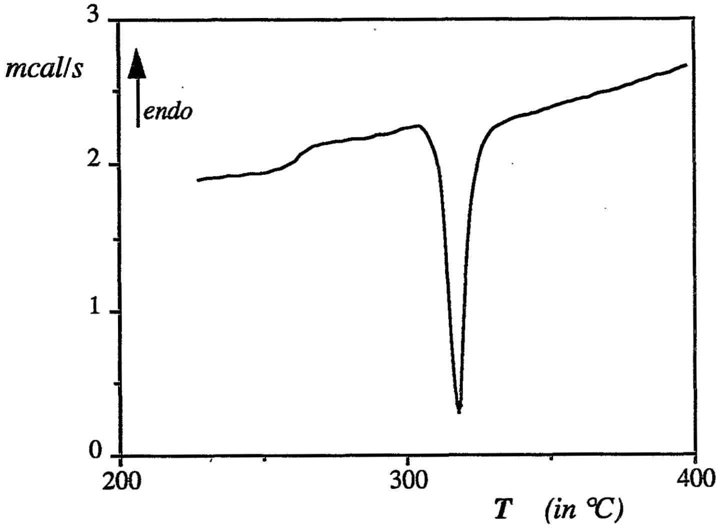

Fig. 7. DSC-thermogram for alternating poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole] (PT-p/m-1) recorded with a heating rate of 20℃/min. under nitrogen.

Poly-1,2,4-triazoles via poly-1,3,4-oxadiazoles.

As precursor polymers, high molecular weight poly-1,3,4-oxadiazole are more easily obtained than polyhydrazides. While the polyhydrazide synthesis requires high purity monomers and necessitates vigorous exclusion water, making this synthesis a laborious one, the direct formation of poly-1,3,4-oxadiazoles from dicarboxylic acids and hydrazine sulphate is relatively simple.

The conversion of poly(*m*-phenylene)-1,3,4-oxadiazoles and poly(*p*-phenylene)-1,3,4-oxadiazoles into the corresponding poly-1,2,4-triazoles was first investigated by D'Yachenko et al.[9] and the preparation is essentially the same as the method described by Holsten and Lilyquist where polyhydrazide is used as a precursor polymer. The reaction differs in its higher reaction temperature, 225 instead of 175℃, and its shorter reaction time, 35 instead of 140 hours. In both cases the precursor polymer should dissolve during the reaction. In our case the poly-1,3,4-oxadiazoles dissolved only to some extent during the reported 35 hours. During prolonged reaction times, up to 140 hours, the precursor poly-1,3,4-oxadiazoles dissolved completely but gave poly-1,2,4-triazoles in only a 5 to 10 % yield. D'Yachenko et al. do not report on slow dissolution of poly(phenylene)-1,3,4-oxadiazole in PPA. Their poly-1,3,4-oxadiazoles may have dissolved readily due to the low molecular weight of their precursor polymers.

We have modified the reaction procedure, and added the as-prepared poly-1,3,4-oxadiazoles to PPA prior to the addition of aniline.

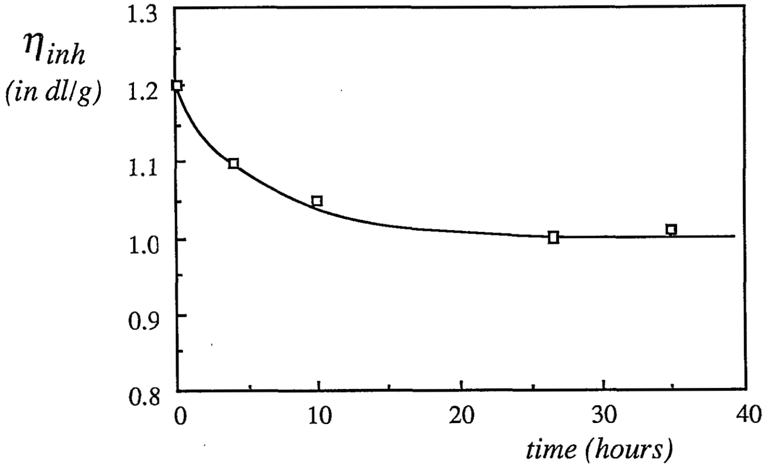

Fig. 8. Inherent viscosity of POD-25/75-2 in PPA at 150°C as a function of time. Inherent viscosities are determined at 30°C of a 0.5 g polymer solution in 100 ml concentrated sulphuric acid.

Due to addition of aniline to the PPA, the "solvent strength" of the latter is decreased. First dissolving poly-1,3,4-oxadiazole in PPA followed by the addition of aniline is dissuaded because of expected degradation of the precursor polymer and thus resulting in low molecular weight poly-1,2,4-triazoles. To show this effect, POD-25/75-2 was dissolved in PPA at 150°C and the inherent viscosity was determined as a function of time, see figure 8. Degradation takes place indeed, and the value of the inherent viscosity decreases with 20% during the first 15 hours and remains constant thereafter until the end of the experiment. The decrease in inherent viscosity is however acceptable and all the poly-1,2,4-triazoles represented in table 3 were prepared by dissolving the precursor polymer in PPA followed by the addition of aniline.

The infrared spectra of these poly-1,2,4-triazoles are identical to the infrared spectrum of the poly-1,2,4-triazole prepared via the polyhydrazide route. The elemental analysis indicates some impurities. Analysis showed residual amounts of phosphorous. Poly-1,2,4-triazoles with moderate inherent viscosities yielding films with good mechanical strength were obtained. These membranes were tested for their gas separation properties[10].

The synthesis of poly-1,2,4-triazoles can further be simplified by performing the complete reaction as a one-pot synthesis[28]. Firstly the reaction between dicarboxylic acid and hydrazine yielding a poly-1,3,4-oxadiazole is carried out in PPA. When this polycondensation reaction is complete extra PPA is added to the reaction mixture followed by the addition of aniline. The reaction temperature is increased and the poly-1,3,4-oxadiazole is converted into the corresponding poly-1,2,4-triazole.

Table 3. Elemental analysis of poly-1,2,4-triazoles.

Polymer	p/m-ratio	η_{inh}* (dl/g)	C (wt.%)	N (wt.%)	H (wt.%)	C/N
PT-p/m-1	alternating	0.85	73.04	18.02	4.06	4.05
PT-0/100-1	0/100	0.73	71.73	17.51	3.87	4.10
PT-25/75-1	25/75	1.36	73.02	17.77	4.07	4.11
PT-50/50-1	50/50	1.37	71.14	17.22	3.78	4.13
PT-75/25-1	75/25	1.84	71.51	17.56	3.99	4.07
PT-75/25-2	75/25	1.60	73.5	18.2	4.1	3.99
Theoretical			76.70	19.17	4.14	4.00

* Inherent viscosity determined in formic acid.

The poly-1,2,4-triazoles were characterised with DSC and TGA techniques. TGA experiments show the occurrence of a weight loss between 250 and 400℃ due to the formation and escape of water caused by a ring closure reaction of unclosed 1,2,4-triazole groups. The reaction between poly-1,3,4-oxadiazole and aniline is believed to occur via an intermediate[18], see figure 9.

If the reaction is not complete, unclosed 1,2,4-triazole rings are present in the final product. These groups will undergo cyclodehydration during a TGA experiment and the percentage unclosed groups can be calculated, see table 4.

These unclosed rings can be closed by means of a heat treatment at 350℃ for 24 hours. Further investigations for the ideal reaction conditions should minimise the amount of unclosed rings because they represent possible weak spots for thermally or chemically induced degradation.

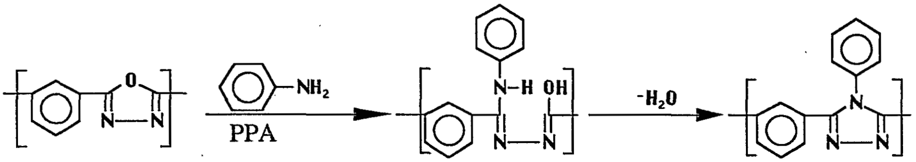

Fig. 9. Formation of a poly(4-phenyl)-1,2,4-triazole out of a poly-1,3,4-oxadiazole via an intermediate.

Table 4. TGA-analysis of poly-1,2,4-triazoles.

Polymer	p/m-ratio	relative weight loss (wt.%)	percentage unclosed rings (%)
PT-p/m-1	alternating	2.07	26
PT-0/100-1	0/100	0.88	11
PT-25/75-1	25/75	1.35	17
PT-50/50-1	50/50	2.47	31
PT-75/25-1	75/25	0.97	12
PT-75/25-2	75/25	1.30	16

An increase in thermal stability with increasing ratio of *para*-phenylene groups in the main chain as found for the poly-1,3,4-oxadiazoles, is not found for the poly-1,2,4-triazoles, see figure 10. This is probably due to the presence of weak spots in the macromolecules, caused by prolonged exposure to the harsh reaction medium, PPA. These weak spots decrease the degradation temperature and overshadow the stability dependence on the ratio *para-/meta-*phenylene groups.

The TGA curve of the alternating poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole] is similar to the curves of the random polymers with respect to degradation and ring closure behaviour.

The glass transition temperature increases with increasing *p*-phenylene ratio as was shown by DSC and torsion pendulum experiments, see figure 11. This is due to an increased chain stiffness of the latter and which is also found by other authors for other copolymers[29,30]. Upon extrapolation, a theoretical glass transition temperature of 380°C is obtained for poly[*p*-phenylene-(4-phenyl)-1,2,4-triazole]. A meaningful estimation of the glass transition temperature of poly[*p*-phenylene-(4-phenyl)-1,2,4-triazole] using the Woods[31] or Gordon-Taylor[32] equation was not possible since too few glass transition temperatures of intermediate copolymers are available.

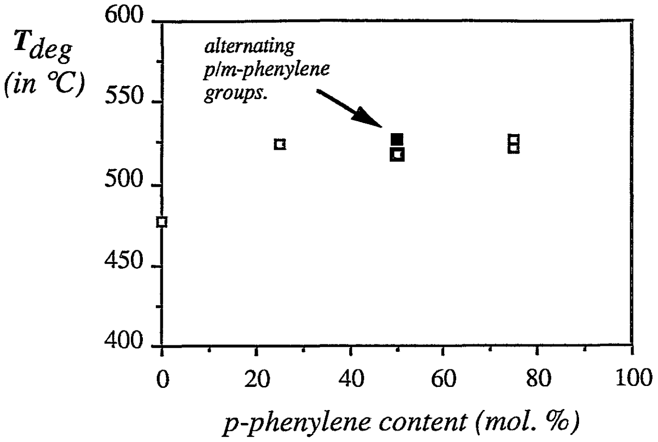

Fig. 10. Degradation temperatures (T_{deg}) of poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles] as a function of the amount of *p*-phenylene groups in the main chain.

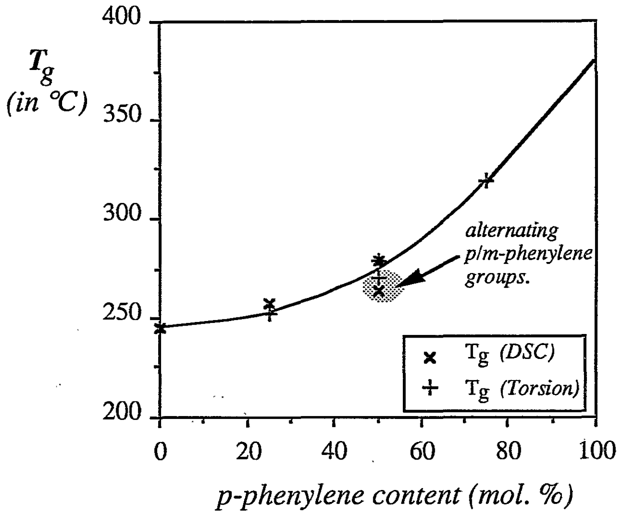

Fig. 11. Glass transition temperatures (T_g) of poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles] as a function of the ratio *p*-phenylene groups in the main chain.

The glass transition temperature of the alternating poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles] is slightly lower than the T_g of the random variant, possibly due to the higher molecular weight of the latter.

When the *p*-phenylene content was 75% no glass transition temperature was detectable with DSC. With a torsion pendulum the glass transition was however readily detected. In the DSC thermogram the magnitude of the heat capacity jump at the glass transition is proportional to the amorphous fraction of the polymer[33]. Increasing the ratio of *p*-phenylene groups gives a more linear polymer which obviously results in a polymer matrix with increased ordering and thus a decreased amorphous fraction. In figure 12, WAXS-diffractograms indicate that this is indeed the case.

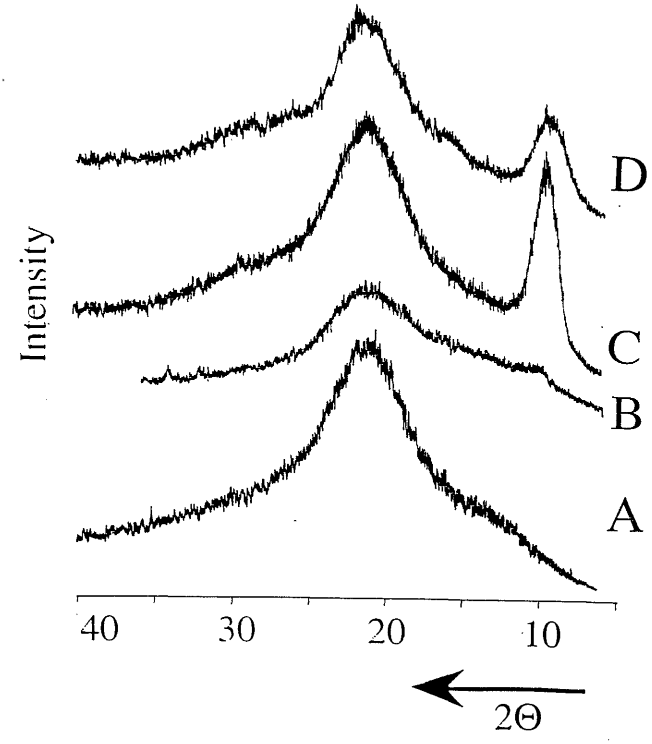

Fig. 12. X-ray diffractograms for PT-0/100-1(A), PT-25/75-1(B), PT-50/50-1(C) and PT-75/25-1(D).

The exothermic peak representing cold crystallisation in the rubbery phase is completely absent in the case of random poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles] including the 100% *meta*-phenylene variant. Alternating and random poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles] films are prepared similarly out of formic acid solutions. If cold crystallisation were to occur in the case of only completely amorphous poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles] then PT-0/100-1 and PT-25/75-1 should also undergo cold crystallisation since they are also completely amorphous as indicated by WAXS-diffractograms, see figure 12. It is therefore believed that cold crystallisation can only occur for poly-1,2,4-triazoles where *para*- and *meta*-phenylene groups are incorporated alternatingly. Similar subtle influences of the macromolecular structure on cold crystallisation have also been reported by Burfield and Tanaka[34]. They found that cold crystallisation in the rubbery phase occurred much more readily in the case of natural rubber, which is a completely *cis*-1,4-polyisoprene product, than in the case of synthetic analogues of 99% *cis*-1,4 purity. The cold crystallisation phenomenon is obviously very sensitive to macromolecular irregularities. In the alternating poly-1,2,4-triazole, *para*- and *meta*-phenylene groups are incorporated in a perfectly alternatingly fashion and are capable to achieve a crystalline morphology upon cold crystallisation whereas in the case of the random poly-1,2,4-triazoles the *p*-/*m*-phenylene groups are incorporated randomly and obviously lack the possibility of increasing their crystallinity through cold crystallisation.

CONCLUSIONS

Aromatic poly-1,3,4-oxadiazoles are prepared by means of a polycondensation reaction of terephthaloyl chloride and isophthalic dihydrazide and by means of a polycondensation reaction between terephthalic and isophthalic acid and hydrazine sulphate. The latter reaction is more simple and yields poly-1,3,4-oxadiazoles with higher inherent viscosities. Flexible poly-1,3,4-oxadiazole films can be obtained only if the inherent viscosities of the polymers used, are higher than 2.7 dl/g. Thermal stability was found to increase with increasing content of *p*-phenylene groups.

Aromatic poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles] were prepared using polyhydrazides with alternating *para*- and *meta*- phenylene groups and poly-1,3,4-oxadiazoles with a random incorporation of *para*- and *meta*- phenylene groups in the main chain as precursor polymers. Poly-1,2,4-triazoles were obtained in high yield after alteration of the original synthesis procedure given by D'Yachenko et al.[9] The glass transition temperature was found to increase with increasing ratio *p*-phenylene groups in the main chain. Cold crystallisation was only observed for the alternating polymer and its occurrence is believed to be directly related to the manner of incorporation of the phenylene groups in the main chain.

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LITERATURE

1. P.E. Cassidy, Thermally stable polymers, Marcel Dekker, New York (1980).
2. B. Gebben, Thermally stable and chemically resistant polymer membranes, Aromatic polyoxadiazoles and polytriazoles, Ph. D. Thesis, University of Twente, The Netherlands, 1988.
3. B. Gebben, M.H.V. Mulder and C.A. Smolders, J. Membrane Sci., 46, 29-41(1989).
4. R.J. Cotter and M. Matzner, "Ring-forming polymerizations" in A.T. Blomquist and H. Wasserman, (Eds.), "Organic Chemistry", Vol. 13B, 1, Academic Press, New York, 1972.
5. A.H. Frazer and F.T. Wallenberger, J. Polym. Sci., A2, 1147-1156(1964).
6. A.H. Frazer, W. Sweeny and F.T. Wallenberger, J. Polym. Sci., A2, 1157-1169 (1964).
7. Y. Iwakura, K. Uno and S. Hara, J. Polym. Sci., A, 3, 45-54(1965).
8. J.R. Holsten and M.R. Lilyquist, J. Polym. Sci.,A, 3, 3905-3917(1965).
9. A.V. D'Yachenko, V.V. Korshak and E.S. Krongauz, Vysokomol. Soedin., Ser. A, 9(10),2231-2235(1967).
10. E.R. Hensema, J.P. Boom, M.E.R. Sena, M.H.V. Mulder and C.A. Smolders, to be published (*Chapter 4 of this thesis*).
11. A.H. Frazer and F.T. Wallenberger, J. Polym. Sci., A2, 1137-1145(1964).
12. Fr. Demande, 2.111.913 (1972).
13. J.A. Zapp, Science, 190, 422(1975).
14. A.H. Frazer and I.M. Sarasohn, J. Polym. Sci.: Part A-1, 4, 1649-1664(1966).
15. A.H. Frazer and D.R. Wilson, Applied Polymer Symposia, 9, 89-106(1969).
16. A.H. Frazer and F.T. Wallenberger, J. Polym. Sci.: Part A, 2, 1171-1179(1964).
17. J. Preston, W.B. Black and W.L. Hofferbert, J. Macromol. Sci.-Chem, A7, 45-65(1973).
18. V.V. Korshak, G.L. Berestneva, I.P. Bragina, G.V. Yeremina and V.V. Krylova, Vysokomol. Soyed. A16, 1714-1722 (1974).
19. V.V. Korshak, G.L. Berestneva, I.P. Bragina and S.A. Astafiev, J. Polym. Sci., Polym. Symp., 47, 25-34(1974).
20. A.H. Frazer and T.A. Reed, J. Polym. Sci., C, 19, 89-94(1967).
21. A. Hetzheim and K. Möckel, "Recent advances in 1,3,4-oxadiazole chemistry", in A.R. Katritzky and A.J. Boulton (Eds.), "Advances in heterocyclic chemistry", Vol. 7, Academic Press, New York, 1966.
22. V.V. Korshak, G.L. Berestneva, AV. Volokhina, A.B. Raskina, D.V. Bibileishvili, P.V. Petrovskii, S.A. Astaf'ev, N.P Okromchedlidze and G.I. Kudryavtsev, Vysokomol. Soyed. A24, 36-42, 1982.
23. I.K. Varma, R.M. Sambadam and D.S. Varma, Makromol. Chem., 170, 117-130(1973).
24. B. Gebben, M.H.V. Mulder and C.a. Smolders, J. Polym. Sci., Polym. Chem. Ed, 26, 1757-1768(1988).
25. Y. Imai, J. Appl. Polym. Sci., 14, 225-239 (1970).
26. V.V. Korshak, E.S. Krongauz and A.V. D'Yachenko Doklady Akademii Nauk SSSR, 176, 338-340 (1967).

27. B. Gebben, M.H.V. Mulder and C.A. Smolders, J. Polym. Sci., Polym. Chem. Ed., 27, 3481-3499 (1989).
28. A.H. Schroeder, P. Denisevich, S. Suzuki and V.P. Kurkov, U.S. Pat. 4,519,940(1985).
29. H.G. Weijland, P.J. Hoftijzer and D.W. van Krevelen, Polymer, 11, 79-87 (1970)
30. D.R. Wiff, M.S. Altieri and I.J. Goldfarb, J. Polym. Sci., Polym. Phys. Ed., 23, 1165-1176 (1985).
31. L.A. Woods, J. Polym. Sci., 38, 319-350(1958).
32. M. Gordon and J.S. Taylor, J. Appl. Chem., 2, 493-500(1952).
33. J. Menczel and B. Wunderlich, Polym. Prepr., 1, 255-256(1986).
34. D.R. Burfield and Y. Tanaka, Polymer, 28, 907-910(1987).

3

Syntheses and properties of related polyoxadiazoles and polytriazoles.

E.R. Hensema, M.E.R. Sena‡, M.H.V. Mulder and C.A. Smolders

SUMMARY

New aromatic poly-1,2,4-triazoles and poly-1,3,4-oxadiazoles are studied as thermally stable membrane materials. Various groups were introduced onto the pendant phenyl groups of poly-1,2,4-triazoles. Glass transition temperature, degradation temperature and cold crystallisation behaviour were studied as a function of these groups. Cold crystallisation appeared to be highly sensitive to macromolecular regularity. The solubility of poly-1,3,4-oxadiazoles was highly improved upon incorporation of 5-*t*-butylisophthalic, 1,1,3-trimethyl-3-phenylindane, 4,4'-(2,2'-diphenyl)hexafluoro propane and diphenyl ether groups into the polymeric main chain whereas the high glass transition temperatures and degradation temperatures typical for aromatic poly-1,3,4-oxadiazoles were maintained.

INTRODUCTION

Aromatic poly-1,2,4-triazoles and poly-1,3,4-oxadiazoles are studied as new thermally stable membrane materials for gas separation applications. Especially poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole] is known for its excellent gas separation properties[1]. The use of these polymers as membrane materials is however hampered due to their poor solubility limiting the number of possibilities of fabricating membranes with a desired morphology, like asymmetric structures. For example, poly(*p*-, *m*-phenylene)-1,3,4-oxadiazole is only soluble in concentrated sulphuric acid, which is a very difficult solvent to handle in practice.

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‡ IMA, Universidade de Rio de Janeiro, Brasil.

In this paper we wish to report on the syntheses and physical properties of poly-1,3,4- oxadiazoles and poly-1,2,4-triazoles where various functional groups are incorporated *into* and *onto* the polymer backbone with the aim to increase their solubility while maintaining their thermal stability. The relation between the gas separation properties and these molecular structure was also studied and is reported elsewhere[2].

The solubility of polymers is often increased when flexible bonds, large pendant groups or polar substituents are incorporated in the polymer backbone. The introduction of large pendant bulky groups along the polymer backbone results in a less ordered polymer matrix increasing the solubility characteristics. This is nicely illustrated by the fact that poly(*p*-, *m*-phenylene)-1,3,4-oxadiazoles are only soluble in concentrated sulphuric acid while poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles], having an extra pendant phenyl group, are also soluble in *m*-cresol and formic acid.

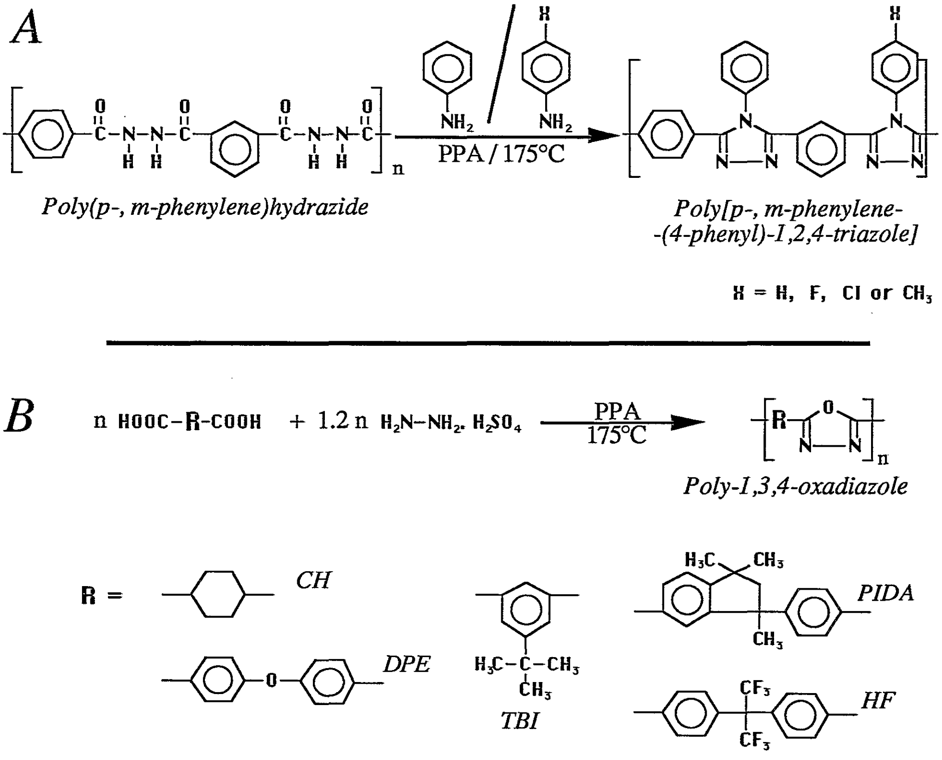

Fig. 1. Preparation of aromatic poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles] out of a polyhydrazide in a reaction medium consisting of polyphosphoric acid and mixtures of aniline and *para*-substituted aniline derivatives (**A**).
Preparation of poly-1,3,4-oxadiazoles using dicarboxylic acids,R(COOH)$_2$, and hydrazine sulphate as monomers (**B**).

