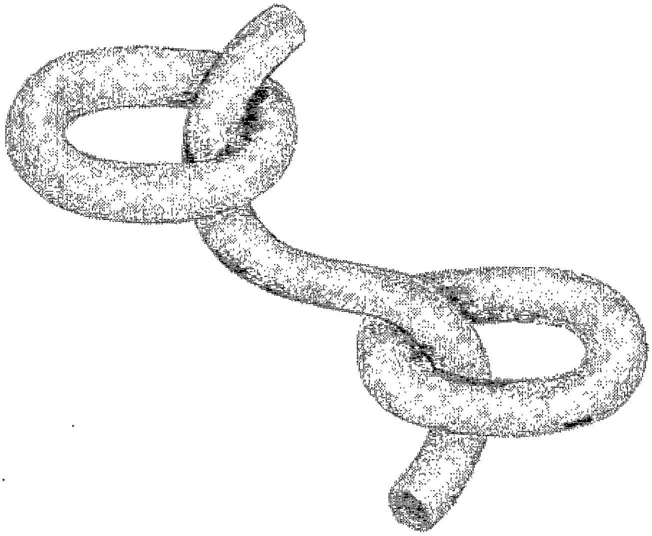
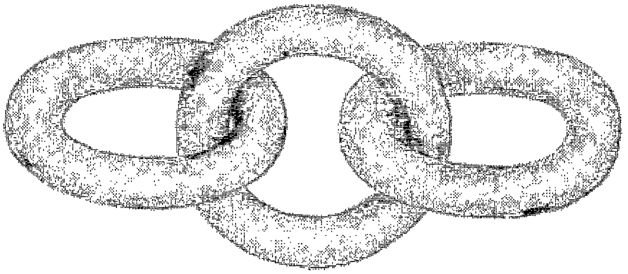
THERMALLY STABLE AND CHEMICALLY RESISTANT POLYMER MEMBRANES

Aromatic Polyoxadiazoles and Polytriazoles





Bert Gebben

9

THERMALLY STABLE AND CHEMICALLY RESISTANT POLYMER MEMBRANES

Aromatic Polyoxadiazoles and Polytriazoles

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus,
prof. dr. ir. van den Kroonenberg,
volgens besluit van het College van Dekanen
in het openbaar te verdedigen
op donderdag 16 juni 1988 te 14.00 uur

door

BERT GEBBEN

geboren op 7 januari 1960 te Hengelo

Dit proefschrift is goedgekeurd door de promotor:
Prof. Dr. Ir. C.A. Smolders
Ass. promotor: Dr. Ing. M.H.V. Mulder

Acknowledgement:
This paper is based upon work financially supported by the Ministiry of Economical Affairs in the Netherlands

Dit onderzoek werd uitgevoerd met geldelijke steun van het Ministerie van Ecomomische Zaken

ISBN 90-9002229-5
Druk: Alfa, Enschede

Voorwoord

Op deze plaats wil ik een aantal mensen bedanken die met mij gewerkt hebben aan het IOP-project TST 44.0654 en zo hebben bijgedragen aan de totstandkoming van dit proefschrift. Ten eerste, de technisch assistenten, die een groot deel van het praktische werk waarop dit proefschrift steunt hebben uitgevoerd. In de eerste jaren was dit Clemens Padberg, een onvervalste Twentenaar, die er zijn grote handen niet voor omdraaide levensgevaarlijke syntheses uit te voeren. Een enkel H_2S wolkje doet niets af aan de goede resultaten die hij boekte en waarmee het project een goede start kende. In het laatste jaar was het de veel rustiger en subtielere Eric Rolevink die met preciese en geduldige metingen een zeer belangrijke bijdrage heeft gelevert met name aan hoofdstuk 4. Naast deze (betaalde) assistentie is er ook hulp geweest van HTS-afstudeerders en stagiaires, waaronder enkele zeer karakteristieke personen. In chronologische volgorde: Peter Schwering, Yvette Roman, Bertha Winter en Hubert Krinkels. Aan het eind van het project verscheen er nog een doctoraal student van de UT: Tjerk Ploeger. Tot slot noem ik nog Marcel Mulder, voor de plezierige begeleiding van het project. Allen hartelijk bedankt!