Solubility is also mostly increased if instead of aromatic groups aliphatic groups are incorporated into the polymer backbone but a significant reduction in thermal stability is also observed. Incorporation of aliphatic groups for that reason was avoided (Nonetheless, cyclohexane was incorporated as a comparison to the aromatic poly(*p*, *m*-phenylene-1,3,4-oxadiazoles).

A number of authors have reported on poly(1,3,4-oxadiazoles) with increased solubility characteristics. Iwakura has, for example, reported on poly-1,3,4-oxadiazoles where the phenylene ring has been replaced by a pyridine ring. These polymers are soluble in formic acid, DMF and DMSO. However these polymers were not synthesised and studied here since low inherent viscosities where reported[3].

Russian workers have developed so called "Cardo" poly-1,3,4-oxadiazoles containing a bulky phthalide group. Poly-1,3,4-oxadiazoles containing this group have extensively been studied and the preparation of porous membranes of poly-1,3,4-oxadiazoles containing this group has been patented[4].

The functional groups that where incorporated into poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles in this study, together with their syntheses are represented in figure 1.

A number of reaction routes are known for the preparation of these polymers[5]. Poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles] with alternating *para*- and *meta*-phenylene groups were prepared by means of a reaction of aniline and aniline derivatives with poly(*p*-, *m*-phenylene)hydrazide in polyphosphoric acid, see figure 1 (A). Holsten and Lilyquist have extensively studied this reaction using polyhydrazide as a precursor polymer in combination with aniline[6]. Poly(*p*-, *m*-phenylene)hydrazide is prepared by means of a polycondensation reaction between terephthaloyl chloride and isophthaloyl dihydrazide[7].

High molecular weight aromatic poly-1,3,4-oxadiazoles were prepared directly using various dicarboxylic acids and hydrazine sulphate as monomers, see figure 1 (B). This reaction route was originally reported by Iwakura et al.[8].

EXPERIMENTAL

Materials

A mixture of *cis*- and *trans*-1,4-cyclohexane dicarboxylic acid was purchased from Aldrich. The pure *cis*- (*c*-CH) and the *trans*-isomer (*t*-CH) were obtained from this mixture by means of a treatment with chloroform[9].

The dicarboxylic acids: 4,4'-diphenyl ether (DPE), 1,1,3-trimethyl-3-phenylindan-4',5-dicarboxylic acid (PIDA) and 5-*t*-butylisophthalic acid (TBI) are Amoco products and 4,4'-(2,2'-diphenyl)hexafluoro propane dicarboxylic acid (HF) was supplied by Hoechst. These dicarboxylic acids were used as received.

All other chemicals were supplied by Merck, and were used as received, except NMP which was distilled under reduced pressure over CaH_2, lithium chloride which was dried in a vacuum oven at 150°C and aniline which was distilled under reduced pressure and its colourless distillate stored under nitrogen in a sealed flask in a refrigerator.

Isophthaloyl dihydrazide was prepared from isophthaloyl dimethyl ester and hydrated hydrazine[10].

Poly(*p*-, *m*-phenylene)hydrazide synthesis[7,10]

Isophthaloyl dihydrazide, 74.24 g (0.382 mol) and 16.21 g LiCl are dissolved in a three necked flask containing 600 ml NMP at 60°C under dry nitrogen. After dissolution the stirred solution is cooled to 0°C and 77.62 g (0.382 mol) terephthaloyl chloride is added in 4 equal portions. Each following portion is added when the terephthaloyl chloride of the previous portion has completely dissolved. Total addition lasts approximately 2 hours. The viscous solution is stirred overnight and the polymer is precipitated and washed in hyperfiltrated water. After additional washing with ethanol the polymer is dried in a vacuum oven at 150°C during at least 24 hours.

Two batches of polyhydrazide were prepared having inherent viscosities of 0.86 and 0.82 dl/g, respectively (0.5 g polymer solution in 100 ml DMSO).

Poly-1,2,4-triazole synthesis using polyhydrazide as a precursor polymer[6]

In a three necked flask 310 g polyphosphoric acid (PPA) is heated to 150°C under nitrogen. Aniline, 76.65 g (0.823 mol), is added dropwise to the stirred solution, meanwhile maintaining the temperature at 150°C. After addition, the temperature is raised to 175°C, and 10 g poly(*p*-, *m*-phenylene)hydrazide is added. The reaction mixture is kept at this temperature during 140 hours and poured into hyperfiltrated water and neutralised with sodium hydroxide under stirring. The product is washed in a 5% sodium hydroxide solution and twice in hyperfiltrated water. Subsequently the product is extracted with ethanol using a Soxhlet extractor after which it is dried in a vacuum oven at 150°C during 24 hours. The product is dissolved in formic acid and insoluble parts are removed by means of filtration over a 5 µm filter. These solutions are directly used for poly-1,2,4-triazole film preparation, as will be discussed below.

The polymers were obtained in a good yield. Instead of aniline, also mixtures of aniline and aniline derivatives have been employed. In all cases a ratio of 0.823 mol aniline and aniline derivative per 310 g PPA has been applied.

Poly-1,3,4-oxadiazole synthesis[8]

In a three necked flask under a dry nitrogen flux 0.05 mol dicarboxylic acid and 0.06 mol hydrazine sulphate are added to 155 g PPA. The mixture is homogenised under stirring and heated to the reaction temperature of 100-175°C and maintained at this temperature for 10 to 21 hours. The reaction medium becomes very viscous with increasing reaction time.
The polymer solution is precipitated in hyperfiltrated water and neutralised with sodium hydroxide. The product is repeatedly washed with hyperfiltrated water and dried in a vacuum oven at 60°C. The polymers were obtained in a quantitative yield.

Preparation of homogeneous films

Poly-1,2,4-triazoles

Homogeneous poly-1,2,4-triazole films are prepared from a 15 wt.% polymer solution in formic acid. Inhomogenities were removed from this solution by filtration over a 5 μm filter. The solution is cast on a glass plate using casting knives with slit heights of 0.3 and 0.5 mm, followed by evaporation of the solvent in a nitrogen atmosphere at room temperature. After evaporation, the glass plate is immersed into a water bath and the poly-1,2,4-triazole film is easily removed from the glass plate. Transparent films are obtained with thicknesses between 20 and 60 μm. The films were dried in a vacuum oven during at least 24 hours at 150°C.

Poly-1,2,4-oxadiazoles

For PIDA-POD and HF-POD the same procedure was followed but in this case trifluoro acetic acid was used as a solvent. For CH-POD, DPE-POD and TBI-POD, formic acid was used while for the 50/50 copolymer HF/DPE-POD NMP was used as a solvent which was evaporated at 150°C.

Characterisation

Inherent viscosity

The inherent viscosities are determined of 0.5 g polymer solutions in 100 ml solvent at 30°C. For the polyhydrazides DMSO is used as a solvent while for the poly-1,2,4-triazoles and poly-1,3,4-oxadiazoles formic acid was used. The inherent viscosities of PIDA-POD and HF-POD were determined in concentrated sulphuric acid, while for the copolymer HF/DPE-POD NMP was used as a solvent.

Differential Scanning Calorimetry (DSC)

DSC measurements are performed on a Perkin-Elmer DSC 4 in combination with a System 4 Microprocessor Controller and a Thermal Analysis Data Station (TADS), model 3700. The polymer samples are placed in aluminium sample pans and the temperature is increased with a heating rate of 20°C/min. from 100 to 400°C under a nitrogen purge gas stream. The sample is cooled with 320°C/min. to 100°C and a second run is recorded from 100 to 450°C again with a heating rate of 20°C/min. As glass transition temperature (T_g) the midpoint of the transition is taken, calculated by means of the TADS software.

Thermo-Gravimetrical Analysis (TGA)

TGA experiments are carried out on a Perkin-Elmer TGS-2 in combination with a system 4 microprocessor Controller and a Thermal Analysis Data Station, model 3700. Experiments are carried out under a nitrogen purge gas stream from 50 to 600°C. The temperature of the polymer samples is increased with a heating rate of 20°C/min. Weight loss over a certain temperature interval is calculated by means of the TADS software.

The degradation temperature (T_{deg}) is defined as the point of intersection of the tangents in the thermogram was taken, see figure 2.

RESULTS AND DISCUSSION

Poly-1,2,4-triazoles via polyhydrazides

The preparation of high molecular weight poly-1,2,4-triazoles using polyhydrazide as a precursor polymer was originally reported by Holsten and Lilyquist[6]. The reaction is carried out in PPA containing an excess of aniline. The ideal concentrations of the reactants were determined as being 10 g polyhydrazide and 0.823 mol aniline per 310 g PPA.

We have incorporated aniline in combination with aniline derivatives and studied the effect on the physical properties of the polymers prepared. The effect on the gas separation properties of these poly-1,2,4-triazoles are reported elsewhere[2].

Poly-1,2,4-triazoles where prepared from two batches of polyhydrazides having inherent viscosities of 0.86 and 0.82 dl/g.

Elemental Analysis.

Elemental analysis of C, H and N were carried out. In table 1, the C/N and C/H ratio of the elemental analysis of the polyhydrazides and the poly-1,2,4-triazoles are given.

The experimental values found were somewhat lower than the theoretical ones. Nevertheless, the C/N and C/H ratios a close to their theoretical values indicating residual impurities, most likely to be polyphosphoric acid[13]. Polyhydrazide and poly-1,2,4-triazole are prepared reproducibly, as is indicated by the elemental analysis of PH-p/m-1, PH-p/m-2, PT-p/m-1, PT-p/m-2 and PT-p/m-3.

Table 1. Inherent viscosities and elemental analyses of polyhydrazides and poly-1,2,4-triazoles.

Polymer	contents aniline/ aniline derivative[*]		η_{inh}[†] (dl/g)	C/N[‡] found	C/N[‡] theor.	C/H[‡] found	C/H[‡] theor.
PH-p/m-1			0.82	3.50	3.43	15.66	15.89
PH-p/m-2			0.86	3.50	3.43	14.32	15.89
PT-p/m-1	100%	aniline	0.85	4.05	4.00	17.99	18.53
PT-p/m-2	100%	aniline	0.94	4.06	4.00	19.42	18.53
PT-p/m-3	100%	aniline	1.01	4.13	4.00	19.57	18.53
PT-p/m-25Cl	25%	*p*-Cl	0.94	4.07	4.00	17.09	19.07
PT-p/m-50Cl	50%	*p*-Cl	0.80	4.08	4.00	16.97	19.64
PT-p/m-75Cl	75%	*p*-Cl	0.80	4.08	4.00	20.70	20.24
PT-p/m-100Cl	100%	*p*-Cl	0.78	4.16	4.00	21.62	20.84
PT-p/m-25F	25%	*p*-F	0.99	4.07	4.00	19.27	19.08
PT-p/m-50F	50%	*p*-F	1.10	4.05	4.00	19.11	19.65
PT-p/m-100F	100%	*p*-F	0.95	4.07	4.00	19.95	20.85
PT-p/m-*p*-Me	100%	*p*-Me	1.12	4.36	4.28	17.08	16.26
PT-p/m-*o*-Me	100%	*o*-Me	0.98	4.21	4.29	17.44	16.26

[*] Proportions aniline/aniline derivative added to the reaction medium, for example PT-p/m-75Cl means that a mixture consisting of 25% aniline and 75% *p*-chloro aniline is applied, *p*-F stands for *p*-fluoro aniline, *p*-Me is *p*-toluidine and *o*-Me is *o*-toluidine.

[†] Inherent viscosities were determined from polymer solutions (0.5 g/dl) at 30°C. DMSO was used as solvent in the case of polyhydrazide and formic acid in the case of the poly-1,2,4-triazoles.

[‡] determined using elemental analysis (wt.%/wt.%).

The chlorine contents of PT-p/m-25Cl and PT-p/m-50Cl were determined being 4.52 and 8.21 wt.%, respectively. This indicates that incorporation of chloro aniline is favoured over aniline itself since incorporation based on stoichiometric concentrations in the reaction medium would have yielded theoretical chlorine values of 3.89 and 7.5 wt.%, respectively.

Aniline or its derivatives forms a complex with PPA. This complex is in equilibrium with the free amines. Since only free amines can react with polyhydrazide, relatively more free chloro aniline must be available than can be accounted for on the basis of the ratio of aniline/chloro aniline present in the reaction medium. This means that equilibrium between complex and free amine has shifted into the direction of the latter one being chloro aniline. Similar incorporations are assumed to have taken place in the case of PT-p/m-75Cl, PT-p/m-25F and PT-p/m-50F.

Cyclodehydration

The results obtained with TGA and DSC techniques are given in table 2. In figure 2, a TGA run of PT-p/m-25F and in figure 3 two successive DSC curves of this poly-1,2,4-triazole are represented.

Table 2. Film appearance and thermal properties of the poly-1,2,4-triazoles*.

Polytriazole	Film* appearance	T_g† 1st run (°C)	2nd run (°C)	T_{cc}‡ (°C)	T_m§ (°C)	T_{deg} (°C)	Δw (200-400°C) (wt.%)
PT-p/m-1	light yellow	264	-	319	425	527	2.07
PT-p/m-2	light yellow	267	282	324	427	524	1.65
PT-p/m-3	light yellow	261	-	315	425	521	1.82
PT-p/m-25Cl	yellow	271	288	-	-	504	1.52
PT-p/m-50Cl	deep yellow	269	276	-	-	489	2.30
PT-p/m-75Cl	blue	271	278	-	-	484	1.45
PT-p/m-100Cl	deep blue	274	279	373	423	486	1.77
PT-p/m-25F	light yellow	257	266	344	407	507	1.11
PT-p/m-50F	light yellow	269	273	-	-	479	1.13
PT-p/m-100F	light yellow	276	283	-	409	453	1.10
PT-p/m-*p*-Me	light yellow	257	254	-	-	506	1.78
PT-p/m-*o*-Me	light yellow	268	272	-	-	493	2.88

* DSC curves were recorded twice using the same sample. The first run from 100 to 400°C and the second run from 100 to 450°C. In all cases a heating rate of 20°C/min. was used. After the first run the sample was cooled down with 320°C/min.

† All films were transparent besides PT-p/m-100F which was opaque.

‡ The peak temperature of cold crystallisation is given.

§ The onset of the melting peak is given.

\- No T_g, cold crystallisation or melting peak detectable using DSC techniques.

Unclosed 1,3,4-oxadiazole and 1,2,4-triazole groups can be present in the final product. During a TGA experiment a distinct weight loss is observed, phase 1 in figure 2, attributable to the loss of water formed during the cyclodehydration of 1,3,4-oxadiazole and 1,2,4-triazole groups. The reaction scheme of this ring closure is represented in figure 4.

Weight loss occurring between 200 and 400°C has been attributed to the ring closure reaction. In all cases weight losses due to ring closure reactions are observed, see table 2, indicating that the reaction between aniline and aniline derivatives and polyhydrazide at 175°C does not result in a fully converted product. Performing the reaction at higher temperatures results however in products with lower inherent viscosities[6]. In a thermogram of a fully converted poly-1,2,4-

triazole this weight loss is of course absent. PT-p/m-*o*-Me shows the highest weight loss. In this case, the reaction between *o*-toluidine and polyhydrazide is most probably sterically hindered. Unclosed groups are also detectable by IR-spectrometry since a carbonyl stretching absorption peak is observed in the IR-spectra at 1650 cm^{-1}.

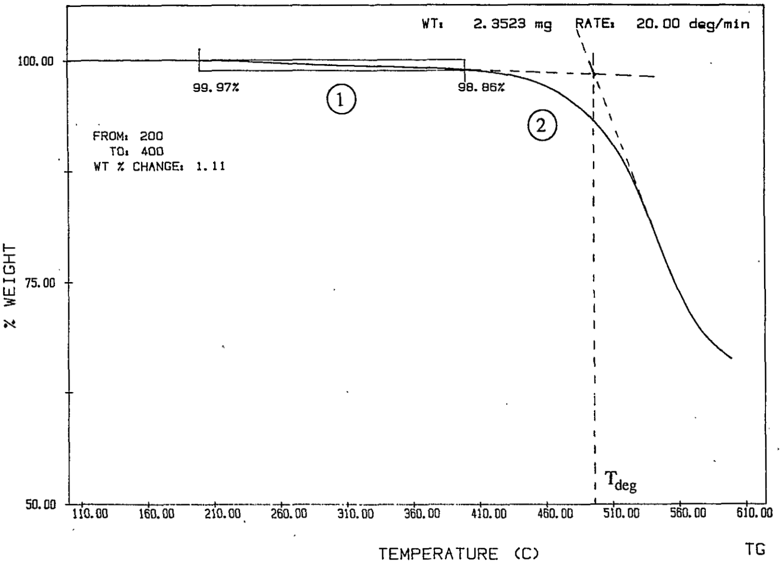

Fig. 2. TGA thermogram of PT-p/m-25F recorded with a heating rate of 20°C/min. from 100 to 600°C under nitrogen. Two phases of weight loss can be observed: (1) loss of water caused by the cyclodehydration of unclosed groups, (2) loss of volatiles caused by the degradation of the polymer. The degradation temperature (T_{deg}) is defined as the intersection of the tangents.

Unclosed rings are possible weak spots for thermal or chemical degradation. A heat treatment will force unclosed rings into their more thermally stable and chemically resistant closed ring forms.

Phase 2 in figure 2 represents the loss of volatiles caused by the ultimate degradation of the polymer. Incorporation of aniline derivatives yields polymers with a slightly decreased thermal stability as compared to unmodified poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles], see table 2. From all polymers, except from PT-p/m-*o*-Me and PT-p/m-100F, flexible films were obtained by solvent casting techniques and these were investigated for their gas separation properties[2]. These films were also used for DSC experiments.

Each sample was subjected to two subsequent DSC heating runs, the first from 100 to 400°C after which the sample was cooled down with 320°C/min., followed by a second heating run from 100 to 450°C, see figure 3. In both experiments a heating rate of 20°C/min. was applied. The glass transition temperatures recorded during both runs are given in table 2.

The glass transition temperature is raised with the incorporation of fluoro and chloro aniline, obviously due to increased polar interactions. Incorporation of *o-toluidine* results in a decreased glass transition temperature compared to the unmodified poly-1,2,4-triazoles, PT-p/m-1, PT-p/m-2 and PT-p/m-3. Differences in glass transition temperatures are however small.

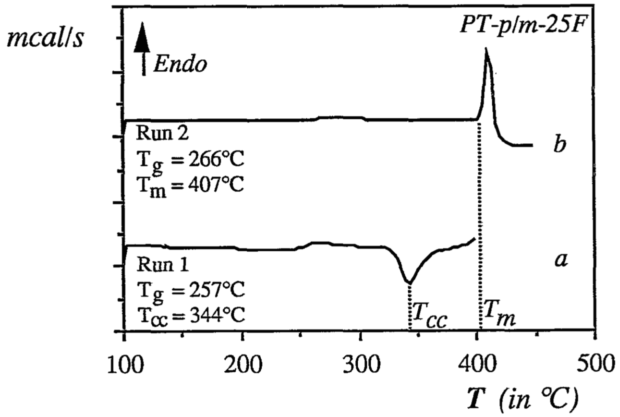

Fig. 3. Two successive DSC curves of PT-p/m-25F recorded with 20°C/min. under nitrogen. After the first run from 100 to 400°C (a) the sample is cooled with 320°C/min. and the second run from 100 to 450°C is recorded (b). T_{cc} is the peak temperature of cold crystallisation and T_m is the on-set temperature of melting.

Except for PT-p/m-*p*-Me the glass transition temperature of the second run is higher than the glass transition temperature of the "as-cast" film. This rise in glass transition temperature is obviously due to quenching effects during cooling[11] and due to cyclodehydration of unclosed groups during the first DSC experiment in which a more flexible structure is converted into a rigid one. The effect of both quenching and ring closure on the glass transition temperature is nicely shown by the following experiment were a sample of PT-p/m-50Cl is subjected to a number of successive DSC heating runs, see table 3. PT-p/m-50Cl was chosen for this experiments since it has a relatively large number of unclosed rings as indicated by its weight loss during the TGA experiments.

During the first run up to 300°C, a glass transition temperature of 268.5°C is measured. After cooling down with 320°C/min. the second run is recorded and the T_g has slightly increased, obviously due to quenching of the sample during cooling but further changes in run 2, 3 and 4 are marginal. Due to the low end temperatures no significant cyclodehydration reactions of the unclosed rings take place. Increasing the end temperature to 400℃ results in a rise in T_g. During these runs the polymer undergoes cyclodehydration resulting in a more rigid polymer. This implies that the greater part of the ring closure reactions takes place when the polymer is in the rubbery phase. During run 6 and 7 the polymer is likely to undergo also some degradation.

Table 3. Influence of subsequent heating runs on the glass transition temperature of PT–p/m–50Cl.

Heating run	limits	glass transition temperature (℃)	Heating run	limits	glass transition temperature (℃)
1	100-300	268.5	5	100-420	278.6
2	100-300	271.0	6	100-455	282.7
3	100-300	271.1	7	100-455	289.3
4	100-420	270.6			

Cold crystallisation

Cold crystallisation is detected for a number of poly-1,2,4-triazoles during the first heating run of a DSC experiment. Cold crystallisation of alternating poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole] has extensively been studied by Gebben et al. who noticed that cold crystallisation is only observed for poly-1,2,4-triazole films and not for the as-prepared reaction powder[12]. The process of cold crystallisation also depends highly on the macromolecular structure of the polymers used. For example, cold crystallisation is only observed for a poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole] where *p*- and *m*-phenylene groups are present in an alternating fashion and not if these groups are incorporated randomly[13]. A highly regular macromolecule is obviously a precondition for cold crystallisation. A similar phenomenon is observed for the modified poly-1,2,4-triazoles as represented in table 2.

During the first DSC heating cycle a number of poly-1,2,4-triazoles undergo cold crystallisation in the rubbery phase. After heating to 300℃ the polymer is quenched with 320℃/min. to 100℃ and subjected to a second heating cycle to 450℃. During cold crystallisation the amorphous fraction in a polymer decreases which results in a decreased heat capacity jump at the glass transition temperature. In the case of PT-p/m-1 and PT-p/m-2 this occurs to such an extent that the glass transition temperature is not detectable anymore in the DSC curve of the second run. The crystalline fraction in poly-1,2,4-triazoles formed during cold crystallisation melts in the second run as is indicated by a clear melting peak, see figure 3 (B). The onset of this melting peak is given since the peak temperature could not be indicated clearly in a number of cases due to simultaneously occurring degradation.

As said, the unmodified poly-1,2,4-triazoles undergo cold crystallisation in the rubbery phase. Incorporation of *p*-chloro aniline in combination with aniline results in a less regular macromolecular structure and the possibility to undergo cold crystallisation vanishes. In the case of PT-p/m-100*p*-Cl the polymer becomes "regular" again and crystallisation is observed. PT-p/m-25F undergoes cold crystallisation indicating that incorporation of 25% *p*-fluoro aniline does obviously not result in a dramatic change in the macromolecular structure due to the small amount and the relative small size of the fluorine atom. No cold crystallisation is observed for PT-p/m-100F. Since the appearance of the "as-cast" polymer film is opaque and since a melting peak is observed with an onset of 453°C this polymer is believed to be already crystalline.

One also might expect cold crystallisation for the regular PT-p/m-*p*-Me but no cold crystallisation or melting peak is observed in the DSC curve. The reason for this behaviour is not understood.

Other pendant groups

Since solubility is often enhanced when larger groups are incorporated onto the polymer backbone as pendant groups, we have investigated the possibility of incorporating biphenylic structures, like 1-naphthylamine, 4-phenoxy aniline and 4-aminobenzotrifluoride, but in this case polymers with insufficient film forming properties were obtained. During the reaction between amine and polyhydrazide polymer degradation occurs due to the strong acidic environment of polyphosphoric acid. This degradation is kept to minimum if the reaction medium consists of 0.832 mol amine per 310 g PPA[6]. It was however not possible to dissolve these amounts of these high molecular weight amines in PPA. Another problem was the sublimation of these amines from the reaction mixture during the reaction resulting in a further deviation from the ideal reaction conditions. Similar problems have been reported by Krongauz et al.[14] who investigated the reaction between 1-naphtylamine and poly(*p*-phenylene-1,3,4-oxadiazole) also in PPA.

Incorporation of cyclohexylamine was also examined. During this reaction, only minor quantities of polyhydrazide are converted into the corresponding poly-1,2,4-triazole. In the case of a normal reaction behaviour the precursor dissolves completely in the course of the reaction and is converted into the corresponding poly-1,2,4-triazole. Due to the strong complex formation between polyphosphoric acid and cyclohexylamine[14], the concentration of free amines is apperently too low to result in a successful reaction.

Poly-1,3,4-oxadiazoles.

Poly(*p*-, *m*-phenylene)-1,3,4-oxadiazoles are comparable with poly(*p*-phenylene) with respect to their thermal stability and chemical resistance which is ascribed to the fact that the 1,3,4-

oxadiazole ring is spectrally and electronically equivalent to the *p*-phenylene ring[15]. High thermal stability and chemical resistance is favoured in most end-use applications. During processing these characteristics can however be a major problem.

Poly(*p*-, *m*-phenylene-1,3,4-oxadiazole can be obtained via a cyclodehydration reaction of the corresponding tractable polyhydrazide. Solid state cyclodehydration of alternating poly(*p*-, *m*-phenylene hydrazide) yielded however brittle membranes[13].

Poly(*p*-, *m*-phenylene-1,3,4-oxadiazoles prepared from isophthalic acid and terephthalic acid with hydrazine sulphate as monomers yielded polymers with higher inherent viscosities from which flexible membranes were prepared. Since this reaction gave poly-1,3,4-oxadiazoles with superior properties it was also used to prepare poly-1,3,4-oxadiazoles with various other functional groups. The physical properties of these polymers were studied as a function of these functional groups. The poly-1,3,4-oxadiazoles were prepared from various dicarboxylic acids, see figure 1. These poly-1,3,4-oxadiazoles were in turn used as precursor polymers for the preparation of poly-1,2,4-triazole on which we hope to report in the future.

Table 4. Elemental analysis of poly-1,3,4-oxadiazoles.

Polymer	dicarboxylic acid	η_{inh}* (dl/g)	C/N found	C/N theor.	C/H found	C/H theor.
c-CH-POD	*c*-CH	1.65	3.46	3.43	9.74	9.54
t-CH-POD	*t*-CH	2.81	3.61	3.43	8.94	9.54
c+*t*-POD	*c*+*t*-CH	1.56	3.42	3.43	8.72	9.54
PIDA-POD	PIDA	0.19†	8.63	8.58	12.75	12.55
TBI-POD	TBI	0.38	5.64	5.15	11.65	11.92
HF-POD	HF	0.40†	7.50	7.29	25.38	25.30
DPE-POD	DPE	0.37	6.05	6.00	15.38	20.87
HF/DPE-POD§	HF & DPE	2.44‡	6.26	6.64	16.88	23.08

* Inherent viscosity is determined in formic acid.

† Inherent viscosity is determined in concentrated sulphuric acid.

‡ Inherent viscosity is determined in NMP.

§ Random copolymer of HF and DPE used in 40% and 60% molar amounts, theoretical values for the polymer elemental analysis were calculated assuming stoichiometric incorporation of both monomers.

Fuming sulphuric acid is mostly favoured over PPA as a reaction medium for the preparation of aromatic poly-1,3,4-oxadiazoles[16]. But in the case of 1,1,3-trimethyl-3-(*p*-carboxy-phenyl)-5-carboxyindan (PIDA) no polymer was obtained possibly due to degradation of the monomer which contains aliphatic groups obviously susceptible to degradation in the strong acidic environment. Performing the reaction in PPA, a much milder dehydrating agent, resulted readily in a very viscous reaction medium and gave a polymer with an inherent viscosity of

0.19 dl/g from which flexible films were prepared. To prevent monomer degradation all syntheses represented in figure 1 (B), were performed in PPA instead of fuming sulphuric acid. Successful preparation of poly-1,3,4-oxadiazoles was confirmed by elemental analysis, see table 4. Also in this case the experimental C, N and H values found were somewhat lower than the theoretical ones. Nevertheless, the C/N and C/H ratios are close to their theoretical values indicating residual impurities in the final product, most likely to be polyphosphoric acid[13]. Flexible films were obtained from all poly-1,3,4-oxadiazoles by solvent casting techniques.

In table 5 the glass transition temperatures and the degradation temperatures are given. Again samples are subjected to two successive heating runs, the first from 100 to 400°C after which the sample is cooled down with 320°C/min. to 100°C followed by a second run with an end temperature of 450°C. Both scans were recorded with a heating rate of 20°C/min. These poly-1,3,4-oxadiazoles all have high glass transition temperatures. The first run yields the glass transition temperature of the as-prepared film. The glass transition temperature recorded during the second run is higher than the first. In this case quenching effects and cyclodehydration of unclosed hydrazide groups into the more rigid 1,3,4-oxadiazole groups probably occur, see figure 4. In the second run the glass transition temperature of a number of poly-1,3,4-oxadiazoles were not detectable with DSC techniques.

Table 5. Film appearance and thermal properties of poly-1,3,4-oxadiazoles.

Polymer	Film appearance	T_g 1st run (°C)	T_g 2nd run (°C)	T_{deg} (°C)
c-CH-POD	light yellow	179	-	441
t-CH-POD	colourless	179	-	449
c+*t*-POD	colourless	180	-	449
PIDA-POD	light yellow	300	330	488
TBI-POD	colourless	315	-	485
HF-POD	colourless	287	295	479
DPE-POD	colourless	333	361	496
HF/DPE-POD	light yellow	339	-	491

- No glass transition temperature detectable with DSC techniques.

The thermal stability of these poly-1,3,4-oxadiazoles is slightly lower than those of the poly-1,2,4-triazoles. Discriminating between weight loss due to cyclodehydration and degradation is in this case not possible to full satisfaction since these two phases of weight loss shade off into one another.

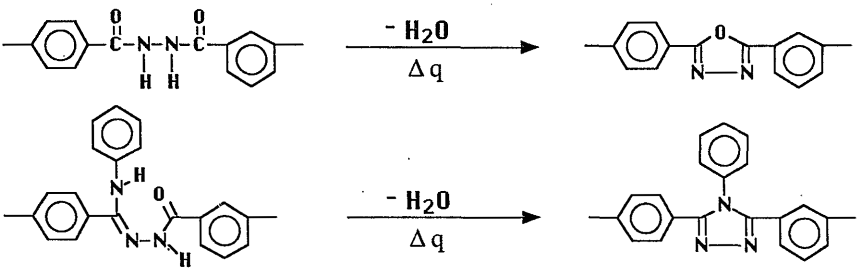

Fig. 4. Cyclodehydration of unclosed 1,3,4-oxadiazole and 1,2,4-triazole groups.

CH-POD

Preparation of alicyclic poly-1,3,4-oxadiazoles was originally reported by Iwakura et al.[9] Poly(1,4-cyclohexane)-1,3,4-oxadiazole was reported to be soluble in formic acid while still a good thermal stability was maintained. Incorporation of the flexible cyclohexane unit results in a decrease of the glass transition temperature compared to its aromatic counterpart, poly(*p*-phenylene)-1,3,4-oxadiazole. The degradation temperature is approximately 100℃ lower than found for poly(*p*-phenylene)-1,3,4-oxadiazole being 542℃[13]. Our results on the thermal stability of CH-POD are in agreement with the observations of Iwakura et al.[9]

Cyclohexane-1,4-dicarboxylic acid was supplied as a mixture of *cis* and *trans*-isomers. Both this mixture as well as the pure *cis* and *trans*-isomers were used as monomers, resulting in three batches of poly(1,4-cyclohexane)-1,3,4-oxadiazole. Flexible films were obtained from all three polymers. No differences were detected between the three batches using elemental analysis, IR-spectroscopy and DSC techniques.

Iwakura synthesised two batches of poly(1,4-cyclohexane)-1,3,4-oxadiazole using the *cis* and *trans*-isomers of 1,4-cyclohexane dicarboxylic acid and concluded that the two polymers had the same geometrical structure on the basis of their identical infrared spectrum, solubility, thermal stability and crystallinity. He assumed that *cis*-1,4-cyclohexane was converted into the more stable *trans*-isomer in the acidic environment of PPA[9]. The identical glass transition temperatures of our three batches of poly(1,4-cyclohexane)-1,3,4-oxadiazole endorses this assumption.

PIDA-POD

The 1,1,3-trimethyl-3-phenylindane unit is used as a solubility increasing unit for a number of polymers. For example, Ciba-Geigy's soluble polyimide "XU-218" also contains this bulky and asymmetrical moiety. We have investigated whether incorporation of this unit had the same effect on solubility behaviour of the poly-1,3,4-oxadiazoles. Compared to the fully aromatic poly(*p, m*-phenylene)-1,3,4- oxadiazoles, the solubility is increased. PIDA-POD is besides its solubility in concentrated sulphuric acid also soluble in trifluoro acetic acid.

Using DSC techniques a glass transition temperature of 330℃ (second run, see table 5) was determined for PIDA-POD which is comparable with the high T_g reported by Wilson[17] of 341℃ (also second run) for a polyamide derived from 1,1,3-trimethyl-3-(*p*-aminophenyl)-5-indanamine and 1,1,3-trimethyl-3-phenylindan-4',5-dicarboxylic acid.

TBI-POD

The preparation of TBI-POD using oleum as reaction mixture has been reported in a patent by Stephens[18]. The preparation of flexible films from TBI-POD/*m*-cresol solutions is claimed in this patent.

We have initially performed this synthesis in PPA. After solvent casting from formic acid a polymer with insufficient film forming properties was obtained possibly due to the low inherent viscosity. Using a mixture of sulphuric acid and chlorosulphonic acid as a reaction medium resulted in a polymer with a higher inherent viscosity, being 0.7 dl/g. Flexible films were obtained from TBI-POD/*m*-cresol solutions after evaporation of the solvent.

HF-POD

Incorporation of the polar and bulky 4,4'-(2,2'-diphenyl)hexafluoro propane moiety into the polymer backbone of, for example, polyimides has shown to be an effective way of substantially increasing the solubility of these polymers[19]. The HF unit has also been incorporated into the polymer backbone of a poly-1,3,4-oxadiazole by Russian workers[20]. This poly-1,3,4-oxadiazole was prepared by cyclodehydration of a polyhydrazide. The polyhydrazide was, in turn, prepared by a low-temperature polycondensation of the dihydrazide and dichloride of 4,4'-(2,2'-diphenyl)hexafluoro propane dicarboxylic acid. We have prepared HF-POD directly by the less laborious one-step synthesis using 4,4'-(2,2'-diphenyl)hexafluoro propane dicarboxylic acid and hydrazine as monomers. Flexible films were cast from a HF-POD/trifluoro acetic acid solution.

The Russian workers reported a glass transition temperature of approximately 333℃ with DTA for their poly-1,3,4-oxadiazole which is somewhat higher than the value we have found using DSC, see table 4. This may be due to the difference in preparation history of the polymer.

Solubility tests showed that HF-POD is soluble in THF, chloroform, NMP, *o*-dichloro benzene and trifluoro acetic acid. The increased solubility of HF-POD compared to the other poly-1,3,4-oxadiazoles is believed to be a result of the more loosely packed polymer matrix as was found by Russian worker for trifluoromethyl containing polyamides[20] allowing enhanced solvent diffusion into the polymer matrix followed by its subsequent dissolution.

DPE-POD

Incorporation of the diphenyl ether unit results in a less rigid poly-1,3,4-oxadiazole as compared with the corresponding poly(*p*-phenylene)-1,3,4-oxadiazole. Elemental analysis indicates a surplus of hydrogen atoms. This deviation from the theoretical value may be due to a combination of the polymers hygroscopic nature and its relative small number of hydrogen atoms in comparison to carbon resulting in a large relative error.

A glass transition temperature of 333℃ was obtained for DPE-POD using DSC techniques, in the second run of the same sample a much broader glass transition area with a midpoint of approximately 361℃ was found. These observation are in agreement with those of Korshak et al.[21]. DPE-POD exhibits a good thermal stability as indicated by its high degradation temperature. During a TGA experiment unclosed 1,3,4-oxadiazole groups undergo cyclo-dehydration.

Flexible films were cast from a polymer solution in formic acid. Besides its solubility in formic acid DPE-POD is soluble in DMSO and NMP.

HF/DPE-POD

Since DPE-POD and HF-POD are each others extremes in permeability and selectivity[2] the random copolymer HF/DPE-POD was also prepared using 40%/60% (mol/mol) mixture of both monomers in combination with hydrazine sulphate.

Flexible films were cast from a polymer solution in NMP. The glass transition temperature and degradation temperature are in agreement with those of the homopolymers.

CONCLUSIONS

The glass transition temperature, degradation temperature and cold crystallisation behaviour have been studied of aromatic poly-1,2,4-triazoles where various groups have been introduced onto the pendant phenyl group. Cold crystallisation was only observed if macromolecular regularity was maintained to a large extent.

The solubility of poly-1,3,4-oxadiazoles was highly improved with the incorporation of 5-*t*-butylisophthalic, 1,1,3-trimethyl-3-phenylindane, 4,4'-(2,2'-diphenyl)hexafluoro propane and diphenyl ether groups into the polymer main chain whereas high glass transition temperatures and degradation temperatures typical for aromatic poly-1,3,4-oxadiazoles were maintained.

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LITERATURE

1. B. Gebben, M.H.V. Mulder and C.A. Smolders, J. Membrane Sci., 46, 29-41(1989).
2. E.R. Hensema, J.P. Boom, M.E.R. Sena, M.H.V. Mulder and C.A. Smolders, to be published. *(Chapter 4 of this thesis).*
3. Y. Iwakura, K. Uno and S. Hara. Makromol. Chem., 108, 160-169(1967)
4. A.P. Bogdanov et al., GB 2093.460 (1982).
5. R.J. Cotter and M. Matzner, "Ring-forming polymerizations" in A.T. Blomquist and H. Wasserman, (Eds.), "Organic Chemistry", Vol. 13B, 1, Academic Press, New York, 1972.
6. J.R. Holsten and M.R. Lilyquist, J. Polym. Sci.,A, 3, 3905-3917(1965).
7. A.H. Frazer and F.T. Wallenberger, J. Polym. Sci., A2, 1137-1145(1964)
8. Y. Iwakura, K. Uno and S. Hara, J. Polym. Sci., A, 3, 45-54(1965).
9. Y. Iwakura, K. Uno and S. Hara, Makromol. Chem., 95, 248-260(1966).
10. A.H. Frazer and F.T. Wallenberger, J. Polym. Sci., A2, 1147-1156(1964).
11. M.J. Richardson and N.G. Savill, Polymer, 16, 753-757 (1975).
12. B. Gebben, M.H.V. Mulder and C.A. Smolders, J. Polym. Sci., Polym. Chem. Ed., 27, 3481-3499(1989).
13. E.R. Hensema, J.P. Boom, M.H.V. Mulder and C.A. Smolders, to be published. *(Chapter 2 of this thesis)*
14. E.S. Krongauz, V.V. Korshak and A.V. D'Yachenko, Vysokomol. Soedin. Ser. B 10, 108-111 (1968).
15. J. Sauer, R. Huisgen and H.J. Sturm, Tetrahedron, 11, 214(1960).
16. Y. Iwakura, K. Uno and S. Hara, Makromol. Chem., 94, 103-113(1966).
17. J.C. Wilson, J. Polym. Sci., Polymer Chemistry Ed., 13, 749-754 (1975).
18. J.R. Stephens, U.S. Patent 4487921, 1984.
19. F.W. Harris and L.H. Lanier, "Structure-solubility relationships in polyimides", *in* F.W. Harris and R.B. Seymour (Eds.), Structure-solubility relationships in polymers, London, Academic Press, 1977.
20. B.R. Livshits, S.V. Vinogradova, I.L. Knunyunts, G.L. Berestneva and T.K.L. Dymoshits, Vysokomol. Soyed., A 15, 961-968(1973).
21. V.V. Korshak, A.V. D'Yachenko, Ye. S. Krongauz and G.L. Berestneva, Vysokomol. Soyed. Ser. A 11, 7-10 (1969).

4

Gas separation properties of new polyoxadiazole and polytriazole membranes.

E.R. Hensema, J.P. Boom, M.E.R. Sena[‡], M.H.V. Mulder and C.A. Smolders

SUMMARY

New aromatic poly-1,2,4-triazoles and poly-1,3,4-oxadiazoles are studied in a directed search for new membrane materials for gas separation applications. The gas separation properties of these closely related polymers have been systematically investigated. Various functional groups were incorporated as pendant groups *onto* the polymer backbone of poly-1,2,4-triazoles. A wide permeability/selectivity spectrum was covered with the choice of functional groups incorporated *into* the polymer backbone of poly-1,3,4-oxadiazoles. High permeabilities were found for poly-1,3,4-oxadiazoles with a 1,1,3-trimethyl-3-phenylindane (PIDA-POD) and a 4,4'(2,2'-diphenyl)hexafluor propane (HF-POD) unit in the polymer backbone while incorporation of a 4,4'-diphenyl ether unit (DPE-POD) results in a polymer with a low permeability but an extremely high selectivity.

While the permeabilities vary over four orders of magnitude, the solubility almost remains constant and the increase in permeability therefore is mainly due to an increase in diffusivity. The permeability will be discussed in terms of the polymer free volume.

INTRODUCTION

Today's gas separation membranes are mostly made of conventional high performance polymers, like polyethersulphone and polyphenylene oxide. The next generation of commercial membranes is likely to be made from "tailor-made" polymers allowing high permeabilities and selectivities, sinces today's research is dedicated to the development of these materials. For example, polyimides containing the diphenylhexafluoroisopropylidene unit are known for their

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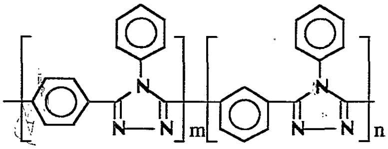
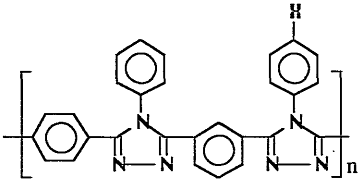
[‡] IMA, Universidade de Rio de Janeiro, Brasil.

Random poly[p-, m-phenylene-(4-phenyl)-1,2,4-triazoles]



1	PT-0/100	m/n = 0/1
2	PT-25/75	m/n = 1/3
3	PT-50/50	m/n = 1/1
4	PT-75/25	m/n = 3/1

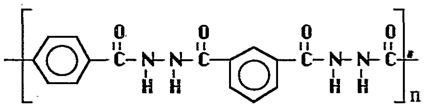
Alternating poly[p-, m-phenylene-(4-phenyl)-1,2,4-triazoles]



R = H, F, Cl or CH_3

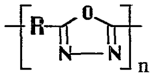
5	PT-p/m-1	100%	phenyl
6	PT-p/m-2	100%	phenyl
7	PT-p/m-3	100%	phenyl
8	PT-p/m-25Cl	25%	*p*-Cl phenyl
9	PT-p/m-50Cl	50%	*p*-Cl phenyl
10	PT-p/m-75Cl	75%	*p*-Cl phenyl
11	PT-p/m-100Cl	100%	*p*-Cl phenyl
12	PT-p/m-25F	25%	*p*-F phenyl
13	PT-p/m-50F	50%	*p*-F phenyl
14	PT-p/m-100F	100%	*p*-F phenyl
15	PT-p/m-*p*-Me	100%	*p*-Me phenyl

Poly(p-, m-phenylene)hydrazide



16 PH-p/m-1

Poly-1,3,4-oxadiazoles



17 TI-POD
18 CH-POD
19 PIDA-POD
20 HF-POD
21 DPE-POD
22 HF/DPE-POD

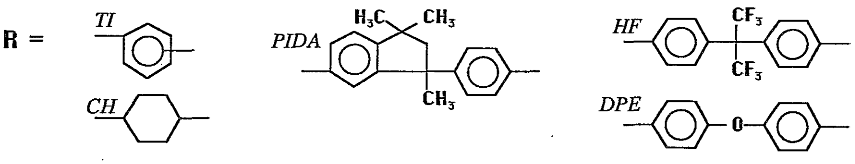


Fig. 1. Random and alternating poly-1,2,4-triazoles, polyhydrazide and poly-1,3,4-oxadiazoles studied as new gas separation membrane materials[3,4]. TI-POD is a random copolymer using a 50/50 mol.% monomer mixture of terephthalic and isophthalic acid while HF/DPE-POD is a random copolymer using a 40/60 mol% monomer mixture of HF and DPE dicarboxylic acids.

good gas separation characteristics[1]. Another interesting material, allowing exceptional high fluxes is poly(1-trimethylsilyl-1-propyn), PTMSP. Surface fluorination of this material results in higher selectivities without loosing too much of the unusual high permeability[2].
In our laboratory related poly-1,2,4-triazoles and poly-1,3,4-oxadiazoles are studied as new "tailor-made" membrane materials. Especially, poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole] is known for its excellent gas separation properties[3].
In this research project the gas separation properties of poly-1,2,4-triazoles and poly-1,3,4-oxadiazoles are studied. In directed syntheses various related poly-1,2,4-triazoles and poly-1,3,4-oxadiazoles were prepared and their gas separation properties were studied as a function of their macromolecular structure and resulting physical properties. The polymers studied are represented in figure 1.

EXPERIMENTAL

Materials

The syntheses and properties of these related thermally stable and chemically resistant polymers are reported elsewhere[4,5]. All other chemicals were supplied by Merck or Janssen Chimica, and were used as received.

Preparation of homogeneous membranes

Poly-1,2,4-triazoles
Homogeneous poly-1,2,4-triazole membranes (polymers 1 to 15, see figure 1) were prepared from a 10-15 wt.% polymer solution in formic acid. Inhomogeneities were removed from the solution by filtration over a 5 µm filter. The solution is cast on a glass plate using casting knives with slit heights of 0.2, 0.3 and 0.5 mm. Prior to use the glass plate is scrupulously cleaned with chromic acid. After casting the solvent is evaporated in a nitrogen atmosphere at room temperature. After evaporation, the glass plate is submersed into a water bath and the poly-1,2,4-triazole membrane is easily removed from the glass plate. Transparent films are obtained with thicknesses between 20 and 60 µm. The membranes were dried in a vacuum oven during at least 24 hours at 150°C.

Poly(p-, m-phenylene)hydrazide

Homogeneous polyhydrazide membranes (polymer 16, see figure 1) were cast from a 10–15 wt.% solution in DMSO using casting knives with slit heights of 0.3 and 0.5 mm. The solvent was evaporated in a nitrogen atmosphere at 80℃.

Poly-1,3,4-oxadiazoles

A 5 wt.% solution of TI-POD (17) in concentrated sulphuric acid is cast on a glass plate followed by immersion precipitation in 50 wt.% water-diluted sulphuric acid solution. Subsequently the membranes are rinsed in demineralised water during at least 24 hours after which they are dried in a vacuum oven at 150℃ during at least 24 hours. Transparent TI-POD films are obtained.

For CH-POD (18) and DPE-POD (21), see figure 1, the same procedure as for the poly-1,2,4-triazoles was used. PIDA-POD (19) and HF-POD (20) were cast from trifluoro acetic acid solution while HF/DPE-POD membranes were cast from a NMP solution followed by evaporation of the solvent at 150℃ in a nitrogen atmosphere.

Characterisation

Differential Scanning Calorimetry (DSC)

DSC measurements were performed on a Perkin-Elmer DSC 4 apparatus in combination with a System 4 Microprocessor Controller and a Thermal Analysis Data Station (TADS), model 3700. The polymer samples were placed in aluminium sample pans and the temperature was increased with a heating rate of 20℃/min. from 100 to 400℃ under a nitrogen purge gas stream. The sample is cooled with a rate of 320℃/min. to 100℃ and a second run is recorded from 100 to 450℃ again with a heating rate of 20℃/min. As glass transition temperature (Tg) the midpoint of the transition was taken, calculated by means of the TADS software.

Thermo-Gravimetrical Analysis (TGA)

TGA experiments were carried out on a Perkin-Elmer TGS-2 in combination with a system 4 microprocessor Controller and a Thermal Analysis Data Station, model 3700. Experiments were carried out under a nitrogen purge gas stream from 50 to 600℃. The temperature of the polymer samples was increased with a heating rate of 20℃/min. Weight loss between 200 and 400℃ was attributed to the formation of water due to a ring closure reaction of unclosed 1,2,4-triazole groups. This weight loss was calculated by means of the TADS software.

Density

The density of the polymers 1 to 17 was determined using a density gradient column of tetrachloro methane and cyclohexanon. For the polymers 18 to 22 a NaBr-water column was used. The densities were verified by extensiometric methods.

Gas permeation experiments

Gas transport properties of polyhydrazide, poly-1,2,4-triazole and poly-1,3,4-oxadiazole membranes for single gases (O_2, N_2, CH_4 and CO_2) and gas mixtures of various compositions (CH_4 and CO_2) were determined on two set-ups on which permeability and diffusivity were determined using standard procedures[6].

On the first set-up[7] steady-state permeability and selectivity towards carbon dioxide/methane mixtures were determined, see figure 2 for a schematic representation. Permeability on this set-up is determined by an accurate measurement of the pressure increase with time in a calibrated volume at the vacuated downstream side of the membrane. The carbon dioxide permeability P_{CO2} is defined as:

$$P_{CO_2} = \frac{l \cdot v \cdot Y_{CO_2,p}}{A \cdot P_f X_{CO_2,f} 76} \cdot \frac{\Delta p}{\Delta t} \qquad (1)$$

and the selectivity is determined using gas chromatography and is defined as:

$$\alpha_{CO_2/CH_4} = \frac{Y_{CO_2,p}/Y_{CH_4,p}}{X_{CO_2,f}/X_{CH_4,f}} \qquad (2)$$

where P_{CO2} is the permeability for CO_2 (cm^3(STP).cm/(cm^2.s.cmHg)), l is the thickness of the membrane (cm), V is the calibrated volume (cm^3), $Y_{CO2,p}$ and $Y_{CH4,p}$ are the CO_2 and CH_4 contents in the permeate (vol.%) respectively, Δp is the pressure increase (mmHg) in the permeate volume during Δt, A is the membrane area (cm^2), $X_{CO2,f}$ and $X_{CH4,f}$ are the CO_2 and CH_4 content in the feed (vol.%) respectively, P_f is the feed pressure (mmHg), Δt is the time (s) needed for pressure increase Δp and *76* is a pressure correction factor (cmHg). P is expressed in Barrer (1 Barrer = $10^{-10}cm^3$.cm/(cm^2.s.cmHg). Gas mixtures consisting of 25 vol.% CO_2 and 75 vol.% CH_4 were applied unless stated differently. The downstream side is vacuum and in all cases a pressure difference of 6 bar over the membrane is applied.