Ondanks de jaarlijks veranderende samenstelling van de onderzoeksgroep "Membraanfiltratie", onder leiding van Kees Smolders, is er altijd een bijzonder prettige sfeer geweest waarin het goed werken was. Tijdens mijn aanwezigheid, maar niet door mijn toedoen, heeft de onderzoeksgroep een enorme groei doorgemaakt, van 1 personal computer en 1 koffiepotje tot 15 pc's en een koffiezetapparaat voor 40 koppen. Graag zou ik iedereen die in mijn aanwezigheid op welke wijze dan ook aan de sfeer in de groep heeft bijgedragen bedanken. Als iemand mij over een jaar of tien aan mijn promotietijd in deze onderzoeksgroep herinnert dan zal er een brede glimlach op m'n gelaat verschijnen.

Contents

Chapter 2 The cyclodehydration reaction of polyhydrazides Part I: kinetic parameters obtained with non-isothermal thermogravimetry

Chapter 3 The cyclodehydration reaction of polyhydrazides Part II: kinetic parameters obtained from isothermal thermogravimetry

Chapter 4 The cyclodehydration reaction of polyhydrazides Part III: the preparation history influence

Chapter 5 Gas separation properties of a thermally stable and chemically resistant polytriazole membrane

Chapter 6 Thermal behaviour of polytriazole films. A thermal analysis study

In a slightly revised version the following chapters have been or will be submitted for publication:
Chapter 2 will be published in J. Polym. Sci., Polym. Chem. Ed., 26 (1988)
Chapter 3 will be published in J. Polym. Sci., Polym. Chem. Ed., 26 (1988)
Chapter 4 has been submitted for publication to J. Polym. Sci.
Chapter 5 has been submitted for publication to J. Membr. Sci.
Chapter 6 will be submitted for publication to J. Polym. Sci.
The preparation and application of polytriazole membranes, discussed in chapter 5 and 6, has been laid down in a patent: NL 8700758 (31/3/1987)

Chapter 1 Introduction

1.1 Historical development

Membranes exist since the early forms of life on this planet. This is because all living cells are surrounded by membranes. The major and most characteristic function of these biological membranes is a selectively permeable boundary which allows water, certain nutrients and metal ions to pass but forms a barrier for other substances. The biological membrane contains about 40% of polar lipids (phosphoglycerides predominantly), which are believed to be arranged in bilayers, and about 60% of proteins, which are penetrated partially or completely in the lipid bilayers[1]. Two different types of biological membranes[2] can be distinguished: the plasma membranes, which surround every cell and intracellular cellular particle, and the epithelial membranes, which are tissues of specific cells which surround the organs as a kind of skin. The epithelial membrane cells are specialized in specific transport of substances from one side of the cell layer to the other. Our whole body is surrounded by such a membrane skin, in fact the Latin word membrana means skin of body.

Some of these epithelial membranes, taken from animals, were the first membranes used for filtration experiments outside the human body. These animal membranes, such as intestines and bladders of cow's and pig's were used for fundamental research on membrane phenomena like osmosis (1748, A.Nollet) and diffusion[3,4]. Although animal membranes are convenient for some separation purposes because they are thin and highly permeable, they never became widely popular, probably owing to a lack of reproducibility[3]. This was a reason for man to look for synthetic membranes of which the properties could be controlled.

In 1855 Fick studied the phenomenon of diffusion through membranes[4]. For his studies he used films of nitrocellulose which he prepared himself from solutions of cellulose nitrate in ether/alcohol. These films can be considered as some of the earliest artificial semi-permeable membranes. The big advantage of these membranes over the animal membranes was the possibility to adjust the porosity and the pore size of the membranes by changing the preparation parameters. Nitrocellulose is a polymer that was discovered shortly before Fick. It not a synthetic polymer but a chemical modification of nature's most important polymer: cellulose. Cellulose is the main material of which the cell wall of plants are made. It forms the natural support for most plant membranes, and can be extracted from wood, cotton(=almost pure cellulose) and leaves[5]. Membranes made of cellulose nitrate are generally called collodion membranes and are probably the first patented artificial membranes(1864)[6]. Collodion membranes remained the main type of membranes used for membrane research and small laboratory scale applications till early this century[7].