Permeability and selectivity measurements were started immediately after the membranes were put into the cells. Since methane is the slower permeating species, small quantities of methane are present in the permeate immediately after the start of an experiment resulting in initially high selectivity values. Constant and reproducible values are found after approximately 24 hours when a steady state is reached. These steady state values are reported.

The same set-up is used to determine the permeabilities of oxygen, nitrogen, carbon dioxide and methane as single gases. In this way the ideal selectivity values of oxygen/nitrogen and of carbon dioxide/methane are obtained. The ideal selectivity is defined as the ratio of the pure gas permeabilities:

$$\alpha_{ij,\,ideal} = P_i/P_j \qquad (3)$$

A second similar set-up was used to determine permeability and diffusion coefficients by means of "time-lag" measurements, see also figure 2.

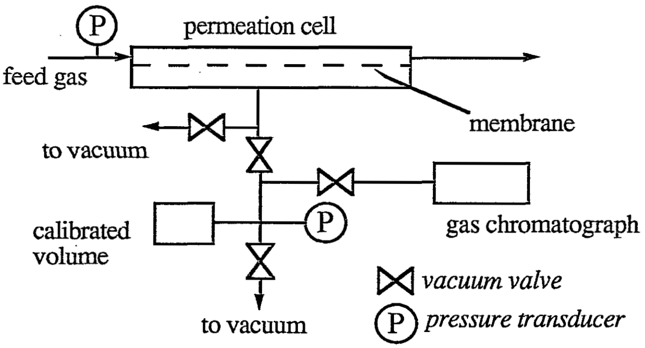


Fig. 2. Schematic drawing of the testing apparatus for the gas separation and time-lag measurements of CO_2/CH_4 gas mixtures and single gases.

Both set-ups are computer-controlled and were calibrated using a polyester standard film (Standard Reference Material 1470) of the National Bureau of Standards in Washington D.C. (U.S.A).

In the dead-end cells used in a previous study[3] soap film capillary meters were used for the permeability determination. These were not used here since permeability values are relatively small and do not allow an accurate determination by this method.

RESULTS AND DISCUSSION

The aim of this paper is to study the influence of the macromolecular structure of the related polyhydrazide, poly-1,2,4-triazoles and poly-1,3,4-oxadiazoles on the gas separation properties. The reproducibility of the polymeric syntheses and the influence of the casting conditions on the gas separation properties must be known before a meaningful discussion on the influence of the macromolecular structure on the gas separation properties is justified. It is known that both permeability and selectivity may be sensitive towards these influences[8,9].

Influence of the poly-1,2,4-triazole batch

Three batches poly[*p*, *m*-phenylene-(4-phenyl)-1,2,4-triazole], polymers 5,6 and 7, were prepared to investigate the influence of the polymer synthesis on the gas separation properties. Besides the permeability and selectivity towards a carbon dioxide/methane gas mixture, the polymers were subjected to thermo-gravimetrical analysis (TGA). During a TGA experiment unclosed groups undergo a cyclo dehydration reaction, see figure 3. The carbonyl and hydrazide groups capable of hydrogen bonding are converted into the less interacting 1,2,4-triazole and 1,3,4-oxadiazole groups. The weight loss due to the formation of water caused by the cyclodehydration of unclosed groups is represented in table 1. It is shown that the permeability increases with decreasing weight loss, so with a decreasing number of unreacted 1,2,4-triazole groups. Poly-1,2,4-triazoles 5, 6 and 7 are prepared out of a poly-hydrazide precursor polymer (16) which has the maximum amount of hydrazide groups capable of hydrogen bonding resulting in increased intermolecular interactions opposing easy passage of gas molecules. This results in low permeability values comparable to those found for polyamides. The polyhydrazide will be discussed later and it has an extremely low permeability for CO_2 of 0.05 Barrer, comparable to the values found for Nylon-6 and Nylon-6,6 being 0.1 and 0.07 Barrer, respectively[10]. The latter two polymers also exhibit strong hydrogen bonding.

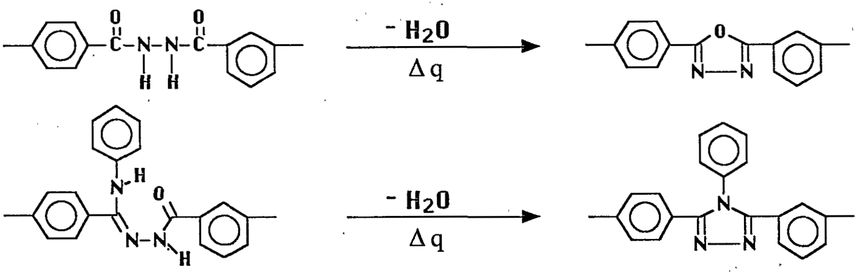


Fig.3. Cyclo dehydration reaction of unclosed 1,3,4-oxadiazole and 1,2,4-triazole groups.

The poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole] studied by Gebben et al.[3] is also included in table 1. The gas separation properties of this polymer were determined under slightly different conditions.

Table 1. Gas separation properties of poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles] for a carbon dioxide/methane gas mixture as a function of the percentage weight loss due to unreacted 1,2,4-triazole groups.

Poly-1,2,4-triazole	P_{CO2} (Barrer)	$\alpha_{CO2/CH4}$	$\Delta w^{\dagger}$ (wt.%)	T_g (°C)
TIPT * (ref. 3)	8.9	63	< 1	270
PT-p/m-1	5.8	47	2.07	264
PT-p/m-2	7.1	50	1.65	267
PT-p/m-3	5.9	51	1.82	261

---

* measured using a pressure difference of 3 bar and a gas mixture consisting of 20 vol.% carbon dioxide and 80 vol.% methane.

† The maximum possible weight loss starting from the corresponding poly(*p*-, *m*-phenylene)hydrazide is 11.1 wt.%.

Influence of the casting conditions

Since it is known that permeability and selectivity can be sensitive to the casting conditions applied[8], the influence of the membrane thickness and the evaporation temperature of formic acid and an additional heat treatment, to remove residual solvent, on the gas separation properties of PT-p/m-1 were studied.

One casting solution of PT-p/m-1 was prepared from which four membranes were cast using casting knives with slit heights of 0.5, 2 samples, and 0.2 mm, also 2 samples. The casting solvent of two membranes with different casting thicknesses was evaporated at 80°C and of the other two at room temperature, see table 2.

After evaporation permeability and selectivity for carbon dioxide towards a carbon dioxide/ methane gas mixture (25/75 vol.%) of the membranes were determined continuously for 7 days. During this period the membranes are continuously exposed to a feed pressure of 6 bar and a vacuum at downstream side of the membrane. Subsequently the membranes were subjected to a heat treatment at 150°C in vacuum for at least 24 hours after which permeability and selectivity were measured again for the carbon dioxide/methane gas mixture. The results are summarised in table 2. Besides carbon dioxide and methane, the permeabilities for oxygen and nitrogen were also measured but as single gases and after the additional heat treatment, see table 3.

Before the heat treatment permeabilities between 12 and 14.2 Barrer for carbon dioxide are found after 1 day. In the course of the first day high selectivities, well above 50 are observed since only small concentrations of the slower permeating species, methane are found during this non-steady situation. From day one to day seven the selectivities almost remain constant. The permeability of the as-cast membranes decreases in time, as can be seen from table 2. After the heat treatment, values for the permeability are lower and constant in time. The time dependence of permeability and selectivity of PT-p/m-1-D before and after the heat treatment is shown in figures 4 (a), (b) and (c). The decrease in permeability with time is representative for all membranes.

Table 2. Gas separation properties of polytriazole (PT-p/m-1) membranes in time, before and after a heat treatment at 150°C in vacuum.

Casting conditions	membrane thickness (µm)	After 1 day		After 7 days		After heat treatment	
		P_{CO2} (Barrer)	$\alpha_{CO2/CH4}$	P_{CO2} (Barrer)	$\alpha_{CO2/CH4}$	P_{CO2} (Barrer)	$\alpha_{CO2/CH4}$
Room Temperature							
PT-p/m-1-A	31	14.2	48.7				
PT-p/m-1-B	62	13.1	49.0	10.4	43.0	6.4	50
80°C							
PT-p/m-1-C	34	12.0	45.5	10.0	40.1	6.22	41
PT-p/m-1-D	60	12.2	44.6	8.9	48.1	5.8	47

IR measurements show a strong absorption peak at 3400 cm^{-1} in the as-cast membranes indicating residual water and formic acid. (The absorption peaks of water and formic acid overlap to a large extent in the IR-spectrum.)

The presence of water in the membrane can be caused by the presence of water in formic acid, up to 4%, or due to absorption of humidity during membrane formation. TGA experiments showed that poly-1,2,4-triazole may contain up to 3% water. The intensity of the peak at 3400 cm^{-1} is lowered during the permeation experiment because both water and formic acid are evaporated from the membrane due to the vacuum at the permeate side of the membrane.

The peak at 3400 cm^{-1} vanishes completely after the heat treatment at 150°C in vacuum. After this heat treatment the membranes become more brittle and upon handling cracks are easily introduced resulting in leaky membranes. This indicates that water and/or residual formic acid acts as a plasticiser. During a permeation experiment the solvents or plasticisers are removed from the membrane due to the vacuum on the permeate side of the membrane. In figure 4 (b) the decrease in permeability is plotted versus the logarithm of time. After a heat treatment all residual low molecular weight components are removed from the membrane and a permeability of 5.8 Barrer is found. In figure 4 (b) it can be seen from extrapolation of the permeability of the non-heat treated membrane to the final value of 5.8 Barrer that all residual solvent will be extracted from the membrane after approximately 1500 hours.

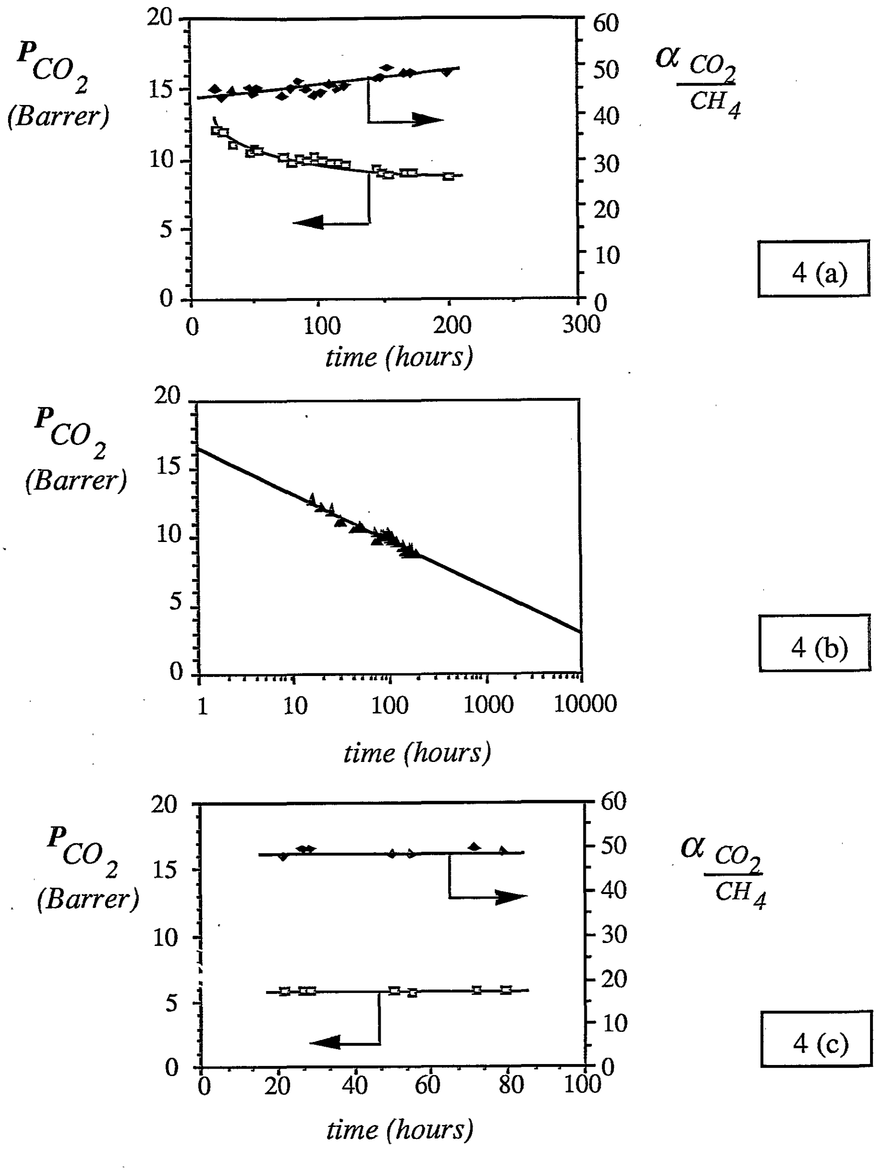


Fig. 4. Influence of residual solvent on the permeability and the selectivity of a PT-p/m-1 membrane freshly prepared without an additional heat treatment (a). Permeability plotted vs. the logarithm of time (b) and permeability and selectivity after an additional heat treatment in vacuum at 150°C during 24 hours (c).

After the heat treatment also the permeabilities for oxygen and nitrogen were determined, being 0.99 and 0.15 respectively resulting in an ideal selectivity of 6.6.

When the membranes are exposed to air the membranes take up moisture and the peak at 3400 cm^{-1} appears again in the IR spectrum. Besides residual solvents, water is able to act as plasticiser for polymers like polyvinyl alcohol, cellulose acetate and cellophane[11]. After an exposure time of 3 months to the atmosphere of a heat treated membrane equilibrium sorption of water is assumed and a carbon dioxide permeability of 6.4 and a carbon dioxide/ methane selectivity of 43-45 was found. This indicates that residual formic acid and not water must have acted as a plasticiser, causing the initial high permeabilities.

In order to explain plasticisation effects, the free volume theory has been proposed in literature[11]. During membrane formation, volume available to the macromolecules is decreased due to the evaporation of the solvent. Residual solvent not evaporated during this process will result in an increased free volume and an increased chain mobility permitting a higher permeability. The polymer matrix compacts in the course of time upon the extraction of the residual solvent, resulting in a decreased free volume, reduced chain mobility and permeability. Besides the change in permeability also the mechanical properties change resulting in an increase in brittleness upon the heat treatment at 150°C in vacuum.

One can conclude that the inherent values for permeability and selectivity are found after the heat treatment when all residual formic acid has been removed and the polymer film has obtained its relaxed state. No significant differences were found between the permeability and selectivity values of thick and thin membranes after the heat treatment. Also the temperature of evaporation did not have a measurable effect on the inherent values of permeability and selectivity.

So, in order to be able to compare the values for the permeability and selectivity of different poly-1,2,4-triazole membranes, the membranes have to be completely free of residual formic acid. It was also found that the gas separation properties of PT-p/m-1 membranes did not depend on the concentration of the original casting solution.

Influence of the feed composition

The permeability and selectivity values of poly-1,3,-4-oxadiazole, poly-1,2,4-triazole and polyhydrazide membranes were determined using oxygen and nitrogen as pure gases while for carbon dioxide and methane a gas mixture consisting of 25 vol.% carbon dioxide and 75 vol.% methane was used. The feed composition will however have its influence on the permeability and selectivity values[14,15].

In figure 5, the influence of the carbon dioxide feed concentration on the membrane performance of a PIDA-POD membrane is represented. Both carbon dioxide permeability and selectivity increase a little with an increasing carbon dioxide feed concentration. On extrapolation to a feed composition of pure carbon dioxide a selectivity of 21.8 is obtained. The methane permeability in the case of a feed composition consisting of pure methane was found to be 3.42 Barrer while for pure carbon dioxide a permeability of 76 Barrer is found. This results in an ideal selectivity using pure gas permeabilities of carbon dioxide and methane of 22.2. The selectivity found using a gas mixture of 25 vol.% carbon dioxide and 75 vol.% carbon dioxide yields thus somewhat lower values for both permeability and selectivity than would be obtained for single gases. Figure 5 shows that the faster permeating gas, carbon dioxide, is slowed down to some extend by the slower permeating methane.

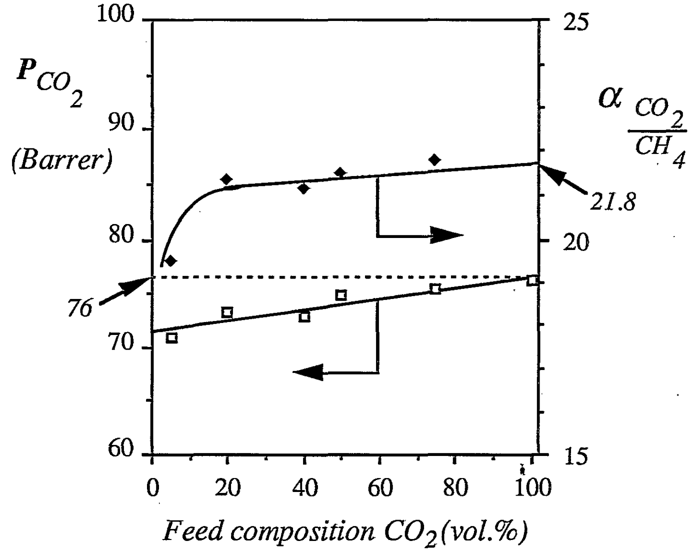


Fig.5. Influence of the carbon dioxide feed composition on permeability and selectivity for a PIDA-POD membrane at 6 Bar.

This experiment was carried out with an 8 months old membrane. The permeabilities and selectivities reported here are somewhat lower than those of freshly prepared PIDA-POD membranes, see table 3. We assume that aging effects are responsible for the decreased permeability.

Influence of the macromolecular structure

Permeability and selectivity

The main objective of the present study is to investigate the relationship between the macromolecular structure, the resulting physical properties and the gas separation properties of polyhydrazide, poly-1,3,4-oxadiazole and poly-1,2,4-triazole membranes. Various functional groups were incorporated into these related polymers to study influence on the gas separation properties, see figure 1.

The two important characteristics of a gas separation membrane material are its permeability and selectivity. In figure 6 permeability is plotted versus selectivity for a carbon dioxide/methane gas mixture (25 vol. %/75 vol.%) of the polymers prepared. The data are also represented in table 3. As can be seen from figure 6, the typical trade-off between selectivity and permeability is found. Introducing a hexafluor unit into the backbone of a poly-1,3,4-oxadiazole gives a polymer with a high permeability typically found for polymers containing this group, like polyimides[1,15] and polycarbonates[16]. Even higher permeabilities were found for PIDA-POD. This polymer contains the bulky and asymmetrical 1,1,3-trimethyl-3-phenylindane moiety also found in Ciba-Geigy's "XU-218".

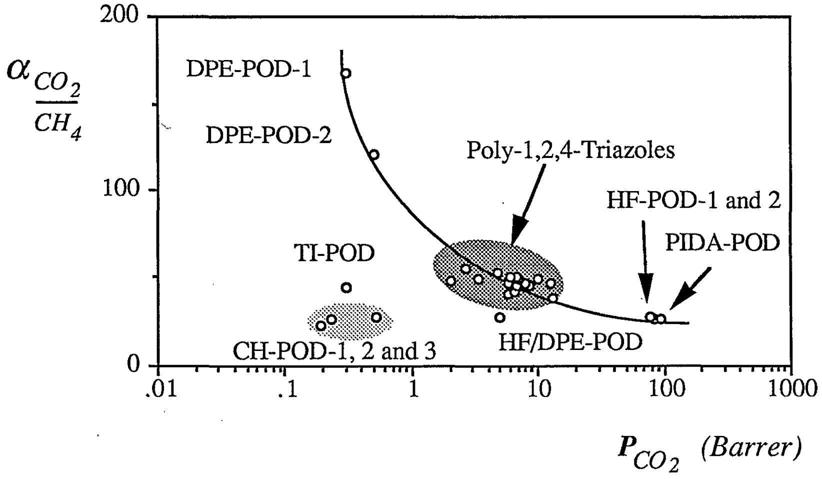


Fig.6. Permeability/selectivity curve for the poly-1,2,4-triazole and poly-1,3,4-oxadiazole membranes.

Table 3. Gas separation properties of poly-1,2,4-triazole, polyhydrazide and poly-1,3,4-oxadiazole membranes

Polymer	P_{CO2} (Barrer)	$\alpha_{CO2/CH4}$	P_{O2} (Barrer)	P_{N2} (Barrer)	$\alpha_{O2/N2}$ (=P_{O2}/P_{N2})	T_g^* (°C)	Density (g/cm^3)	V_f (=V-1.3V_w)/M) (cm^3/g)
1 PT-0/100	2.7	55	0.52	0.09	5.8	242	1.20	0.0956
2 PT-25/75	3.3	49	0.59	0.10	5.9	257	1.20	0.0956
3 PT-50/50	6.7	50	1.17	0.18	6.5	279	1.22	0.0819
4 PT-75/25-1	10.1	50	1.46	0.23	6.3	319	1.25	0.0622
PT-75/25-2	12.6	47	2.00	0.30	6.7	319	1.25	0.0622
5 PT-p/m-1	5.8	47	0.99	0.15	6.6	264	1.21	0.0901
6 PT-p/m-2	7.1	50				267	1.21	0.0860
7 PT-p/m-3	5.9	51				261	1.21	0.0860
8 PT-p/m-25Cl	8.5	46	1.43	0.22	6.5	271	1.24	0.0796
9 PT-p/m-50Cl	6.8	46	1.11	0.17	6.5	269	1.26	0.0819
10 PT-p/m-75Cl	6.8	46	1.32	0.20	6.6	271	1.26	0.0917
11 PT-p/m-100Cl	6.6	42	1.21	0.18	6.7	274	1.31	0.0718
12 PT-p/m-25F	5.8	41	1.11	0.18	6.2	257	1.26	0.0647
13 PT-p/m-50F	8.0	47	1.53	0.22	7.0	269	1.27	0.0669
14 PT-p/m-100F†						276	1.30	0.0646
15 PT-p/m-Me	13.0	38	2.21	0.35	6.3	256	1.15	0.1098
16 PH-1	0.05	‡	‡	‡	‡	§	1.43	0.0610
17 TI-POD	0.3	45	‡	‡	‡	¶	1.38	0.0342
18 *c*CH-POD-1	0.2	27	‡	‡	‡	179	1.21	0.0898
*t*CH-POD-2	0.5	28	‡	‡	‡	179	1.21	0.0898
(*c*+*t*)CH-POD-3	0.2	23	‡	‡	‡	180	1.21	0.0898
19 PIDA-POD	93.0	26	17.1	3.3	5.2	300	1.04	0.2066
20 HF-POD-1	78.0	28	20.0	4.0	5.0	282	1.36	0.1109
HF-POD-2	84.0	26				287	1.36	0.1109
21 DPE-POD-1	0.3	168	‡	‡	‡	333	1.45	-
DPE-POD-2	0.5	120	‡	‡	‡	306	1.45	-
22 HF/DPE-POD	5.0	28				339	1.45	0.0748

* Glass transition temperatures were determined using DSC-techniques except for PT-75/25-1 and PT-75/25-2 their T_g is determined using a torsion pendulum[4].

† PT-p/m-100F films were too brittle to allow permeation experiments.

‡ Methane, oxygen and nitrogen permeabilities were too low to allow an accurate measurement.

§ Glass transition temperature of polyhydrazide cannot be determined directly; Gebben et.al. have found a glass transition of 278°C upon extrapolation[13].

¶ No T_g detected using DSC-techniques[4].

\- Discussed below

The extreme in both permeability and selectivity in comparison with HF-POD and PIDA-POD is DPE-POD. This poly-1,3,4-oxadiazole exhibits a low permeability and an extremely high permeability. Other polymers also containing this group like Kapton® and 6FDA-ODA[12], see figure 7, also exhibit higher selectivities in comparison with corresponding polymers not containing this group. The high selectivity of Kapton® is thought to originate from the high concentration of carbonyl groups in this polymer[17]. However in the case of DPE-POD these carbonyl groups are not present while nevertheless this polymer exhibits a high selectivity meaning that the impressive selectivity must be due to the diphenyl ether structure being a part of the main chain.

The low permeability of DPE containing polymers is likely due to the relatively efficient packing of DPE-POD due to its flexible ether linkage. Chern et al. have related the carbon dioxide/methane selectivity of a number of gas separation membrane materials to the solubility parameters of these polymers[12]. A similar study is under way in our laboratory and the results will be reported in due course.

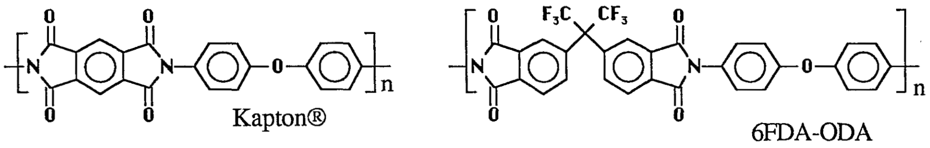


Fig. 7. Chemical structure of two DPE-containing polymers.