In membrane science, nowadays, the polymers form the most applied and studied class of materials. From about 1920 on when new synthetic polymers were discovered, like for example polyamid (nylon), polystyrene and polyvinylchloride (PVC), various polymers have been applied for membrane manufacturing. Cellulose based polymers, like cellulose acetate, however are still the most exploited types. One of the first major membrane applications was the use of hemodialysis membranes, made from cellophane (=pure cellulose with a trace of glycerol[7]), in the artificial kidney in 1944[4].

Besides polymers several different materials have been and are still being used for the preparation of membranes. Already in 1861 Thomas Graham reported the use of natural rubber for dialysis and diffusion measurements[4] and at the same time the first inorganic membranes were prepared by Traube, Pfeffer and van't Hoff by precipitating cupric ferrocyanide in the pores of thin layers of earthenware pots, used for the study of osmotic pressures[4,7]. Also materials like paper (again cellulose based!), ceramics, carbon[8], glasses, salts, crystals, inorganic polymers, metals and even liquids have been or are being studied.

One important argument for the search for new materials, besides improvement of separation properties is mechanical, thermal and chemical stability. Membranes of cellulose acetate and of most other polymers are rather poor in their thermal and chemical stability and therefore their applicability is restricted to only very mild separation conditions, such as temperatures below 100°C, no acidic or caustic environments (pH between 4 and 7) and no contact with organic solvents. Therefore there is a need for membranes which can function under more severe conditions. These membranes would open up new possibilities for membrane separations and increase the competitive position of membrane separations amongst other physical separation methods.

When the Dutch ministry of Economic Affairs started their national innovative research program on membranes (IOP-M) in 1984 one of the projects accepted was the development of thermally stable and chemically resistant polymer membranes. The aims of the project were clear: a polymer membrane which could withstand high temperatures (~250 °C), agressive chemical environments, a broad pH-range and organic solvents. In this thesis part of the work done in this project is described. The work has been concentrated upon the preparation of membranes from two polymers with high thermal and excellent chemical stability and which have not been used before as membrane material.

1.2 Membrane filtration

Membrane filtration is a separation process which can be used for the separation of molecular mixtures into their components. For molecular separations a whole series of separation processes is available nowadays, such as distillation, crystallization, adsorption, extraction, centrifugation, flotation and complexation. Each separation process makes use of one or more differences in chemical or physical nature of the components to be separated[9]. In membrane filtration use is made of all possible physical or chemical properties. The main characteristic of membrane filtration is that the separation is achieved by a difference in transport rate of the molecular components through a thin interfacial wall, the membrane. This is represented schematically in figure 1.1.

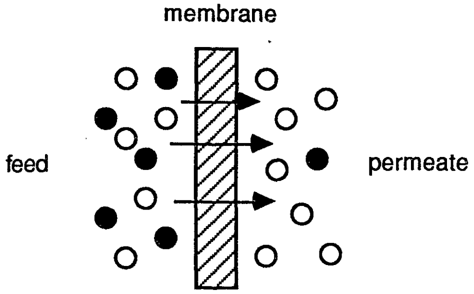


Figure 1.1: Schematic representation of a membrane filtration process

The membrane separates two phases and there is selective transport of components of one phase to the other. In order to accomplish transport of a component through the membrane a driving force, which is a difference in thermodynamic potential across the membrane, is needed.

The transport rate or permeability, of one component through the membrane can be effected by its size, shape, weight, affinity to the membrane, charge, chemical nature or combinations of these in relation to the structure of the membrane.

Three main transport mechanisms can be mentioned:
a. convectional flow through pores
b. solution and diffusion through dense, non-porous media
c. facilitated transport

Membrane process	chem./phys. property	driving force	F/P phase	membrane morphology	application
Microfiltration	size	pressure	L/L	porous	removal of small particles
Ultrafiltration	size	pressure	L/L	porous	separation of macromolecules
Reverse osmosis	size/affinity	pressure	L/L	dense/ porous	separation of low M molecules
Dialysis	diffusivity	concentration	L/L	porous	removal of low M molecules
Electrodialysis	charge	electric potential	L/L	porous	separation of ions
Gas separation	solubility/ diffusivity	pressure	G/G	dense	separation of gases
	mass	pressure	G/G	porous	"
Vapour permeation	solubility/ diffusivity	activity	V/V	dense	separation of vapours
Pervaporation	solubility/ diffusivity	activity	L/V	dense	separation of solvents
Membrane distillation	partial vapour pressure	temperature	L/L	porous	removal of volatile components

N.B. F=feed, P=permeate, L=liquid, G=gas, V=vapour

Table 1.1: *Membrane processes and their characteristics*

The different membrane processes and their characteristics are presented in table 1.1. For a more detailed description of the various processes other sources have to be consulted.