Two batches of DPE-POD and HF-POD were prepared and the reproducibility of the gas separation data is good, see table 3. The large difference in selectivity values found for the two DPE-POD batches is caused by a relatively large impact of a small difference in methane permeability.

Polymers with a completely aromatic backbone are located on the hyperbolic line in figure 6. The alicyclic CH-POD deviate which obviously is due to their flexible aliphatic cyclohexane ring. Three batches of CH-POD were prepared, see table 3, using pure *cis-* and *trans-*cyclohexane dicarboxylic acid and a mixture of both isomers as monomers.

Using DSC, TGA and IR-techniques it was found that the three polymers batches were identical[5,18]; this must be due to a conversion in the acidic reaction medium of *cis*-isomers into the more stable *trans*-isomer. This implies that the differences in permeabilities as found here must be due to minor configurational differences or must lie within experimental error.

The high selectivities of the completely aromatic and rigid poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles are believed to originate from their high chain stiffnesses also indicated by their high glass transition temperatures. These polymers are believed to behave as "molecular sieves" generally exhibiting high diffusivity selectivities[20] based on their ability to discriminate more effectively between permeant sizes and shapes.

Permeability, diffusivity and solubility

Permeability is considered to be the product of diffusivity and solubility:

$$P = D.S \tag{4}$$

where P is the permeability for a given gas in cm^3(STP).cm/(cm^2.s. cmHg), D is the diffusion coefficient in $cm^2.s^{-1}$ and S is the solubility in cm^3(STP)/cm^3.(cmHg).

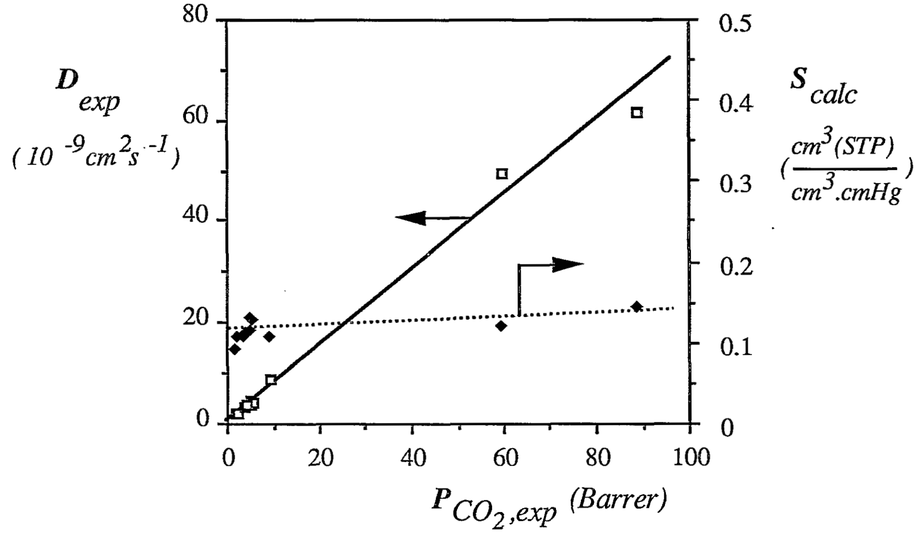


Fig.8. Experimental diffusivity and calculated solubility values for a number of poly-1,2,4-triazole and poly-1,3,4-oxadiazole membranes as a function of the measured permeability.

The diffusion coefficient is calculated from a transient state permeation experiments revealing the time-lag Θ:

$$D = l^2/6\Theta \tag{5}$$

where l is the membrane thickness. The permeability was determined from the slope of the time-lag curve following the transient state. Equations 4 and 5 allow the calculation of solubility coefficients. Detailed discussions on theory[21] and measuring techniques[6] have excellently been reviewed, and are therefore not discussed in detail here. Permeability and diffusivity values for a number of polymers were obtained from time-lag experiments with vacuum at the downstream side and 6 bar at the feed side using carbon dioxide as a single gas, see figure 8. Solubility was calculated from these diffusivity and permeability values using equation 5.

The carbon dioxide permeability values differ slightly from those represented in figure 6 where a gas mixture consisting of 25 vol.% carbon dioxide and 75 vol.% methane is employed resulting in a partial pressure of 1.5 bar for carbon dioxide.

From figure 8 it can be seen that the solubility remains almost constant while diffusivity increases linearly with permeability. This means that the increase in permeability is mainly caused by an increase in diffusivity.

Influence of the *p*- and *m*-phenylene content in poly-1,2,4-triazoles

Several authors have investigated the influence of the ratio *p*-/*m*-phenylene groups on the gas separation properties of polyimides[15], polyesters[22], poly(phenolphthalein phthalate)s[23], and poly(ethylene tere/isophthalates[24]. In all cases the *p*-phenylene substituted polymers exhibited higher permeabilities than the corresponding *m*-phenylene polymers.

Gebben at al. have extensively investigated poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole] for its gas separation properties[3]. The *p*-phenylene and *m*-phenylene groups are incorporated in alternating fashion in this polymer. But what is the influence of the sequence of incorporation of these groups, viz. alternating versus random incorporation and what are the permeability and selectivity values for the two isomers: poly[*p*-phenylene-(4-phenyl)-1,2,4-triazole] and poly[*m*-phenylene-(4-phenyl)-1,2,4-triazole]?

For the various *p*-/*m*-isomers prepared permeability and selectivities values together with the glass transition temperatures and densities are represented in table 3. All poly-1,2,4-triazoles were soluble in formic acid, except for poly[*p*-phenylene-(4-phenyl)-1,2,4-triazole] which was only soluble in concentrated sulphuric acid. No flexible membranes could however be prepared from the latter polymer solutions.

For the poly-1,2,4-triazoles an increase in permeability is found with increasing *p*-phenylene content in the polymer backbone, see figure 9. Selectivity almost remains constant for this series of isomers despite the increasing permeability. The increase in permeability is mainly due to an increasing diffusivity, the solubility is hardly changed. This could be expected since the chemical composition of the polymers, and thus the polymer-permeant interaction, is not changed at all.

A semi-logarithmic relation between permeability and *p*-phenylene content is observed. A similar dependence of permeability has been found by Schmidhauser and Longley for aromatic polycarbonates[25] and by Barnardeo et al. for various random copolymers[26]. The following relation has been proposed to describe the relation between permeability and polymer composition:

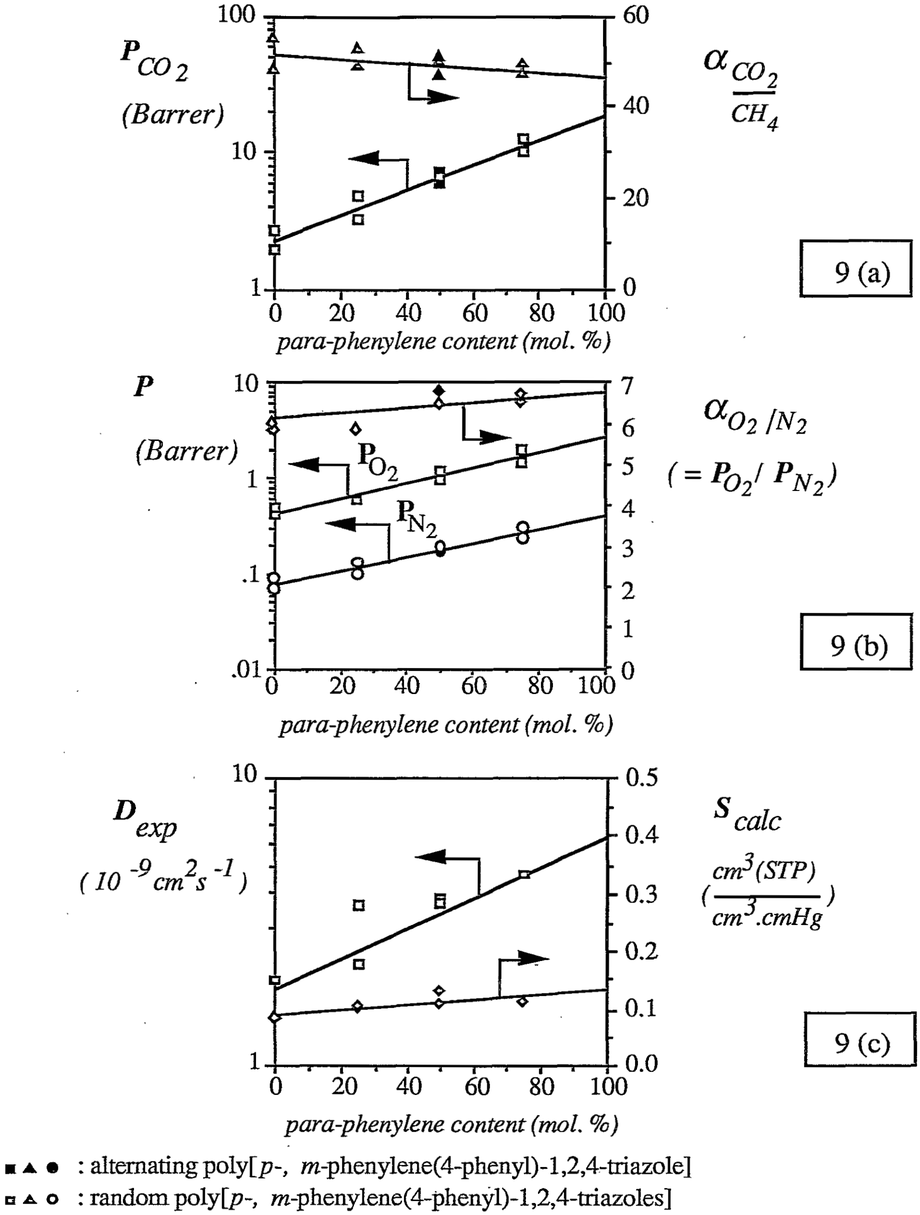


Fig.9. Permeability and selectivity values for poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles] for a carbon dioxide/methane mixture (a), oxygen and nitrogen (b) as function of the *p*-phenylene content in the main chain. Carbon dioxide diffusivity and sorption as a function of the *p*-phenylene content in the main chain (c).

$$\log P_{AB} = X_A \log P_A + X_B \log P_B \qquad (6)$$

The relation allows calculation of the permeability of intermediate and homopolymers.
Upon extrapolation permeability, diffusivity and solubility values for poly[*p*-phenylene-(4-phenyl)-1,2,4-triazole] can be determined, see figure 9. The permeability values for carbon dioxide, oxygen and nitrogen are 21, 2.7 and 0.4 Barrer respectively. Selectivity is less dependent on the ratio *p*-/*m*-phenylene groups and selectivities of 48 for carbon dioxide/methane and 6.8 for oxygen/nitrogen are found upon extrapolation.
Besides the random copolymers also the permeability and selectivity values of the alternating copolymers are plotted in figure 9. These values do not deviate significantly from those found for the random copolymers.
Considering these results and results of other authors[22,23,24], we can conclude that an increasing permeability with increasing ratio *p*-phenylene over its *m*-isomer is likely to be a general phenomenon. The increase in permeability was found to be mainly due to the increase in diffusivity which was also reported by Coleman and Koros for two isomeric *m*- and *p*-connected fluorinated polyimides[15].

Glass transition and free volume
Besides the permeability also the glass transition temperature for the *p*-phenylene polymer is higher than for the *m*-phenylene polymer. The density of the *p*-isomer is in all cases lower[15,23,24]. (No data on density and glass transition temperatures are reported by Schmidhauser and Longley[22].)

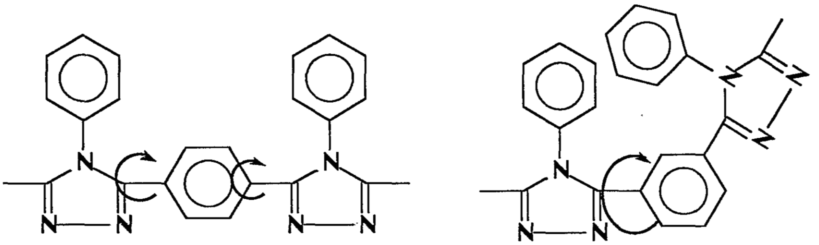


Fig.10. Chain segments of poly[*p*-phenylene-(4-phenyl)-1,2,4-triazole] and poly[*m*-phenylene-(4-phenyl)-1,2,4-triazole].

Sheu and Chern[23] have attributed the increase in permeability to the increasing free volume of the *para* -isomer caused by its lower density. Since these copolymers have the same Van der Waals volume a lower density results in a higher free volume. Differences in density are however very small. In our case the density increases with increasing *p*-phenylene content

which seems to be in contradiction with the explanation of Sheu and Chern, see table 3.
Other authors have attributed the increasing permeability to an increasing torsional mobility or "revolving door" effect of the *p*-phenylene group allowing passage of a gas molecule[15], see figure 10. This rotation is not likely in the solid state in the case of the *m*-isomer since this would also require the rotation of the adjacent groups. Gillham and Gillham[27] have shown by means of thermo-mechanical techniques of related polyimides that the *m*-isomer has indeed suppressed sub-T_g motions. These motions were also found by Light and Seymour[24] for *meta*-connected polyester in comparison to the para-isomer. Several authors have speculated that these sub-T_g motions may be responsible for the higher gas permeability of the *para*-isomers because they would allow diffusional jumps to occur.
Dynamical mechanical analysis on these poly-1,2,4-triazoles showed ß-relaxations at -113℃ (recorded on a Myrenne Torsion pendulum with a frequency of 1 Hz and a heating rate of 1.8℃/min.). We could however not observe distinct differences between the isomers. Recently Schmidhauser and Longley[25] have shown that this particular motion cannot be the rate limiting step. McHattie et al.[28] studied the gas transport in various polysulphones and reported that the temperature of the peak maximum of the sub-T_g motions of various polysulphones is inversely related to their free volume. In other words; a higher free volume allows small scale motions at lower temperatures indicating that sub-T_g motions are a function of free volume. Lee[29] has shown that permeability can be expressed as a function of the free volume. It seems that the (amount of) free volume is the rate limiting factor for both sub-T_g motions and gas permeability. Although segmental motions may be necessary to allow the passage of a permeating gas molecule, the amount of free volume seems to be the controlling factor.
We therefore speculate that the increased permeability upon increased *para*-content is due to a difference in packing between the poly-1,2,4-triazole isomers resulting in a different free volume and a different distribution of free volume and we would like to follow the illustrative explanation of Dimarzio and Gibbs[30] on the difference in packing of rigid polymers versus flexible polymers.
All poly-1,2,4-triazole membranes were prepared by casting a polymer solution in formic acid onto a glass plate followed by evaporation of the solvent. During the evaporation process the macromolecules approach each other. From entropy considerations it follows that during this process of polymer matrix formation, the macromolecules will try to occupy the space available as equally as possible, resulting in a narrow free volume distribution. The only difference between the isomeric *m*- and *p*-phenylene poly-1,2,4-triazoles is the extra axis of rotation available to the *m*-isomer through which it can change its conformation during membrane formation. The *p*-isomer is a rod-like macromolecule and rotation does not change its conformation to the same extent as in the case of the *m*-isomer, see figure 10. An amorphous polymer matrix of the *p*-isomer can be compared to a heap of strands of uncooked spaghetti, requiring substantially more free volume than the more flexible *m*-isomer which can be compared to cooked spaghetti which will pack into a much more tight form during membrane

formation[30]. This extra axis of rotation of the *m*-isomer, through which it can change its conformation during membrane formation, will yield a polymer matrix which has a much more narrow free volume distribution. The rigid *p*-isomer has a smaller number of possible conformations resulting in a smaller probability to achieve optimal relaxation of non-equilibrium free volume. This results in a larger free volume and a broader free volume distribution and consequently a higher permeability. In macroscopic terms this difference is small as is indicated by the small differences in densities[15,23,24] and may be easily overshadowed by measuring inaccuracies. Since differences in densities are very small, these results should not be overinterpreted. Their reliability may be influenced by side effects like polymer/solvent interactions in the density column or by residual impurities in the polymer matrix. Density measurements reveal an integrated determination of free volume. Of equal importance is the distribution of free volume since diffusion is assumed to take place only through holes with a minimal critical hole size, depending on the size of the permeant. This free volume distribution may be estimated using for example probe techniques[31].

Gas transport is believed to be much more sensitive to subtle changes in the polymer matrix than other techniques, like density measurements, can reveal. A technique sensitive to the same conformational differences in the polymer matrix as gas diffusion molecules is positron annihilation which has been studied extensively by Durgar'yan et al.[32]. They reported an increased fraction of free volume with increasing glass transition temperature for various polymers. This behaviour was also found for the polymers studied: with increasing *p*-phenylene content the glass transition temperature increases and also the permeability increases. Fritzsche et al.[33] have prepared polysulphone hollow fibre membranes using Lewis acid/base solvent systems which resulted in an acceleration of the coagulation process. This results in membranes with an increased non-equilibrium free volume which is reflected by an increased glass transition temperature. Van Krevelen[34] allows us to interpret this increase in free volume on the basis of the increase in glass transition temperature, as follows:

Thermal expansion below and above the glass transition temperature can be visualised using the concept of Simha and Boyer[35], see figure 11. Decreasing the temperature from the rubbery state results in a decreasing free volume above T_g. Below the glass transition temperature, movements of only small parts of the chain are possible and the non-equilibrium free volume is assumed to be constant in the glassy state as is visualised in figure 11.

Van Krevelen found that the molar thermal expansivities in the rubbery and glassy state (E_r and E_g) of most polymers is related to the Van der Waals volume:

$$E_r = 1.00*10^{-3}*V_w \qquad [\text{in cm}^3/\text{mol.K}] \qquad (6)$$

$$E_c = E_g = 0.45*10^{-3}*V_w \qquad [\text{in cm}^3/\text{mol.K}] \qquad (7)$$

E_c stands for the expansion coefficient of the crystalline materials, or in the case of amorphous materials for the total solid including interstitial volume.

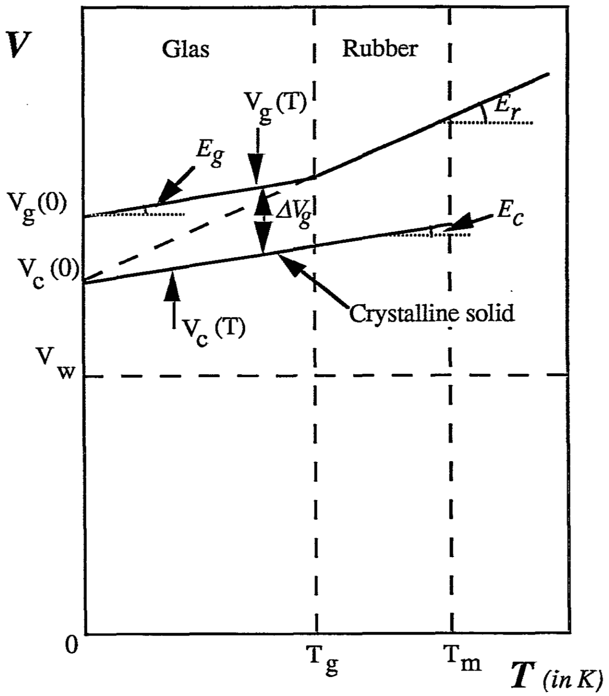


Fig. 11. Thermal molar expansions of polymers in the rubbery state (E_r), glassy state (E_g) and crystalline state (E_c)(ΔV_g, V_w, V_g and V_c are in cm^3/mol)[34,35].

Since ΔV_g is constant over the whole region below the glass transition:

$$\Delta V_g(0) = \Delta V_g(T_g) \tag{8}$$

At T_g the molar volumes in rubbery and glassy state are equal, see figure 11:

$$V_g(0) + E_g.T_g = V_c(0) + E_r.T_g \tag{9}$$

Thus,

$$\Delta V_g = V_g(0) - V_c(0) = (E_r - E_g).T_g =$$

$$=(1.00 - 0.45).10^{-3}V_w.T_g = 0.55.10^{-3}.V_w.T_g \tag{10}$$

In order to obtain the specific free volume, ΔV_g is divided by the molecular weight M:

$$V_f = \Delta V_g/M \qquad \text{[in cm}^3\text{/g]} \tag{11}$$

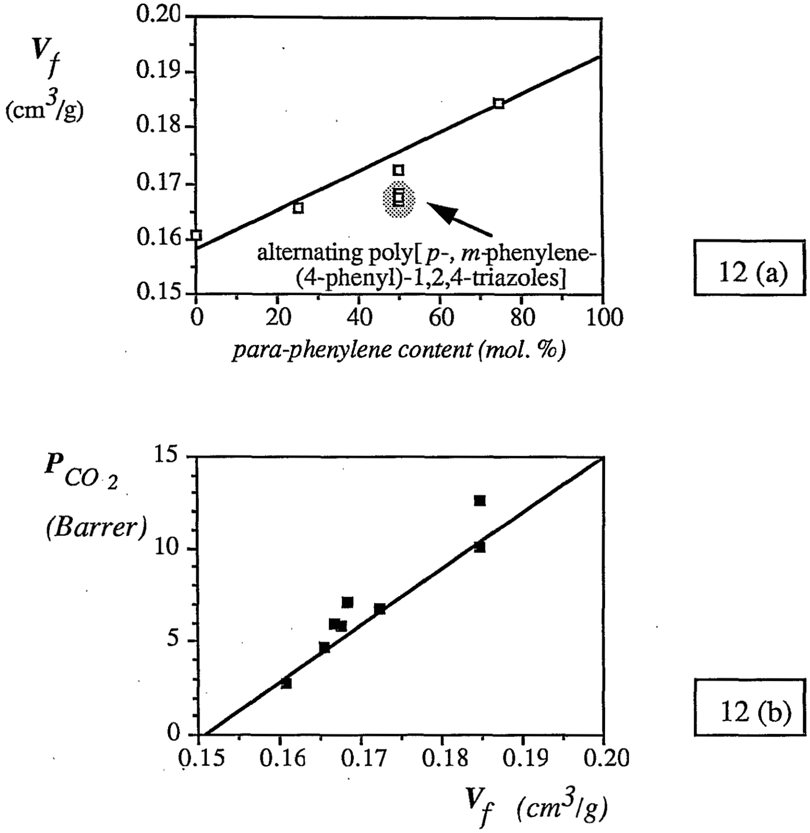


Fig. 12. Free volume (V_f) calculated using equation (10) and (11) as a function of the p-phenylene content in the main chain (a) and permeability as a function of free volume for these series of isomeric poly[p-, m-phenylene(4-phenyl)-1,2,4-triazoles] (b) (V_f in cm^3/g).

In figure 12 (a) the specific free volume V_f defined by equation 10 and 11 is plotted versus the percentage *para*-phenylene groups in the main chain. It can be seen that the specific free volume increases with increasing percentage of p-phenylene groups. The alternating poly-1,2,4-triazoles exhibit a somewhat lower specific free volume. This simple calculation allows us to estimate the specific free volume using T_g values instead of density measurements. This approach is believed to yield a more accurate approximation of the free volume for these closely related poly[p-, m-phenylene-(4-phenyl)-1,2,4-triazoles]. In figure 12 (b) the carbon dioxide permeability is plotted as a function of the free volume thus calculated. Polymers with high glass transition temperatures mostly exhibit high permeabilities which is due to the larger free volume as is indicated by equation (10).

Influence of *p*-phenyl substitution in poly-1,2,4-triazoles

Various pendant p-substituted phenyl groups in different ratio's were incorporated onto the polymer backbone of alternating poly[*p*-, *m*-phenylene-(4–(phenyl)-1,2,4-triazole], see figure 1, and table 3. Aim is to relate the change in gas separation properties to the change in steric and polar interactions caused by the incorporated specific group. A similar study for substituted polystyrenes has been carried out by Puleo et al.[37].

Compared to unmodified poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole] incorporation of a methyl group results in an increased permeability whereas the selectivity slightly decreases. This increase in permeability is due to an increased free volume, see table 3. The methyl groups obviously reduce the chain packing efficiency.

The halogen substituted poly-1,2,4-triazoles all have a lower free volume than the unmodified ones. Due to the increased polarity, cohesive forces are increased resulting in a more densely packed polymer matrix with a lower free volume. Since fluorine is more electronegative than chlorine, higher intermolecular forces are responsible for the lower free volume of the fluorine-substituted poly-1,2,4-triazoles.

Variations in permeability due these modifications are however small. Larger pendant groups may increase permeability more dramatically. The possibilities to incorporate larger structures, like biphenylic structures, appeared however to be limited[5].