Membrane technology is a still growing market with good prospects. Some industrial important large scale applications are desalination of brackish- or sea-water by reverse osmosis and concentration of fruit juice by ultrafiltration. There are also a lot of small scale applications which are of importance, for example the artificial kidney (dialysis), the membrane lung or oxygenator (gas separation), pH electrodes and other sensors (electrodialysis), lab scale filters (microfiltration), controlled release for drug deliverance (dialysis), batteries and accu's[9].

1.3 Polymer membranes

As already mentioned polymers form the most studied and applied group of materials used for the manufacturing of membranes. Ceramics (inorganic materials) are the second important class of material which becomes more and more interesting mainly aiming at the superior stability and lifetime of these materials at extreme conditions compared to polymers. Comparison between both membrane materials is difficult because of the many different types of both polymeric and inorganic materials. In general polymers have some clear advantages over ceramics like flexibility, ease of processing, possibility to realize any configuration, low density, high strength-to-weight ratio[10], availability of wide structure variations, ability to have properties tailored to a specific use by structural changes and last but not least lower costs. The general disadvantages are the inferior stability at high temperatures and the time dependent relaxation phenomena by which membrane properties change in time.

Before the preparation methods of polymer membranes will be discussed three distinct types of (polymer) membranes will be distinguished[4]:

(a) dense, non-porous polymer membranes, which act as permselective barriers through which molecules permeate by a solution-diffusion process using the intermolecular space between the polymer molecules. Molecules are separated according to their interaction with the polymer and their size. The nature of the polymer material is essential for the separation properties of these type of membranes.
(b) porous polymer membranes (pore diameter>10 nm), which act as filters separating molecules mainly according to size and shape. Especially the pore size and pore size distribution of the membrane determine the separation properties of the membrane, so that in principle any material can be used.

(c) an intermediate class of polymer membranes not belonging to the above two types (pore diameter<10 nm), which separate molecules according to a combination of the above mentioned mechanisms. The pores in these films are so small that their magnitude is in the order of the intermolecular space between the polymer molecules. Both the size of the 'pores' and the chemical nature of the membrane material determine the separation properties.

Polymer membranes can be prepared in many different ways, but the chosen preparation method is dependent on the type of membrane wanted and on the properties of the polymer. Below the possible preparation techniques are classified according to the starting phase of the polymer:

I Solid

Solid polymer powder (and possible additives for pore building) can be pressed into films followed by a sintering process at high temperatures (350-380°C). Porous PTFE membranes (pore radius >0.2 mm) are prepared in this way. This process is therefore restricted only to the porous membrane type (b) and for high temperature resistant polymers. The method is useful for insoluble and infusible polymers which can not be processed in any other way.

II Polymer melt

The polymer melt can be shaped into any kind of membrane configuration, for example by extrusion or molding, followed by solidification and/or crystallization of the polymer. In this way the dense membrane type (a) is obtained. Additional treatments can change the structure into a porous structure:

1] Semi crystalline polymer films can be stretched which introduces micro crazes between the crystalline regions.

2] Polymer films can be exposed to high energy particle radiation followed by etching away the material along the created tracks.

The melt process is restricted to polymers with not too high melting temperatures (T_m<400°C) and which do not show severe degradation upon melting.

III Polymer solution.

A concentrated polymer solution can be shaped into any configuration by extrusion or brought on a support of any kind of configuration by casting, coating or spraying followed by a phase inversion of the polymer into a solid phase. The phase inversion can be accomplished by evaporation of solvent, temperature decrease, addition of non-solvent or removal of solvent by filtration (filtration deposition). If the phase inversion process is accomplished by immersing the solution into a non-solvent bath an asymmetric film structure consisting of a dense, thin, toplayer, the actual membrane, and a porous sublayer can be the result. By changing the parameters influencing this phase inversion process any type of membrane structure can be obtained[11,12]. The phase inversion process from the solution therefore is the most versatile membrane preparation process. It is the most important and applied technique only restricted by the solubility of the polymer[11].