Relation between permeability and free volume of the polymers studied

The free volume model describing gas permeability as a function of the polymer free volume received much attention lately[38,39,40]. Lee[29] was the first to correlate permeability of polymers to their specific free volume. For this purpose the hole theory of diffusion was adopted postulating that the rate of diffusion depends on the number and size distribution of existing holes in the polymer matrix[40]. This theory assumes that diffusion of a gas only then takes place if the local specific volume in the polymer matrix exceeds a minimum value allowing diffusion of a gas molecule. The free volume is defined as

$$V_f = V - V_0 \qquad (12)$$

Where, V is the polymer specific volume and V_0 is the volume occupied by the chains. The latter is the molar volume at 0 K. This volume is assumed to be impermeable for diffusing gas molecules. Lee calculated V_0 using the relation proposed by Bondi[42]:

$$V_0 = 1.3V_w \qquad (13)$$

The Van der Waals volume (V_W) is calculated using a group contribution method. We have used the tabulation of Askadskii[43] to calculate V_W.
In the case of densely packed polymers the free volume will be small. In equation 12, V_0 is subtracted from V, obtained through a density measurement and through a summation of group contributions, respectively. Subtraction of these large numbers yields a small value for V_f with a relative large error. For the DPE-POD polymers a negative value for V_f was obtained which is likely to be due to errors in the measured specific volume. On the other hand the factor 1.3 is arbitrary and may not be justified in all cases. DPE-POD has flexible ether bonds probably allowing the polymers to pack more efficiently to such an extent that the factor 1.3 is not appropriate in this case. One may therefore conclude that $V - 1.3.V_W$ offers an approximation of the free volume available for permeation but that it may in some case be an oversimplification of the considered phenomena. In table 3 the free volumes calculated are represented.
Lee has shown that the permeability can be correlated with the specific free volume V_f using in $P = D.S$ the following expression for D:

$$D = D_0 \, exp(-B/(V_f) \qquad (16)$$

This gives for P:

$$P = S. D_0 \, exp(-B/(V_f) \qquad (17)$$

Since S is practically constant in our case, see figure 8, equation 17 can be written as

$$P = A.exp \, (-B/V_f) \qquad (18)$$

in which the parameters A and B depend on the type of gas. This simple free volume treatment allows a direct insight in the influence of the macromolecular structure on the gas transport properties.
In figure 13 the carbon dioxide permeabilities are plotted versus the reciprocal V_f values. A linear dependency can be observed although much scattering is observed, especially CH-POD and PH show deviating behaviour which is attributed to their essentially different macromolecular structure. Whereas all the other polymers have a rigid aromatic backbone, CH-POD and PH have a more flexible backbone. This likely enables these polymers to achieve a different packing compared to the other all-aromatic polymers. CH-POD and PH can obviously achieve a more optimal and thus a more narrow free volume distribution due to their flexible bonds. Schmidhauser and Longley[25] also found decreased permeabilities upon incorporation of cyclohexane units in polycarbonates which was attributed to the ability of this moiety to adopt a sterically compact conformation. PH is capable of strong cohesive forces due to hydrogen bonding between amide and carbonyl groups making passage of permeant molecules more

difficult. A good correlation between permeability and reciprocal V_f values is obviously only obtained if intermolecular forces and chain flexibility or rigidity are comparable in magnitude[36].

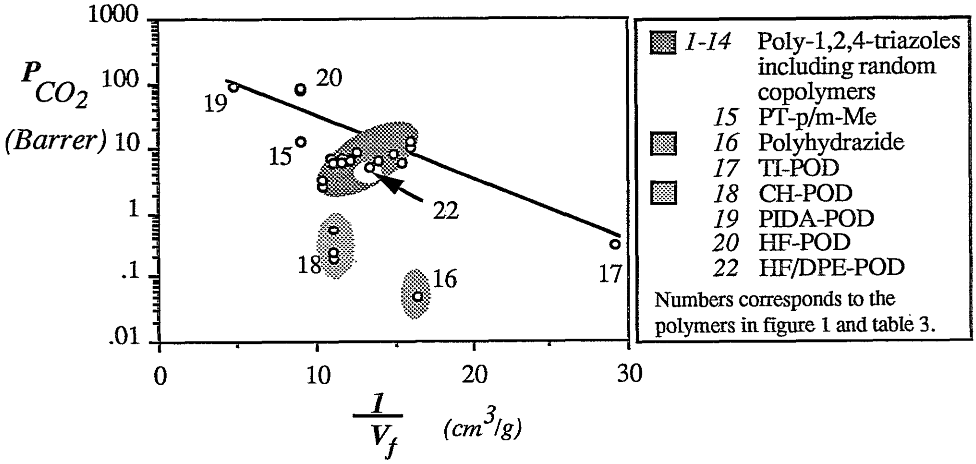


Fig. 13. Carbon dioxide permeability as a function of the reciprocal free volume V_f.

CONCLUSIONS

Poly-1,2,4-triazoles and poly-1,3,4-oxadiazoles are two interesting polymer families of new membrane materials for gas separation purposes. A wide variety of permeabilities and selectivities can be found for these two polymer families. Incorporating a diphenyl ether (DPE) moiety into the polymer backbone of a poly-1,3,4-oxadiazole yields a polymer with a remarkable high selectivity. Incorporation of a hexafluor (HF) or phenyl indane (PIDA) unit results in poly-1,3,4-oxadiazoles with very high permeabilities in combination with reasonable selectivities.

The permeability of the poly-1,2,4-triazoles appears to depend on the amount unclosed triazole groups; the highest permeabilities are to be found for the fully converted poly-1,2,4-triazole.

The casting conditions have no significant effect on the gas separation properties, however residual formic acid may act as a plasticiser. Formic acid can be removed from the membrane by a heat treatment at 150°C during at least 24 hours.

The gas separation values are to a minor extent a function of the feed composition and the permeabilities of single gases and the resulting ideal selectivity may deviate from permeability and selectivity values found employing real gas mixtures.

The differences in permeability are in all cases due to differences in diffusivity, both may increase over several orders of magnitude while solubility hardly changes.

The permeability of polyhydrazide, poly-1,3,4-oxadiazole and poly-1,2,4-triazole membranes can be expressed as a function of their free volume. Permeability also increases with increasing *p*-phenylene content in the isomeric poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles] which is most likely to be due to an increase in free volume available for permeation.

ACKNOWLEDGEMENT

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LITERATURE.

1. T.H. Kim, W.J. Koros, G.R. Husk and K.C. O'Brien, J. Membrane Sci., 37, 45-62(1988).
2. M. Langsam, M. Anand, and E.J. Karwacki, Gas separation and Purification, 2, 162-170(1988).
3. B. Gebben, M.H.V. Mulder and C.A. Smolders, J. Membrane Sci., 46, 29-41(1989).
4. E.R. Hensema, J.P. Boom, M.H.V. Mulder and C.A. Smolders, to be published. *(Chapter 2 of this thesis).*
5. E.R. Hensema, M.E.R. Sena, M.H.V. Mulder and C.A. Smolders, to be published. *(Chapter 3 of this thesis).*
6. R.M. Felder and S.S. Huvard, "Methods of experimental physics", in L. Marton (Ed.), "Solid State Physics", Academic Press, New York, 1980, Vol. 16, Chapter 17.
7. J.A. van't Hof, Wet spinning of asymmetric hollow fibre membranes for gas separation, Ph.D. Thesis, University of Twente, 1988.
8. M. Moe, W.J. Koros, H.H. Hoehn and G.R. Husk, J. Applied. Pol. Sci., 36, 1833-1846(1988).
9. J.S. McHattie, W.J. Koros and D.R. Paul, Polymer, 32, 840-850(1991).
10. H.J. Bixler and O.J. Sweeting, "Barrier properties of polymer films", *in* O.J. Sweeting (Ed.), "The science and technology of polymer films", Vol. 2, New York, 1977.
11. J.K. Sears and N.W. Touchette, "Plasticizers", in Kroschwitz (ed.), "Encycl. Polym. Sci. Eng." Vol. 18, Wiley, New York, 1987.
12. R.T. Chern, W.J. Koros, H.B. Hopfenberg and V.T. Stannet, "Material Selection for Membrane-Based Gas separations", *in* D.R. Lloyd (ed.), "Materials Science of Synthetic Membranes", ACS Symposium Series, Vol. 269, Washington, 1985.
13. B. Gebben, M.H.V. Mulder and C.A. Smolders, J. Polym. Sci., Polym. Chem. Ed., 26, 1757-1768(1988).
14. W.J. Koros, R.T. Chern, V.T. Stannet and H.B. Hopfenberg, J. Polym. Sci., Polym. Phys. Ed., 19, 1513-1530 (1981).
15. M.R. Coleman and W.J. Koros, J. Membrane Sci., 50, 285-297(1990).
16. M.W. Hellums, W.J. Koros, G.R. Husk and D.R. Paul, J. Membrane Sci., 46, 93-112(1989).
17. W.J. Koros, J. Polym. Sci., Polym. Phys Ed., 23, 1611-1628 (1985).

18. B. Gebben, M.H.V. Mulder and C.A. Smolders, J. Polym. Sci., Polym. Chem. Ed., 26, 1757-1768(1988).
19. Y. Iwakura, K. Uno and S. Hara, Makromol. Chem., 95, 248-160(1966).
20. S.A. Stern, V.M. Shah and B.J. Hardy, J. Polym. Sci., Polym. Phys. Ed., 25, 1263 (1987).
21. H.L. Frisch and S.A. Stern, "Diffusion of small molecules in polymers" in CRC Critical Rev. Solid State and Mat. Sci., 11, 123-187(1983).
22. J.C. Schmidhauser and K.L. Longley, Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., Vol. 30, 13-14(1989).
23. F.R. Sheu and R.T. Chern, J. Polym. Sci., Polym. Phys. Ed., 27, 1121-1133(1989).
24. R.R. Light and R.W. Seymour, Polym. Eng. Sci. 22, 857 (1982).
25. J.C. Schmidhauser and K.L. Longley, J. Appl. Polym. Sci., 39, 2083-2096(1990).
26. A.E. Barnardeo, W.S. Creasy and L.M. Robeson, J. Polym. Sci., Polym. Phys. Ed., 13, 1979-1986(1975).
27. J.K. Gillham and H.C. Gillham, Pol. Eng. Sci., 13, 447-454(1973).
28. J.S. McHattie, W.J. Koros and D.R. Paul, Polymer, 32, 840-850(1991)
29. W.M. Lee, Polym. Eng. Sci., 20, 65-69(1980).
30. E.A. Dimarzio and J.H. Gibbs, J. Polym. Sci., 40, 121-131(1959).
31. J.G. Victor and J.M. Torkelson, Macromolecules, 20, 2241-2250(1987).
32. S.G. Durgar'yan, Yu. P. Yampol'skii and N.A. Plate, Russian Chemical Reviews, 57, 549-558(1988).
33. A.K. Fritzsche, R.E. Kesting and M.K. Murphy, J. Membrane Sci., 46, 135-155(1989).
34. A. K. Van Krevelen, Properties of polymers, Chapter 4, Third edition, Elsevier, Amsterdam, 1990.
35. R. Simha and R.F. Boyer, J. Chem. Phys., 37, 1003(1962).
36. E.R Hensema, M.H.V. Mulder and C.A. Smolders, to be published *(Chapter 5 of this thesis).*
37. A.C. Puleo, N. Muruganandam and D.R. Paul, J. Polym. Sci., Polym. Phys. Ed., 27, 2385-2406(1989).
38. T.A. Barbari, W.J. Koros and D.R. Paul, J. Polym. Sci., Polym. Phys. Ed., 26,709(1988).
39. N. Muruganandam, W.J. Koros and D.R. Paul, J. Polym. Sci., Polym. Phys. Ed., 25, 1999 (1987).
40. K.E. Min, W.J. Koros and D.R. Paul, J. Polym. Sci., Polym. Phys. Ed., 26, 1021 (1988).
41. V.T. Stannet, "Simple gases" and H. Fujita, "Organic vapors above their glass transition temperature", and C.A. Kumins and T.K. Kwei,"Free volume and other theories", *in* J. Crank and G.S. Park (eds.), "Diffusion in Polymers", Academic press, London, 1968.
42. A. Bondi, Physical properties of molecular crystals, liquids, and glasses, Elsevier, Amsterdam, 1968.
43. A.A. Askadskii, "Predictions of physical properties of polymers", in R.A. Pethrick and G.E. Zaikv (Eds), "PolymerYearbook", Vol. 4, Harwood Acad. Publ., London, 1987.

5

On the mechanism of gas transport in rigid polymer membranes.

E.R. Hensema, M.H.V. Mulder and C.A. Smolders

SUMMARY

Conventional polymers are compared with "tailor-made" polymers as gas separation membrane materials. The increased permeability of the latter are due to their higher free volume available for gas transport. The increased free volume is associated with the rigidity polymer backbone. Free volume is obtained by subtracting the occupied volume calculated using group contributions from the polymer specific volume. Wide Angle X-ray techniques are used to obtain average d-spacings that are interpreted in terms of average intermolecular space and related to permeability data. These highly permeable rigid polymer membranes have high glass transition temperatures. The physical parameters, i.e. T_g and the jump in heat capacity (ΔC_p), are obtained with Differential Scanning Calorimetry and are used to obtain an estimation of free volume. A good correlation for a series of random copoly[*p*, *m*-phenylene(4-phenyl)-1,2,4-triazoles] is obtained. A relationship between permeability and a free volume term which can be estimated from thermodynamic properties is equally valid for a wide variety of conventional polymers.

INTRODUCTION

In a previous paper we have reported on the gas transport and separation properties of poly-1,3,4-oxadiazoles and poly-1,2,4-triazole membranes[1]. Increase in permeability appeared to be a function of the diffusivity only since the latter increased linearly with permeability whereas solubility almost remained constant.

Permeability and diffusivity could be expressed as a function of the polymer free volume using a Doolittle type equation previously used by Fujita[2] and later successfully employed by Lee[3] who used this equation to correlate the carbon dioxide and oxygen permeability in various commercial polymers to the polymer specific free volume:

$$P = S.\,D\ exp(-B/(V_f) \tag{1}$$

in which *P* is the permeability, *S* is the solubility, *B* is a constant depending on the penetrant and V_f is the polymer specific free volume. Since S can practically be considered as a constant, equation 1 can be written as

$$P = A.exp\ (-B/V_f) \tag{2}$$

In which the parameters *A* and *B* depend only on the type of gas. Free volume here is defined as

$$V_f = V - V_0 \tag{3}$$

where, V is the polymer specific volume and V_0 is the volume occupied by the polymer chains at 0 K. This volume is assumed to be impermeable for diffusing gas molecules. Lee calculated V_0 using the relation proposed by Bondi[4]:

$$V_0 = 1.3V_w \tag{4}$$

The Van der Waals volume (V_w) is calculated using a group contribution method. We have used the tabulation of Askadskii[5] to calculate V_w. This simple free volume treatment allows a direct insight on the influence of the macromolecular structure on the gas transport properties.

The factor 1.3 is however arbitrary and may sometimes result in a faulty interpretation, i.e. giving rise to a negative value of V_f[1].

The free volume treatment is gaining increasing interest since various authors were able to correlate the permeability and diffusivity of various polymer *classes* to their free volume. For example, Maeda and Paul used this equation to interpret the reduction in transport in polysulphone and polyphenylene oxide containing low molecular weight antiplasticisers[6]. The reduction in transport due to the addition of these additives could be explained nicely in terms of a decrease in free volume. Barbari et al. related the free volume of polymers based on bisphenol-A to the diffusivity[7]. Muruganandam et al.[8] and Schmidhauser and Longley[9] did this for polycarbonates whereas Min et al.[10] studied the influence of the tacticity of polymethyl methacrylate using this equation.

Equation (2) implies that for one penetrant all polymers lay on one straight line. This equation does however not account for special polymer/penetrant interactions, differences in macromolecular cohesive forces and chain flexibilities. Since solubility almost remains constant for one class of related polymers, e.g. the poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles studied, it is justified to neglect polymer/penetrant interactions in theses cases.

Vrentas et al. have introduced a modified version of equation (1) accounting for specific polymer/penetrant interactions[11,12,13]. Their approach may better describe the process of permeation in polymers but their equation contains parameters not directly accessible for the poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles studied.

Free volume is a quantity which depends on the definition used, like hole-, excess-, configurational-, expansion- or fluctuation-volume[14]. The concept of unrelaxed free volume of glassy polymers is except for gas transport theories also applied successfully for understanding and describing many other properties including impact strength, physical aging and creep.

Aim of this paper is to compare the previously reported gas separation properties of poly-1,3,4-oxadiazole and poly-1,2,4-triazole membranes[1] with other conventional membrane materials and to evaluate other means of free volume determinations.

EXPERIMENTAL

Materials

The syntheses, membrane preparation and gas separation properties of poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles are reported elsewhere[1,15,16].

Characterisation

Differential Scanning Calorimetry (DSC).

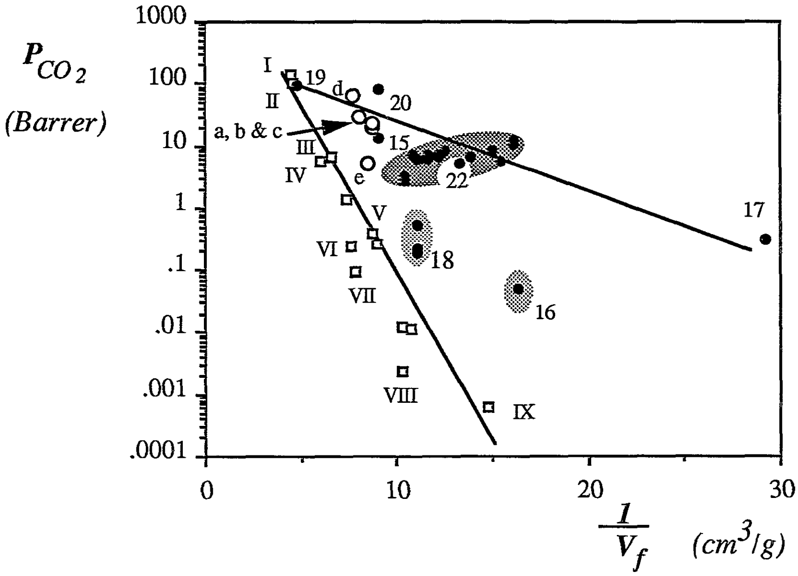
DSC measurements were performed on a Perkin-Elmer DSC 4 in combination with a System 4 Microprocessor Controller and a Thermal Analysis Data Station (TADS), model 3700. The polymer samples were placed in aluminium sample pans and the temperature was increased with a heating rate of 20℃/min. from 100 to 400℃ under a nitrogen purge gas stream. As glass transition temperature (T_g) the midpoint of the transition was taken, calculated by means of the TADS software. The jump in heat capacity (ΔC_p) at this point was also calculated using the TADS software.

Wide Angle X-ray Scattering (WAXS).

Wide angle X-ray diffractograms were record on a Philips Röntgen diffractometer, PW1710 using copper radiation (CuKα = 1.5418Å)[15].

RESULTS AND DISCUSSION

In figure 1 the permeabilities of conventional polymers as reported by Lee[3] are compared with hexafluoro-substituted aromatic polyimides[17,18] and the previously reported poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles[1].



□ *Conventional polymers studied by Lee (ref. 3) including polybutadiene (I), polyethylene (II), polycarbonate (III), polystyrene (IV), polyethylene terephthalate (V), polymethyl methacrylate (VI), polyvinyl chloride (VII), polymethacrylonitrile (VIII) and polyacrylonitrile (IX).*

○ *Hexafluoro-substituted polyimides.*
(a) 6FDA-ODA (ref. 17)
(b) 6FDA-MDA (ref. 17)
(c) 6FDA-IPDA (ref. 17)
(d) 6FDA-6FpDA (ref. 18)
(e) 6FDA-6FmDA (ref. 18)

● *Polyhydrazide, poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles. Numbers and abbreviations are similar to those in ref. 1*

▨	*1-14*	*Poly-1,2,4-triazoles including random copolymers*		*17*	*TI-POD*
			▨	*18*	*CH-POD*
	15	*PT-p/m-Me*		*19*	*PIDA-POD*
▨	*16*	*Polyhydrazide*		*20*	*HF-POD*
				22	*HF/DPE-POD*

Fig. 1. Carbon dioxide permeability in commercial polymers, hexafluoro-substituted polyimides, poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles.

According to equation 1 the carbon dioxide permeability of all polymers should be on one line but instead a considerable scattering is found in which two lines can be drawn; one connecting the commercial polymers studied by Lee while the other line connects the "tailor-made" polyimides, poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles.

Lee's polymers all have a relatively flexible backbone and a low glass transition temperatures. The polyimides and the poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles all have rigid aromatic backbones and higher glass transition temperatures, except for the polyhydrazide (PH) and the poly(1,4-cyclohexane-1,3,4-oxadiazole) (CH-POD). Figure 1 suggests that rigid polymers exhibit higher permeabilities at the same specific free volumes. In other words rigid polymers seem to have a higher effective free volume available for the passage of gas molecules. This experimental fact is in contrast with our intuitive feeling that flexible polymers would allow higher permeabilities.

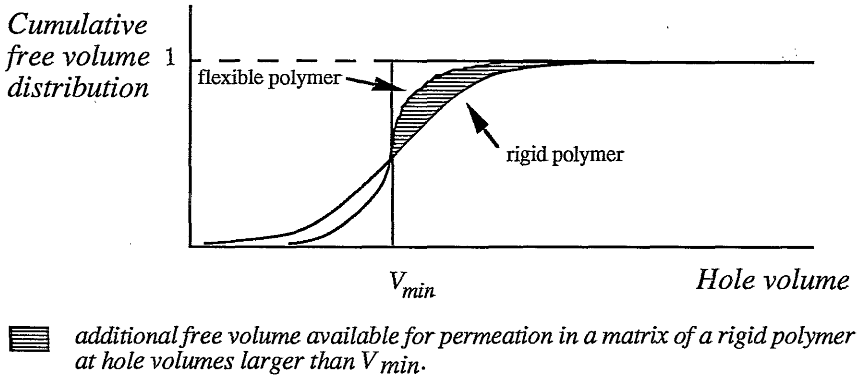
We can again visualise the difference between rigid and flexible polymers using the "spaghetti"-model of Dimarzio and Gibbs[19] which was previously used to explain the increasing permeability with increasing *p*-phenylene ratio in random poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazoles][1]. An amorphous matrix of rigid polymer molecules can be compared to a heap of strands of uncooked spaghetti, requiring substantially more free volume than flexible polymers comparable to cooked spaghetti which can pack into a much tighter form. This difference in packing density will result in a different free volume and in its distribution.

From energy and entropy considerations follows that a polymer matrix will strive after a narrow free volume distribution during membrane formation. It is easily seen that flexible polymers will be able to achieve a narrow distribution while rigid polymers will lack this possibility since these polymers are limited in achieving the same variety of conformations, resulting in a broader free volume distribution through which the number of larger holes is substantially increased. This is of importance since it is believed that the larger holes contribute substantially more to the permeation process then smaller ones. This is obvious since the passage of a permeant with a certain volume requires a minimum hole volume V_{min} to become possible. The importance of the free volume distribution on the gas transport in polymer membranes has also been discussed by Chen[20] and Allen et al.[21].

The existence of free volume distributions has been shown experimentally by means of probe techniques by Victor and Torkelson[22], by means of computer Monte Carlo simulations[23] and by means of measurements of the jump in specific heat at the glass transition temperature[24]. Frisch[25] has discussed the influence of free volume and its distribution on the permeation process.

In figure 2 two hypothetical cumulative free volume distributions of a flexible and a rigid polymer are drawn both having the same total free volume, the rigid polymer has a larger number of large holes allowing an increased permeability.

The hexafluoro substituted polyimides and the poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles are of interest as new membrane materials since they allow higher permeabilities in combination with higher selectivities. Their increased permeability is a result of their rigidity resulting in an increased free volume available for gas transport.



▤ *additional free volume available for permeation in a matrix of a rigid polymer at hole volumes larger than* V_{min}.

Fig. 2. Hypothetical cumulative free volume distributions of a flexible and a rigid polymer, after Frisch[25].

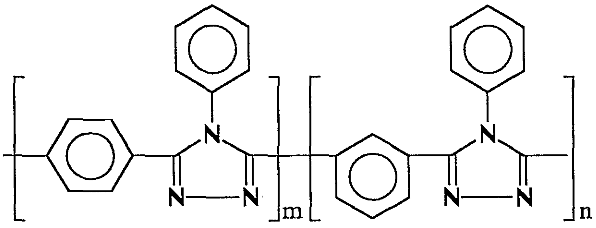
Figure 1 shows that the free volume determination by means of density measurements and calculation of Van der Waals volumina by means of group contribution methods yields an approximate average free volume value. A more accurate and correct determination of the free volume available for permeation of gas molecules is highly desirable so that permeability or diffusivity values of various polymers can be described and compared.

Below a series of methods and techniques to obtain relevant data will be discussed in detail.

Wide Angle X-ray Scattering (WAXS)

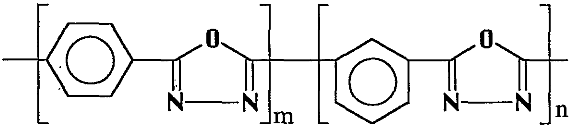
WAXS experiments are often used to obtain average d-spacings of a polymer matrix. The d-spacing is assumed to be a measure for the openness of the polymer matrix. A higher average d-spacing corresponds to higher average intermolecular distances allowing easy passage of gas molecules. Differences in the average d-spacing can be small although considerable differences in permeabilities may be found[26].

The WAXS curves of TI-POD and of the random copolymers poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles], see figure 3, are reported elsewhere[15] but the average d-spacings of these polymers are represented in table 1.



PT-0/100	m/n = 0/1
PT-25/75	m/n = 1/3
PT-50/50	m/n = 1/1
PT-75/25	m/n = 3/1

Random poly[p-, m-phenylene)-4-phenyl-1,2,4-triazoles]



TI-POD m/n = 1/1

Random poly(p-, m-phenylene)-1,3,4-oxadiazole

Fig. 3. Random poly(*p*-, *m*-phenylene-1,3,4-oxadiazole), TI-POD and poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles], PT-0/100, PT-25/75, PT-50/50 and PT-75/25 with increasing *p*-phenylene content.

Table 1. Carbon dioxide permeabilities and average d-spacings of random poly(*p*-, *m*-phenylene)-1,3,4-oxadiazole and poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles][15].