IV Monomers

For these processes reactive monomers have to be deposited on the surface of a chosen support layer where polymerization will occur. Membranes which consist of a porous support layer of any kind of material and thereupon a polymeric top layer, the actual selective membrane, are called "composite membranes". The deposition can be achieved by several methods. One of them is an interfacial polymerization, where the reactive interface is chosen to coincide with the surface of a support layer. A thin layer of polymeric reaction product will be formed onto this support[13]. Another process is a vacuum deposition of reactive monomers from the gas phase on a substrate followed by immediate polymerization. Reactive monomers can be induced by radiation (plasma polymerization) or high temperature pyrolysis. The polymer membranes so obtained are all of the dense type (a).

1.4 Thermally stable polymers

1.4.1 Introduction

In the late 1950's the search for thermally stable polymers started, mainly initiated by the aerospace industries. The ability for polymers to withstand extreme temperatures was first recognized after the discovery of aromatic polyamid and heterocyclic polymers. In the sixties innumerable different polymers have been synthesized and patented. In figure 1.2 a graph is presented showing the range of stabilities of newly discovered polymers against their year of discovery. It is very obvious from this graph that the maximum stability is not improved at all after the early discoveries of these types of polymers[14]. This lack of any great improvement leads to the opinion that the limit of thermal stability for polymers with organic backbones had been reached early.

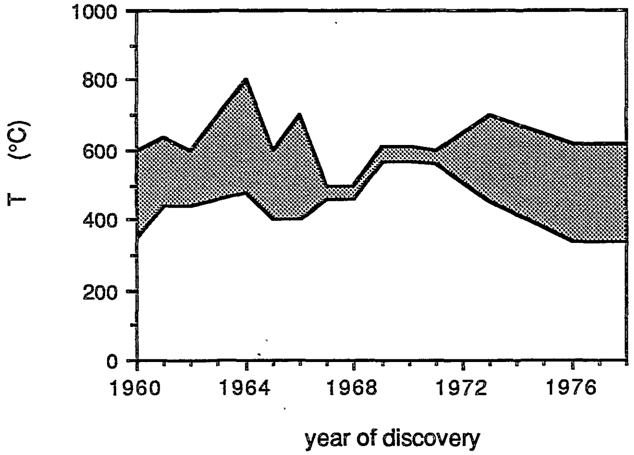


Figure 1.2: Range of thermal stabilities of newly discovered polymers; determined using thermogravimetry, data obtained from literature[10]

The main effort of research after the first important polymer discoveries has therefore not been the discovery of new polymer backbones but the improvement of the processability and tractability of these polymers without loss of stability. Generally the most stable polymers are insoluble and infusible (the "brick dust syndrome") and there is an inverse relationship between stability and tractability. In section 1.4.4 these efforts will be discussed. Some examples of general molecular structures of thermally stable polymers are given in appendix A. For more specific information other sources have to be consulted[10,15,16,17].

1.4.2 Thermal stability

No exact definition of thermal stability of polymers can be found in literature. In his book on thermally stable polymers P.E.Cassidy[10] refers to vague definitions such as: "above 300°C by TGA in air.." or "maintenance of physical properties for long periods of time at 250°C in air measured by IGA". An important reason for this confusion is the fact that there are different mechanisms for loss of properties and there are different conditions/circumstances which determine the stability.

The two main mechanisms for thermal property loss (deterioration) are:

1. Softening

This is a reversible process, which leads to loss in mechanical stability. The softening process is mainly determined by intermolecular attraction forces, chain flexibility and crystallinity. Solvent induced softening or swelling is also classified under this type of mechanism. Significant parameters determining this deterioration mechanism are the glass-rubber transition temperature (T_g), the softening temperature (T_s) and the melt temperature (T_m).

2. Decomposition and degradation

This is an irreversible process caused by chemical reactions on the polymer (thermolyses /pyrolysis) and is therefore determined by the chemical nature of the polymer and ultimately by the bond energies of the polymer backbone. This process can lead to chain cleavage resulting in reduction of the molecular weight. The environmental condition is also an important determining factor for this deterioration mechanism.