Polymer	T_g (°C)	P_{CO2} (Barrer)	2Θ*	d-spacing (Å)
TI-POD†	-	0.3	26	3.5
PT-0/100	242	2.7	21.5	4.2
PT-25/75	257	3.3	21.5	4.2
PT-50/50	279	6.7	21.5	4.2
PT-75/25	319	10.1	21.5	4.2

* WAXS curves are presented in ref. 15.

† Gas separation properties were only determined for a poly(*p*-, *m*-phenylene-1,3,4-oxadiazole) containing 50/50 wt.% *p*-phenylene and *m*-phenylene groups. No glass transition temperature was detected using DSC-techniques.

Comparing the average d-spacing of TI-POD with those of the PT's shows that addition of a pendant phenyl group onto the molecular backbone does obviously result in an increased intermolecular distance which in turn allows a higher permeability due to the increased free volume.

Interpretation of the poly-1,2,4-triazole WAXS spectra is less straightforward. All poly-1,2,4-triazoles exhibit the same average d-spacing although permeability varies over a factor of four.

However, a second "hump" can be found in the spectra at a 2Θ value of 9.5 - 10 or a d-spacing of 8.9 - 9.3 Å. The intensity of this "hump" relative to the main "hump" increases with increasing *p*-phenylene content. This suggests that besides the average d-spacing, its distribution at higher d-values may be of importance for the interpretation with respect to permeability data.

Besides WAXS, Small-Angle X-ray Scattering (SAXS) may also be a valuable technique to interpret the distribution of free volume[27].

Glass transition and quenching

Malhotra and Pethrick[28] have performed positron annihilation studies on polysulphone and polycarbonate and found a free volume consisting of holes with radii of 1.85 and 2.2 Å respectively. The carbon dioxide permeability for both polymers increases with hole sizes being 4.4 and 6.8 Barrer[29,30], respectively. Gol'danskii et al.[31] also have performed positron annihilation studies in combination with permeability experiments and found a linear relation between free volume and diffusion coefficients of methane and hydrogen in rubbers. Positron annihilation is an appreciated technique since it is sensitive to the same structural and molecular dynamic features as the permeating gas molecules[31].

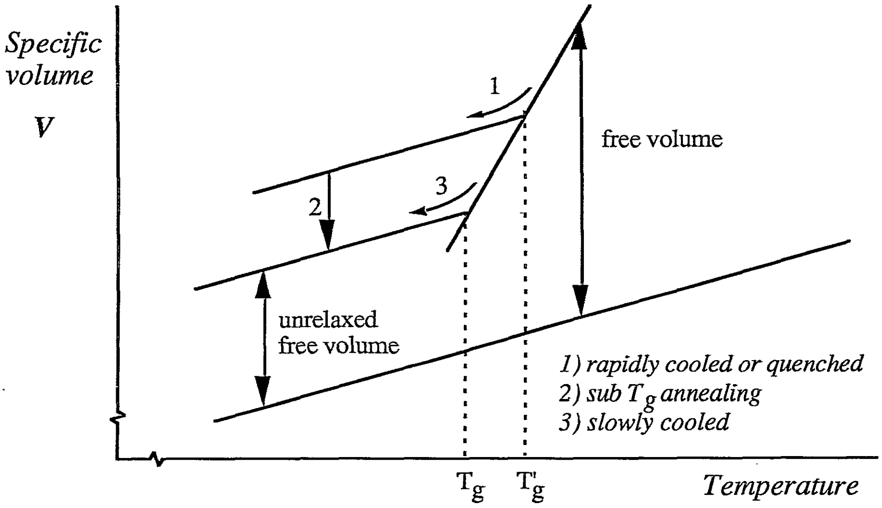


Fig. 4. Schematic representation of the polymer specific volume V as a function of temperature of an annealed and a quenched polymer[34].

This technique also revealed that there exists a linear relation for glassy polymers between their free volume and glass transition temperature. An increasing glass transition temperature was found to lead to an increase in free volume and diffusivity[32].

Fritzsche et al.[33] also explained the increased permeability of asymmetric polysulphone membranes in terms of an increased free volume.These hollow fibre membranes were prepared from Lewis acid/base complex solvents. Due to the use of these solvents the coagulation process is accelerated and a process similar to the quenching from a rubbery to a glassy polymer is believed to occur. The increased free volume was indicated by the higher glass transition temperature. These phenomena were interpreted in terms of increased free volume for a rapidly cooled or quenched polymer sample as proposed by Kovacs[34], see figure 4.

Gebben et al.[35] have extensively investigated alternating poly[*p*-,*m*-phenylene(4-phenyl)-1,2,4-triazole] regarding its gas separation properties and found an increase in carbon dioxide permeability after a heat treatment at 295°C for an hour. The polymer properties before and after the heat treatment are reproduced in table 2.

Table 2. Carbon dioxide permeability, selectivity ($\alpha_{(CO2/CH4)}$) and physical properties of a homogeneous poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazole] membrane[35].

Property		Before heat treatment	after heat treatment
P_{CO2}	(Barrer)	8.9	9.2
$\alpha_{(CO2/CH4)}$		62.5	60.5
T_g	(°C)	270.4	275.6
Density	(g/cm^3)	1.243	1.234

These data can be interpreted in accordance with the explanation of Fritzsche et al.[33] using the model of Kovacs[34]: The poly-1,2,4-triazole membrane in table 2 was cast from a formic acid solution. During evaporation the polymer solidifies and a homogeneous film is obtained. This process is comparable with slow cooling of a polymer from the rubbery state into the glassy state. Gebben et al.[35] heated this polymer membrane during 1 hour at 295°C after which it is quenched followed by permeability and selectivity measurements. An increased permeability and glass transition temperature and a decreased density are found after this heat treatment all being in accordance with the mechanism put forward in figure 4.

During the heat treatment poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazole] also undergoes cold crystallisation complicating a quantitative interpretation of this phenomena. One would expect a lower permeability for a polymer with increased ordering but the opposite is found, see table 2. Quenching obviously dominates over the possible effect of cold crystallisation on permeability.

In table 1 the glass transition temperature of random poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles] are represented where it can be seen that permeability increases with increasing glass transition temperature. Van Krevelen[36] reports an increase in free volume with increasing glass transition temperature for a wide variety of polymers. A reasonable correlation is observed although a considerable scattering is found. Since the Van der Waals volumina of the isomeric random poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles] remains constant, see table 1, the increase of free volume with increasing glass transition temperature is plausible.

The opposite of quenching, sub-T_g annealing, results in a decreased free volume and permeability. Chan and Paul[37] performed Differential Thermal Analysis (DTA) studies in combination with carbon dioxide sorption experiments on sub-T_g annealed polycarbonates and also used the approach of Kovacs to interpret their results, see figure 4.

The discussion above suggests that parameters describing processes occurring at the glass transition and the glass transition temperature itself obtained by means of the appropriate techniques like DSC, may provide an appropriate means to estimate the free volume.

Glass transition and jump in specific heat (ΔC_p).

Various authors have used the change in the specific volume or specific heat at the glass transition as a measure for the free volume. For example, Vrentas et al. have used thermal expansion coefficients to calculate changes in free volume of glassy polymers containing low molecular weight diluents[38]. Koros and Paul[39], Toi et al.[40] and Burgess et al.[41] have estimated free volume fractions by means of expansion coefficients and glass transition temperatures using empirical rules as proposed by Boyer and Spencer[42] and Simha and Boyer[43], respectively:

$$\alpha_l \cdot T_g = K_1 = 0.164 \tag{5}$$

$$(\alpha_l - \alpha_g)T_g = \Delta\alpha \cdot T_g = K_2 = 0.113 \tag{6}$$

where α_l and α_g are the expansion coefficients in the liquid or rubbery state and glassy state respectively and $\Delta\alpha$ is the change in thermal expansivity at T_g. The expansion coefficients follow from volumetric determinations.

Differential Scanning Calorimetry (DSC) can be used to obtain the specific heat of a polymer in its rubbery and glassy state. At T_g a jump in specific heat is observed: ΔC_p. Boyer[44] has proposed a similar relationship between T_g and ΔC_p as for the thermal expansion coefficient:

$$\Delta C_p \cdot T_g = K_3 = 25\ cal/g. \tag{7}$$

Both ΔC_p and $\Delta\alpha$ are parameters of the same physical process[45] which is shown in figure 5. The expansion coefficient α and heat capacity C_p are the derivatives of the thermodynamic entities specific volume V and enthalpy H. Since ΔC_p is quickly and easily obtained by standard DSC techniques, this parameter may have the potential of being a valuable polymer characteristic for newly synthesised polymers.

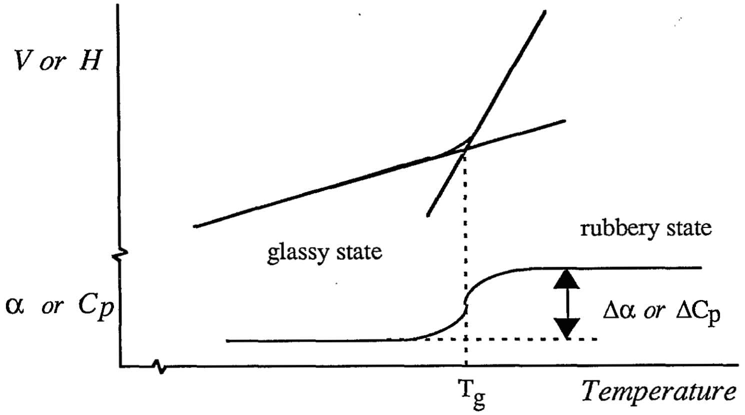


Fig. 5. Schematic representation of the polymer specific volume V and enthalpy H and their derivatives α and C_p as a function of temperature above and below the glass transition temperature[45].

Boyer[44] has plotted $\Delta C_p \cdot T_g$ versus T_g for various commercially available polymers and a considerable scattering can be observed. In our case also a considerable scattering is observed if $\Delta C_p \cdot T_g$ is plotted versus T_g for all poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles studied. If we however limit ourselves to the homologous series of the random poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles] a fairly good correlation in accordance with equation 7 is observed.

In figure 6, the glass transition temperatures together with the ΔC_p values (a) and $\Delta C_p \cdot T_g$ (b) are plotted as a function of the increasing *p*-phenylene content in random poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles].

It is shown that the glass transition temperature increases with increasing *p*-phenylene content whereas ΔC_p decreases with increasing *p*-phenylene content being in accordance with equation 7. The alternating poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazole] show deviating value for $\Delta C_p \cdot Tg$ being only constant for the random poly-1,2,4-triazoles with a *p*-phenylene content less than 75%. The jump in specific heat becomes undetectable at a *p*-phenylene content of 75% resulting in $\Delta C_p \cdot T_g$ value of zero. The same phenomenon has also been observed for polystyrenes. The ΔC_p value was found to decrease in that case with increasing degree of crosslinking[46].

A polymer's heat capacity is the result of molecular rotations and vibrations. At the glass transition the number of rotations and vibrations increases step-wise when the polymer enters the rubbery state since then large chain segments are able to move. In the case of a crosslinked or a stiff macromolecule, as for the poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazole] with 75% *p*-phenylene groups, motions in the rubbery state are substantially hindered and the increased rotational and vibrational possibilities are obviously very small or negligible since no jump in specific heat is observed.

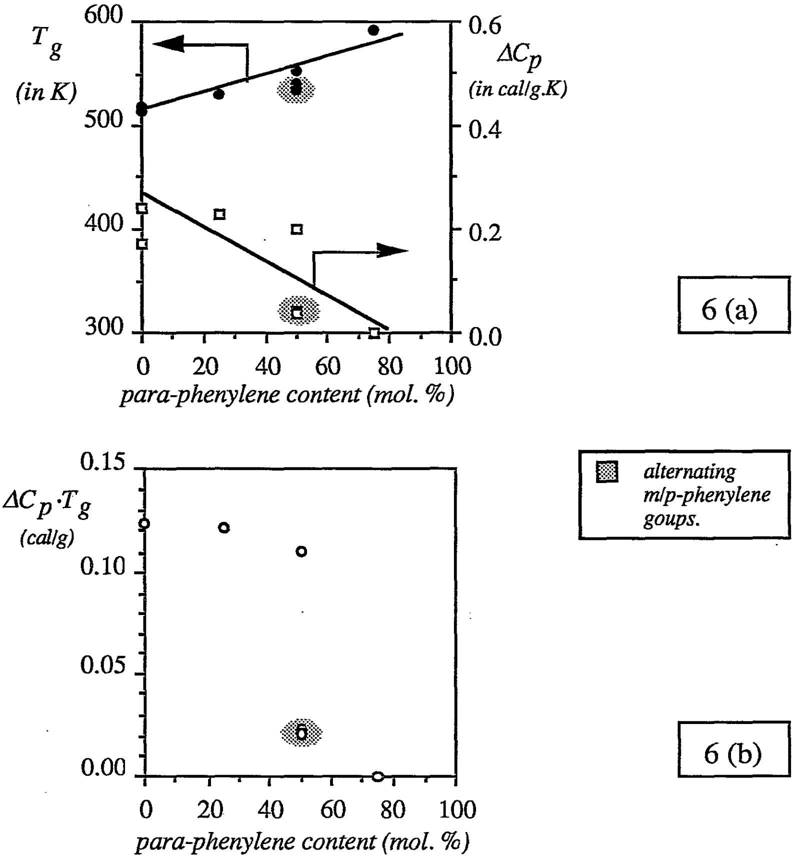


Fig. 6. Glass transition temperature and ΔC_p (a) and $\Delta C_p \cdot T_g$ as a function of the *p*-phenylene content in random and alternating poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles]. The glass transition becomes undetectable with DSC techniques at a *p*-phenylene content of 75%. The glass transition was determined with a torsion pendulum in this case and a value of $\Delta C_p = 0$ was used[15].

In a previous paper[1] it was shown that the permeability increased with an increase in glass transition temperature of the homologous series of poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles]. Since the jump in specific heat decreases with increasing glass transition temperature, permeability or diffusivity can also be expressed as a function of ΔC_p.

In figure 7 the carbon dioxide permeabilities of poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles] are plotted versus the jump in heat capacity of the polymers. As a comparison the carbon dioxide permeability is also plotted versus *p*-phenylene content in the poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles][1]. A reasonable relation between permeability and ΔC_p is observed, although considerable scattering is observed.

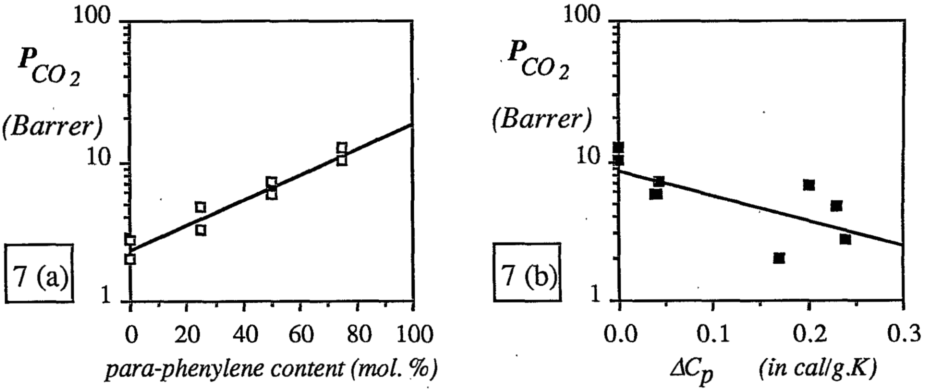


Fig. 7. Carbon dioxide permeability as a function of the *p*-phenylene content in poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles] and as a function of the jump in specific heat at the glass transition.

The relationship between ΔC_p and diffusivity was originally observed by Smit et al. for a series of hexafluoro-substituted polyimides[47]. The relationship between both quantities was explained in terms of the molecular model of Meares originally derived for rubbers[48]. Meares suggested that a diffusional "jump" of a permeant would require a certain amount of energy, E_D, and that diffusivity can be described by an Arrhenius type equation:

$$D = D_0 exp(-E_D/RT) \qquad (8)$$

The magnitude of E_D is assumed to depend on the Cohesive Energy Density (CED) of the polymer:

$$E_D = 0.25\pi d^2 \lambda N_{AV} CED \qquad (9)$$

Smit calculated the CED of a series of hexafluoro substituted polyimides using the emperical relation between ΔC_p and CED proposed by Lee[49]:

$$\Delta C_p = 1.25CED + 2.17\,(cal/molK) \qquad (10)$$

Meares assumes that in order to allow the passage of a permeant molecule contiguous chains or chain segments have "to open up". This treatment suggests that diffusivity is a function of polymer mobility alone and that increasing polymer flexibility will enhance permeability. This is however often not the case for glassy polymers. Higher permeabilities are often found for glassy polymers with higher glass transition temperatures[9,17,18] as in the case for the poly[p-, m-phenylene(4-phenyl)-1,2,4-triazoles].

A polymer backbone is considered to be in a frozen state below T_g and segmental chain motions are drastically reduced compared to the rubbery state; gas transport is therefore likely to be not primarily dependent of polymer chain motion[50].

In addition, a higher glass transition temperature or an increased stiffness was discussed in terms of a larger free volume or a broader free volume distribution. Gas transport in the glassy state is therefore assumed to take place via fixed holes. A gas molecule must "find its way" from hole to hole along pathways involving only minor segmental rearrangements. This means that the magnitude of diffusivity or permeability depends largely on the concentration of holes with an appropriate size able to accommodate a diffusing gas molecule.

Mobility of chain segments in a polymer matrix is however strongly related to the polymer free volume. Struik[51] has visualised this dependence, see figure 8. Free volume has a substantial effect on the mobility in the glassy state and is obviously needed to allow chain segments to move or to rotate "into". For example, the rate of a sub-T_g annealing process decreases with decreasing free volume.

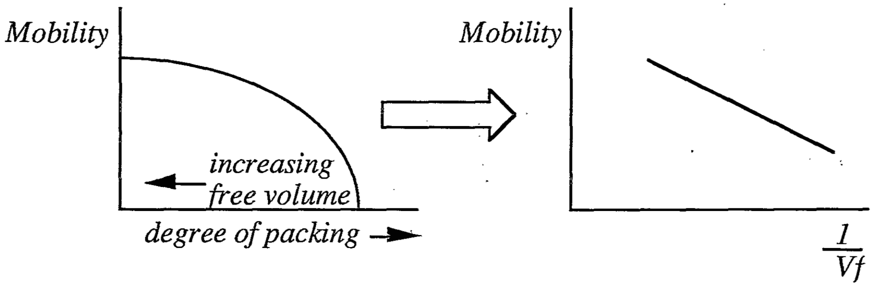


Fig. 8. Qualitative relation between free volume and chain mobility[51].

This discussion suggests that the amount of free volume is the rate limiting factor for both the transport process and chain mobility. Chen and Edin[52] came to the same conclusion in their study on gas transport in polycarbonate. A flexible polymer will have an efficiently packed polymer matrix limiting segmental mobility. A rigid polymer will have a large free volume allowing increased segmental mobility in the glassy state. Free volume is both rate determining for gas transport and for segmental mobility.

But how can we explain the observed relationship between permeability or diffusivity and the jump in specific heat at the glass transition?

A high ΔC_p means that there is a large difference in heat uptake between the non-equilibrium situation in the glassy state and the equilibrium situation above T_g in the rubbery state. This means that ΔC_p may give valuable information concerning the glassy state of the polymer in comparison with the rubbery state. Wunderlich[24,45,53] has interpreted the physical process behind the jump in heat capacity in terms of the hole theory of Hirai and Eyring[54,55].

When a glassy polymer is heated it takes up a certain amount of energy per degree rise in temperature. This amount depends on the heat capacity of the material C_{p0}:

$$C_{p,\text{total,glass}} = C_{p0} \qquad (11)$$

The uptake of energy is used for increased lattice vibrations. In the rubbery state an extra term, C_{ph} (*h* stands for hole), is added to the heat capacity:

$$C_{p,\text{total, rubber}} = C_{p0} + C_{ph} \qquad (12)$$

In the rubbery state molecular rearrangement of neighbouring molecules or molecule segments are possible allowing the creation or disappearance of a hole. The presence of holes is assumed to be necessary for molecular motion.

The second term of the specific heat capacity, C_{ph}, is due to the creation of new holes in the rubbery phase. Each hole is characterised by its molar volume v_h and the molar excess energy over the "no hole" situation ε_h.

The part of interest, C_{ph}, is due to the change in number of holes with temperature and can be written as:

$$C_{ph} = \varepsilon_h \left(\frac{\partial N_h}{\partial T}\right)_p \qquad (13)$$

where N_h is the number of holes present. Using the equilibrium value of Hirai and Eyring:

$$\frac{N_h}{N_0} = \frac{v_0}{v_h} e^{-\varepsilon_h/RT} \qquad (14)$$

where N_0 is the number chain segments in moles and v_0 is the volume of one mol of chain segments. (N_0v_0= occupied volume and N_hv_h=free volume), equation (13) becomes:

$$\Delta C_{ph} = R\frac{v_0}{v_h}\left(\frac{\varepsilon_h}{RT}\right)^2 e^{-\varepsilon_h/RT} \tag{15}$$

On cooling a polymer from the rubbery into the glassy state the mechanism responsible for decreasing the number of holes is blocked at the glass transition temperature so that at lower temperatures the number of holes is constant and corresponds to the equilibrium at the transition interval, see also figure 5 where on the ordinate also the number of holes can be thought[45]. At, and above T_g the additional term ΔC_{ph} or ΔC_p, due to the increase in hole concentration, has to be added. This term should account solely for the rise in heat capacity at T_g:

$$\Delta C_p = \Delta C_{ph} = R\frac{v_0}{v_h}\left(\frac{\varepsilon_h}{RT_g}\right)^2 e^{-\varepsilon_h/RT_g} \tag{16}$$

In equation (16), ΔC_p is expressed as a complicated function of the molar free volume, the energy for hole formation and the glass transition temperature. The hole energy ε_h is a function of the polymer Cohesive Energy Density (CED). Wrasidlo has calculated the hole energies of a wide variety of polymers and found that the hole energy increased linearly with the glass transition temperature[56]. This is in agreement with our intuitive feeling that upon increasing rigidity of a polymer system its possibility of hole formation on passing the glass transition will be restricted. For example, in the case of crosslinked systems or extremely rigid polymers the difference between the glassy and rubbery state decreases and a sudden increase in the number of holes at T_g is unlikely, due to the large hole energy ε_h. Since polymers with high glass transition temperatures often exhibit high permeabilities this implies that hole formation in terms of the Hirai and Eyring theory is not likely or necessary to restrict gas transport through glassy membranes, although it was assumed to be a necessary precondition in the derivation of equation (9). According to equation (16) the hole free volume increases with decreasing ΔC_p. This means that permeability or diffusivity will increase with decreasing ΔC_p.

In the glassy state the number of holes is fixed and no hole redistributions are likely and it is therefore assumed that gas transport mainly takes place via pre-existing holes.

If we neglect the influence of the glass transition temperature on the magnitude of ΔC_p, which seems to be allowed since the quotient ε_h/T_g is constant[56], then instead of ΔC_p, v_h^{-1} can be written on the horizontal axis in figure 7b in the case of the poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles] studied. This would also mean that equation 2 can be modified into:

$$P = A \cdot exp\ (-B \cdot \Delta C_p) \tag{17}$$

Comparing equation 17 and 8 reveals that both the treatment of ΔC_p using the model of Meares and that of Wunderlich results in a similar type of relation.

Kanig[14] has also studied the ΔCp approach extensively and has shown on the basis of equation (16) that rigid polymers or polymers with bulky side groups have a higher free volume, being in agreement with the discussion above.

The next question of interest of course is that of the general validity of this theory with respect to other classes of polymers. Wrasidlo has tabulated related thermodynamic properties including ΔC_p, v_0/v_h and N_0/N_h values, of commercial available polymers[56]. Combined gas transport parameters and thermodynamic properties are only available for a limited number of polymers. Since values for both transport parameters and thermodynamic properties may differ considerably from source to source, we have limited ourselves to three sources. Instead of diffusivity, the oxygen permeability was plotted. Permeability is largely independent of sorption and its increase mainly depends on the increase in diffusivity[1,49].

Bixler and Sweeting have published a vast amount of oxygen and carbon dioxide permeabilities of commercially available polymers[57]. Permeabilities were measured at 25 or 30°C.

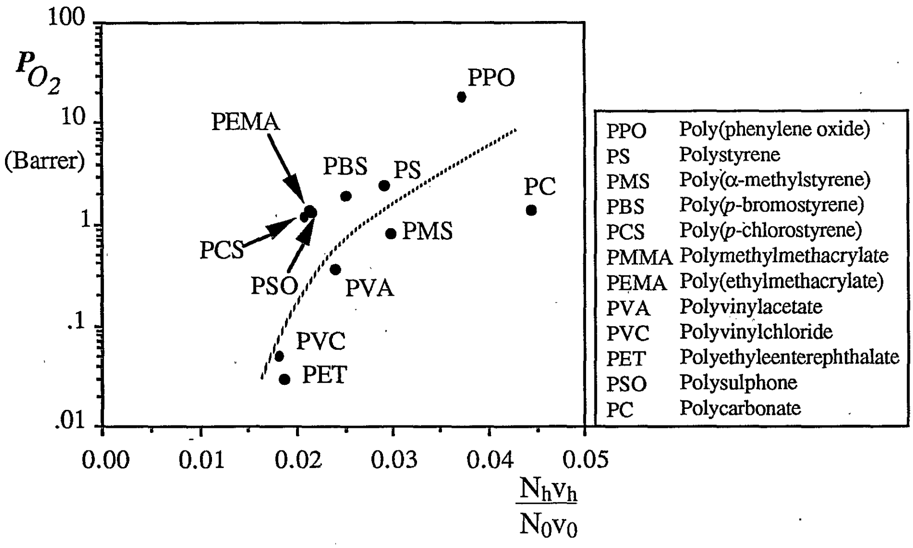


Fig. 9. Oxygen permeability as a function of the ratio nonoccupied/occupied volume $N_h v_h/N_0 v_0$ (ref. 48). Oxygen permeability data are taken from ref. 57, for PMS, PCS and PBS from ref. 58 and for PPO from ref. 59.

In figure 9 the ratio free volume to occupied volume $N_h v_h/N_0 v_0$, see equation 14, is plotted versus the oxygen permeability of conventional glassy polymers. Although care should be taken when using data from different sources, a fairly good correlation is observed between the quantities plotted for these glassy polymers although they belong to a wide variety of different polymer classes. The ratio $N_h v_h/N_0 v_0$ is calculated at the glass transition temperature from the thermodynamic quantities T_g, $\Delta\alpha$, ΔC_p and CED[56]. The free volume in the glassy state can be calculated since the free volume at and below T_g is constant[56], see figure 4. Note that the free volume calculated in this manner is considerably lower, only a few percent, than in the case of the specific free volume and group contributions as used in figure 1. The variation in free volume contradicts the assumption of William, Landel and Ferry of a universal value of 0.025 at the glass transition[60].

Further combined study of gas transport and thermodynamic parameters for a wider range of polymers should reveal the general validity of the relation between permeability or diffusivity and the ratio $N_h v_h/N_0 v_0$.

CONCLUSIONS

In this paper conventional polymers were compared with "tailor-made" polymers as gas separation membrane materials. The increased permeability of the latter was shown to be due to their higher free volume available for gas transport. The increased free volume is associated with their rigid polymer backbone not allowing an efficient packing and thereby favouring increased permeability.

Wide Angle X-ray studies show a marked increase in average d-spacing between the related aromatic poly-1,3,4-oxadiazole and poly-1,2,4-triazoles obviously due to the extra phenyl group attached to the polymer backbone of the former. Explaining the increase in permeability with increasing *p*-phenylene content in the poly-1,2,4-triazoles is less straight forward since all copolymers have the same average d-spacing. The "hump" at smaller angles is found to increase with increasing *p*-phenylene content and suggests a difference in free volume distribution at larger intermolecular distances.

The physical processes occurring at the glass transition and its parameters obtained via DSC techniques offer a convenient and interesting method to calculate the polymer free volume using the hole theory of Hirai and Eyring and the derived relationship between the jump in heat capacity and free volume parameters by Wunderlich. A fair relationship was observed for the aromatic copoly-1,2,4-triazoles with increasing *p*-phenylene content between carbon dioxide permeability and jump in heat capacity at the glass transition temperature. Also for a wide range of well studied conventional polymers a correlation between free volume and oxygen permeability was found.

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LITERATURE

1. E.R. Hensema, J.P Boom, M.E.R. Sena, M.H.V. Mulder and C.A. Smolders, to be published *(Chapter 4 of this thesis).*
2. H. Fujita, Fortschr. Hochpolym. Forsch., 3, 1-47 (1961).
3. W.M. Lee, Polym. Eng. Sci., 20, 65-69(1980).
4. A. Bondi, Physical properties of molecular crystals, liquids, and glasses, Elsevier, Amsterdam, 1968.
5. A.A. Askadskii, “Predictions of physical properties of polymers”, in R.A. Pethrick and G.E. Zaikv (Eds), “Polymer Yearbook”, Vol. 4, Harwood Acad. Publ., London, 1987, p. 93-147.
6. Y. Maeda and D.R. Paul, J. Polym. Sci., Polym. Phys. Ed., 25, 1005-1016(1987).
7. T.A. Barbari, W.J. Koros and D.R. Paul, J. Polym. Sci., Polym. Phys. Ed., 26, 709-727(1988).
8. J.C. Schmidhauser and K.C. Longley, J. Appl. Polym. Sci., 39, 2083-2096(1990).
9. N. Muruganandam, W.J. Koros and D.R. Paul, J. Polym. Sci., Polym. Phys. Ed., 25, 1999-2026(1987).
10. K.E. Min,W.J. Koros and D.R. Paul, J. Polym. Sci., Polym., Polym. Phys. Ed., 26, 1021-1033(1988).
11. J.S. Vrentas, J.L. Duda and H.-C. Ling, J. Membrane Sci., 40, 101-107(1989)
12. J.S. Vrentas, J.L. Duda and H.-C. Ling, J. Polym. Sci., Polym. Phys. Ed, 23, 275-288(1985).
13. J.S. Vrentas, J.L. Duda, H.-C. Ling and A.-C. Hou, J. Polym. Sci., Polym. Phys. Ed, 23, 289-304(1985).
14. G. Kanig, Kolloid-Z. Z. Polym., 233, 829-845(1969).
15. E.R. Hensema, J.P Boom, M.H.V. Mulder and C.A. Smolders, to be published *(Chapter 2 of this thesis).*
16. E.R. Hensema, M.E.R. Sena, M.H.V. Mulder and C.A. Smolders, to be published *(Chapter 3 of this thesis).*
17. T.H. Kim, W.J. Koros, G.R. Husk and K.C. O’Brien, J. Membrane Sci., 37, 45-62(1988).
18. M.R. Coleman and W.J. Koros, J. Membrane Sci., 50, 285-297(1990).
19. E.A. Dimarzio and J.H. Gibbs, J. Polym. Sci., 40, 121-131(1959).
20. S.P. Chen, Polymer Prep., 15, 77-83(1974)
21. S.M. Allen, V. Stannet, H. Hopfenberg and J.L. Williams, Polymer, 22, 912-917(1981).
22. J.G. Victor and J.M. Torkelson, Macromolecules, 20, 2241-2250(1987).
23. S. Trohalaki, L.C. DeBolt and J.E. Mark, Macromolecules, 23, 813-816(1990).
24. B. Wunderlich, D.M. Bodily and M.H. Kaplan, J. Appl. Phys., 35, 95-102(1964).
25. Frisch, J. Pol. Sci., Pol. Lett. Ed., 3, 13-16(1965).
26. M. Moe, W.J. Koros, H.H. Hoehn and G.R. Husk, J. Appl. Pol. Sci., 36, 1833-1846(1988).
27. R.-J. Roe and J.J. Curro, Macromolecules, 16, 428-434(1983).
28. B.D. Malhotra and R.A. Pethrick, Eur. Pol. J. 19, 457-459(1983).
29. A.J. Erb and D.R. Paul, J. Membrane Sci., 8, 11-21(1981).
30. M.W. Hellums, W.J. Koros, G.R. Husk and D.R. Paul, J. Membrane Sci., 46, 93-112(1989).
31. A.V. Gol’danskii, V.A. Onischchuk, V.P. Shantarovich, V.V. Volkov and Yu. P. Yampol’skii, Khim. Fiz, 7, 616-621(1988).
32. S.G. Durgar’yan, Yu. Yampol’skii and N.A. Plate, Russian Chemical Reviews, 57, 549-558(1988).
33. A.K. Fritzsche, R.E. Kesting and M.K. Murphy, J. Membrane Sci., 46, 135-155(1989).
34. A.J. Kovacs, J. Polym. Sci., 30, 131-167(1958).

35. B. Gebben, M.H.V. Mulder and C.A. Smolders, J. Membrane Sci., 46, 29-41(1989).
36. A. K. Van Krevelen, Properties of polymers, Third edition, Elsevier, Amsterdam, 1990, Chapter 4.
37. A.H. Chan and D.R. Paul, Pol. Eng. Sci., 20, 87-94(1980).
38. J.S. Vrentas, J.L. Duda and H.-C. Ling, Macromolecules, 21,1470-1475(1988).
39. W.J. Koros and D.R. Paul, J. Polym. Sci., Polym. Phys. Ed, 16, 1947-1963(1978).
40. K. Toi, G. Morel and D.R. Paul, J. Appl. Pol. Sci., 27, 2997-3005(1982).
41. W.H. Burgess, H.B. Hopfenberg and V.T. Stannet, J. Macromol. Sci.-Phys., B5, 23-40(1971).
42. R.F. Boyer and R.S. Spencer, J. Appl. Phys., 15, 398-405(1944).
43. R. Simha and R.F. Boyer, J. Chem. Phys., 37, 1003-1007(1962).
44. R.F. Boyer, J. Macromol. Sci.-Phys., B7, 487-501(1973).
45. B. Wunderlich, Thermal Analysis, Academic Press, Boston, 1990, Chapter 4.
46. L. H. Judovits, R.C. Bopp, U. Gaur and B. Wunderlich, J. Polym. Sci., Polym. Phys. Ed., 24, 2725-2741(1986).
47. E. Smit, Ph. D. Thesis, University of Twente, 1991, Enschede.
48. P. Meares, J. Am. Chem. Soc., 76, 3415-3422(1954).
49. C.J. Lee, Pol. Eng. Sci., 27, 1015-1017(1987).
50. K.D. Ziegel and F.R. Eirich, J. Polym. Sci., Polym. Phys. Ed., 12, 1127-1135(1974).
51. L.C.E. Struik, "Physical aging of amorphous polymers and other materials", Elsevier, Amsterdam, 1978 Chapter 2.
52. S.P. Chen and J.A. Edin, Pol. Eng. Sci., 20, 40-50(1980).
53. B. Wunderlich, J. Phys. Chem., 64, 1052-1056(1960).
54. N. Hirai and H. Eyring, J. Appl. Phys., 29, 810-816(1958).
55. N. Hirai and H. Eyring, J. Polym. Sci., 37, 51-70(1959).
56. W. Wrasidlo, Fortschr. Hochpolym. Forsch., 13, 3-99(1974).
57. H. J. Bixler and O.J. Sweeting, "Barrier properties of polymer films", in O.J. Sweeting (Ed.), "The science and technology of polymer films", Vol. 2, John Wiley and Sons, New York, 1971.
58. A.C. Puleo, N. Muruganandam and D.R. Paul, J. Polym. Sci., Polym. Phys. Ed, 27, 2385-2406(1989).
59. W.J. Koros, B.J. Story, S.M. Jordan, K. O'Brien and G.R. husk, Pol. Eng. Sci., 27, 603-610(1987).
60. M.L. Williams, R.F. Landel and J.D. Ferry, J. Am. Chem. Soc., 77, 3701-3707(1955).

SUMMARY

Gas separation with membranes is a growing technology having distinct advantages over the more mature technologies like cryogenic and ab- and adsorption processes. Today's main applications are the preparation of nitrogen enriched air for applications requiring inert gas blanketing, like the storage and shipment of flammable liquids, fresh fruits and vegetables, and the separation of carbon dioxide from natural gas. This technology is relatively young and membrane systems are still being improved. The performance of a membrane system depends for all on the membrane material utilised determining the two major membrane characteristics: permeability and selectivity.

Membranes of poly[*p*-, *m*-phenylene-(4-phenyl)-1,2,4-triazole] posses a moderate permeability in combination with a high selectivity compared to the presently commercially used membrane materials. In this study the gas separation properties towards carbon dioxide, methane, oxygen and nitrogen of the closely related poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles have been studied and the gas separation properties have been expressed as a function of the molecular structure and the physical properties of these polymers.

Various functional groups were incorporated into the polymer backbone of poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles. In the chapters 2 and 3 the syntheses and the physical properties of these thermally stable and chemically resistant polymers are discussed and in the chapters 4 and 5 the gas separation properties of membranes of these polymers is dealt with.

Poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles] with different ratio's *p*- and *m*-phenylene groups have been prepared using poly(*p*-, *m*-phenylene)-1,3,4-oxadiazoles and poly(*p*-, *m*-phenylene)hydrazide in which the *p*- and *m*-phenylene groups are incorporated randomly and in alternating fashion, respectively. The corresponding poly-1,2,4-triazoles are obtained after a reaction of aniline with the precursor polymer. The glass transition temperature increased from 242°C for poly[*m*-phenylene(4-phenyl)-1,2,4-triazole] to 319°C for the poly-1,2,4-triazole containing 75% *p*-phenylene groups and 25% *m*-phenylene groups while the carbon dioxide permeability was found to increase with an increasing *p*-phenylene content from 2.7 Barrer for the first to 12.6 Barrer for the latter poly-1,2,4-triazole. The carbon dioxide/methane selectivity meanwhile remained constant at a value of 50. The increase in permeability is explained in terms of an increase in free volume and a broader free volume distribution caused by the increasing *p*-phenylene content which results in a more rod-like macromolecule and which in its turn limits the possibilities of achieving an efficiently packed polymer matrix.

Cold crystallisation in the rubbery phase was found only for the poly-1,2,4-triazoles were the *p*- and *m*-phenylene groups are incorporated alternatingly in the polymer backbone. Only this polymer has the regular structure needed, to achieve a crystalline morphology upon crystallisation.

Besides aniline, *p*-substituted anilines are incorporated into alternating poly[*p*-, *m*-phenylene(4-phenyl)-1,2,4-triazoles]. The glass transition increased with the incorporation *p*-fluoro and *p*-

chloro aniline, and decreased upon incorporation of *p*-methyl aniline which was attributed to the alteration in cohesive forces. Permeability was only increased significantly in the latter case.

Poly(*p*-, *m*-phenylene-1,3,4-oxadiazoles) have been prepared through cyclodehydration of a precursor poly(*p*-, *m*-phenylene)hydrazides and directly using isophthalic and terephthalic acid and hydrazine sulphate as monomers. Flexible membranes were only obtained using the latter synthesis route but only if the inherent viscosity was higher than 2.7 dl/g.

Incorporation of 1,1,3-trimethyl-3-phenylindane, 4,4,'-(2,2'-diphenyl)hexafluoro propane and diphenyl ether structures into poly-1,3,4-oxadiazoles also gave polymers with high glass transition temperatures. Incorporation of the first two moieties gave polymers with high permeabilities while the latter gave a poly-1,3,4-oxadiazole with an extremely high selectivity.

The permeability of the polymers prepared can be expressed as a linear function of their reciprocal free volume, the latter being calculated from density measurements and group contributions methods. Free volume and its distribution is considered to be the rate limiting step in the gas transport process.

Comparing conventional polymers, all having a relative flexible backbone, with the rigid poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles shows that the latter polymers allow higher permeabilities at the same free volume, implying that these polymers have broader free volume distributions allowing an increased transport of gas molecules.

The amount of free volume can also be estimated using the jump in heat capacity (ΔC_p) occurring at the glass transition. From the ΔC_p value, the glass transition temperature and the cohesive energy density, the free volume can be estimated. The permeability values of a wide variety of conventional polymers is expressed as a function of the free volume calculated in this manner giving a reasonable relationship.

SAMENVATTING

Gasscheiding met membranen is een technologie die een grote groei doormaakt en die duidelijke voordelen heeft ten opzicht van de meer conventionele technieken zoals cryogene destillatie en ab- en adsorptie processen. De belangrijkste toepassingen zijn op dit moment de bereiding van stikstofverrijkte lucht, voor de bereiding van een inerte atmosfeer voor de opslag en het vervoer van brandbare vloeistoffen, fruit en groenten, en de verwijdering van kooldioxyde uit aardgas.

Deze technologie is relatief jong en de membraan systemen worden nog steeds verbeterd. De prestaties van dergelijke systemen worden in grote mate bepaald door het gebruikte membraanmateriaal. De permeabiliteit en selectiviteit, de twee belangrijkste membraanparameters, worden bepaald door deze materiaalkeuze.

Membranen van poly[*p*-, *m*-fenyleen-(4-fenyl)-1,2,4-triazool] bezitten een redelijke permeabiliteit in combinatie met een hoge selectiviteit vergeleken met de polymeren die worden toegepast in de huidige gasscheidingsmembraan systemen. Tijdens dit onderzoek zijn de gasscheidingseigenschappen ten aanzien van zuurstof, stikstof en kooldioxyde/methaan gasmengsels van gerelateerde poly-1,3,4-oxadiazolen en poly-1,2,4-triazolen onderzocht. Deze gasscheidingseigenschappen worden bepaald door de macromoleculaire structuur en de fysische eigenschappen van de onderzochte polymeren.

Verschillende functionele groepen zijn ingebouwd in de polymere hoofdketen van poly-1,3,4-oxadiazolen en poly-1,2,4-triazolen. In de hoofdstukken 2 en 3 worden de syntheses en fysische eigenschappen van deze thermostabiele en chemisch resistente polymeren beschreven. In de hoofdstukken 4 en 5 worden vervolgens de gasscheidingseigenschappen van de membranen van deze polymeren beschreven.

Poly[*p*-, *m*-fenyleen-(4-fenyl)-1,2,4-triazolen] met verschillende verhoudingen *p*- en *m*-fenyleen groepen zijn bereid uitgaande van de precursor polymeren: poly(*p*-, *m*-fenyleen)-1,3,4-oxadiazolen en poly(*p*-, *m*-fenyleen)hydrazide. In deze polymeren zijn de *p*- en *m*-fenyleen groepen respectievelijk op random en alternerende wijze in de hoofdketen aanwezig. De overeenkomstige poly-1,2,4-triazool word verkregen na een reactie van het precursor polymeer met aniline in polyfosforzuur. De glasovergangstemperatuur nam toe van 242°C voor poly[*m*-fenyleen-(4-fenyl)-1,2,4-triazool] tot 319°C voor de poly-1,2,4-triazool met 75% *p*- en 25% *m*-fenyleen groepen in hoofdketen. De kooldioxyde permeabiliteit nam toe van 2.7 Barrer voor de eerste tot 12.6 Barrer voor de laatste poly-1,2,4-triazool. De kooldioxyde/methaan selectiviteit behield een vrijwel constante waarde van 50. Deze toename in permeabiliteit wordt veroorzaakt verondersteld door een toenemend vrij volume en breder wordende vrij volume verdeling met een toenemend gehalte *p*-fenyleen groepen. De macromoleculen krijgen hierdoor een meer lineair karakter waardoor een minder efficiënt gepakte polymere matrix ontstaat.

Koude kristallisatie in de rubber fase werd alleen gevonden bij poly[*p*-, *m*-fenyleen-(4-fenyl)-1,2,4-triazolen] waar de *p*- en *m*-fenyleen groepen alternerend in de polymere hoofdketen zijn

ingebouwd en niet bij de random copolymeren. Een dergelijke regelmatige structuur is blijkbaar noodzakelijk om een kristallijne morfologie te kunnen bereiken tijdens het kristallisatie proces.

Naast aniline, zijn ook *p*-gesubstitueerde anilines in alternerend poly[*p*-, *m*-fenyleen-(4-fenyl)-1,2,4-triazole] ingebouwd. Door de inbouw van *p*-fluoro en *p*-chloroaniline nam de glasovergangstemperatuur toe terwijl deze afnam, indien *p*-methylaniline werd ingebouwd, hetgeen valt toe te schrijven aan de gewijzigde intermoleculaire interacties. De permeabiliteit nam alleen significant toe bij de laatste poly-1,2,4-triazool.

Poly(*p*-, *m*-fenyleen-1,3,4-oxadiazolen) zijn bereid door cyclodehydratatie van poly(*p*-, *m*-fenyleen)hydrazide en op directe wijze door isoftaal- en tereftaalzuur en hydrazinesulfaat als monomeren te gebruiken. Flexibele membranen konden alleen bereid worden van poly(*p*-, *m*-fenyleen-1,3,4-oxadiazolen) die op de tweede wijze waren bereid maar alleen indien de inherente viscositeit hoger dan 2.7 dl/g. was.

Inbouw van 1,1,3-trimethyl-3-fenylindane, 4,4,'-(2,2'-difenyl)hexafluoropropaan en difenyl ether structuren in poly-1,3,4-oxadiazolen gaf polymeren met hoge glasovergangstemperaturen. Inbouw van de eerste twee structuren gaf poly-1,3,4-oxadiazolen met een hoge permeabiliteit terwijl inbouw van de difenylether structuur resulteerde in een poly-1,3,4-oxadiazool met een extreem hoge selectiviteit.

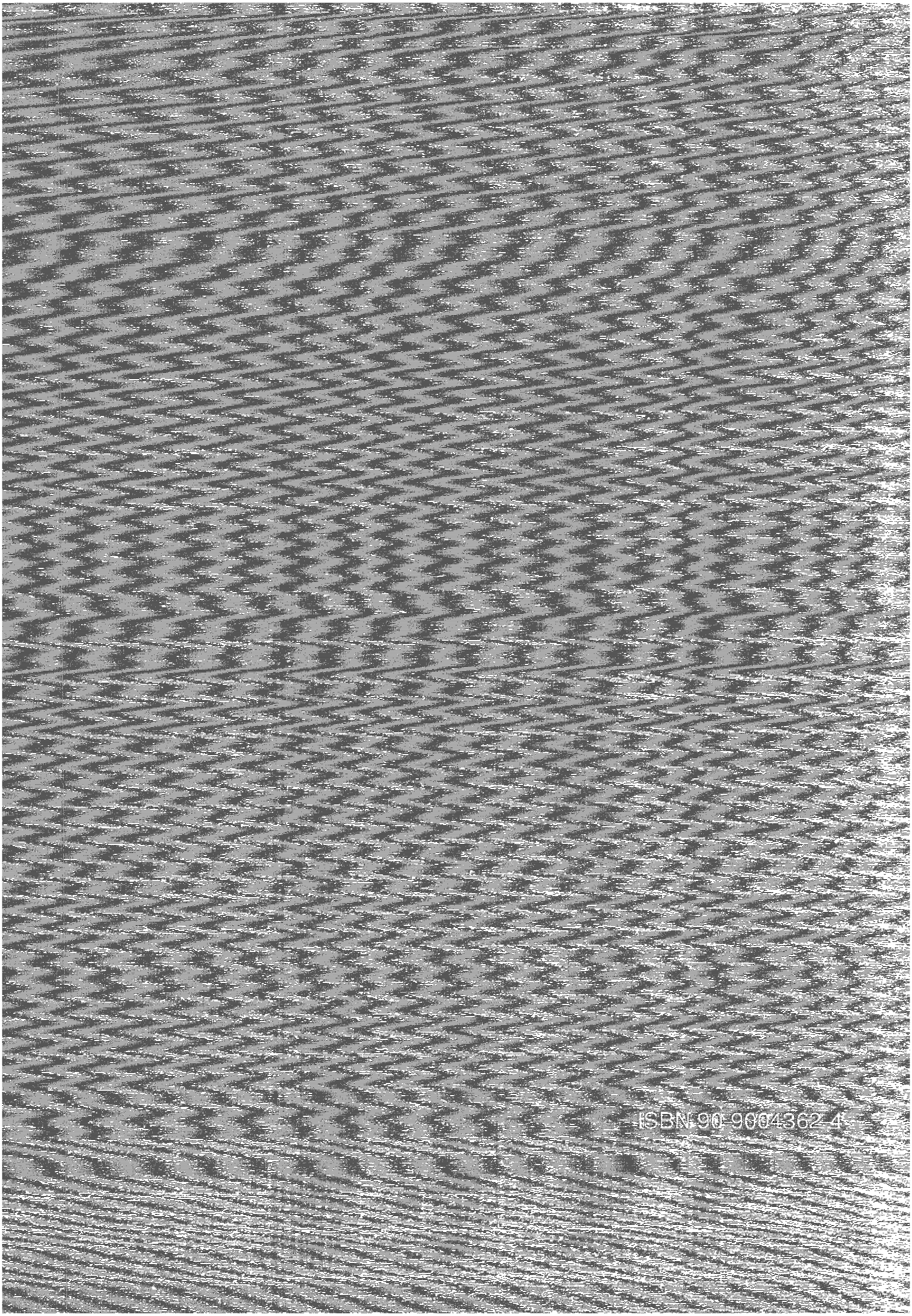
De permeabiliteit van de bereidde polymeren kan worden uitgedrukt als een lineaire functie van hun reciprook vrij volume. Het vrij volume wordt berekend aan de hand van dichtheidsmetingen en groepsbijdragen methoden en wordt als de snelheidsbepalende stap voor het gas transport in polymeren beschouwd.

Indien conventionele polymeren, allen met een relatief flexibele hoofdketen, worden vergeleken met de rigide poly-1,3,4-oxadiazolen en poly-1,2,4-triazolen dan blijken de laatste twee klassen van polymeren hogere permeabiliteiten te bezitten bij een even groot vrij volume, wat betekent dat deze polymeren een bredere vrij volume verdeling hebben hetgeen het gastransport in deze bevordert.

De grootte van het vrij volume kan ook worden bepaald uit de sprong in de soortelijk warmte (ΔC_p) bij de glasovergangstemperatuur. Uit deze ΔC_p-waarde, de glasovergangstemperatuur (T_g) en de Cohesive Energy Density (CED) kan het vrij volume worden berekend. Er blijkt een redelijke relatie te bestaan tussen het op deze wijze berekende vrij volume en de permeabiliteit van een groot aantal polymeren die tot zeer verschillende klassen gerekend worden.

LEVENSLOOP

Edwin Hensema werd op 20 november 1962 geboren te Enschede. Hij volgde de lagere en de middelbare school in Hengelo en behaalde 1981 het Atheneum B diploma aan de openbare scholengemeenschap "De Bataafse Kamp".
In datzelfde jaar begon hij de studie Chemische Technologie aan de Universiteit Twente waar hij in 1987 afstudeerde bij de onderzoekgroep Materiaaltechniek/Biomedica van Prof. dr. A. Bantjes. Per 1 september 1987 trad hij vervolgens in dienst bij de onderzoekgroep Membraantechnologie van Prof. dr. C.A. Smolders alwaar het in dit proefschrift beschreven onderzoek werd uitgevoerd.



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