Chemical stability is the resistance against chemical reactions of the polymer with attacking chemicals from the environment. This stability criterion in general is closely related to thermal stability. Mostly the same structural and chemical features of the polymer influence both stabilities in the same way. Especially the so called "weak spots", such as alkylic, alicyclic and unsaturated groups, non-aromatic hydrocarbons and -NH groups, which can easily be attacked for example by free chlorine or water, have to be avoided in trying to make a polymer more chemically stable[13]. Mostly chemical stability is specified in terms of hydrolytic stability, chlorine resistance and pH resistance.

Knowing the main deterioration mechanisms one can come to a general set of structural and chemical requirements a thermally and chemically stable polymer should meet[10,15]:

For softening stability:

- factors that increase T_g and T_m:
  rigid backbones, preferably para substituted rings, no flexible groups in the backbone, bulky side groups for loss of rotational freedom, high molecular weights, no plasticizers, crosslinking, crystallinity.
- factors that increase crystallinity:
  structural symmetry, intermolecular attraction forces such as hydrogen bonds, no random side groups.

An illustration for the influence of some of these factors is given in table 1.2, where T_g and T_m are presented for some polymers with different structural features.

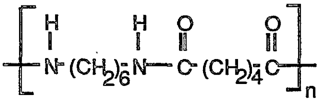
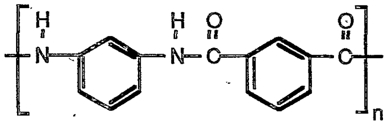
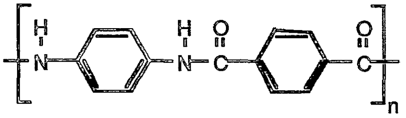
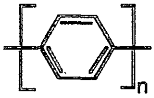
polymer structure	T_g	T_m (°C)
$-\left[CH-CH \right]_n-$	-125	135
 $-\left[N(H)-(CH_2)_6-N(H)-C(=O)-(CH_2)_4-C(=O) \right]_n-$	80	265
	273	380
	-	~500
	-	>500

Table 1.2: Some polymer structures and their corresponding transition temperatures

For decomposition stability:
- aromatic and/or heterocyclic backbones instead of aliphatic backbones
- resonance structures
- rings with normal bond angles
- no weak spots, such as non-aromatic hydrogen, aliphatic groups, pendant hydroxyl groups etc.
- strong chemical bonds with high bond enthalpies
- as much as possible polybonding (=atoms linked with more than two bonds to the main chain)

Thermally stable polymers can be divided into distinct categories, each meeting one or more of the above mentioned requirements. The polymer categories are ordered according to increasing, general thermal stability. (the specific stability requirements realized are placed between brackets)

A Thermosets	(insolubility, high T_g)
B Fluorinated polymers	(high C-F bond energy, shielding of carbon chain)
C Inorganic polymers	(high bond energies)
D Aromatic polymers	(resonance stability, stiff chains, high T_g)
E Heterocyclic polymers	(resonance stability, stiff chains, high T_g)
F Ladder polymers	(polybonding, stiff chains, high T_g)

In appendix A an overview of the most important polymers is given for each of the categories, with general structural formulae added.

1.4.3 Thermal analysis

Thermal stability is generally determined using thermal analysis techniques such as Thermogravimetry (TG), Differential Scanning Calorimetry (DSC) and Thermal Mechanical Analysis (TMA). All these techniques measure a physical property as a function of temperature or time. Using TG the change in weight is measured, for DSC the specific heat and for TMA a mechanical parameter is measured. TG is applicable for determining the decomposition or degradation processes as these are mostly accompanied by weight loss. It is a simple and most frequently used technique. Often the temperature at which a certain fraction of weight loss occurs is used as the definition of thermal stability. In combination with TG a technique which analyses the gas evolving from the heated samples can be very useful (EGA, Evolving Gas Analysis).
During DSC experiments heat effects are measured as a sample is heated with constant heating rate. These heat effects correspond to softening processes like rubber-glass transitions and melting but also decomposition processes. Parameters for the softening stability like T_g and T_m can be determined accurately using DSC. TMA is also suitable for following softening processes. For a good understanding of the thermal stability of a certain polymer at least several techniques should be used at a time to complete each other.

The above mentioned techniques are dynamic ones. There is also a trend to rely more on static methods, such as isothermal thermogravimetry (IGA)[10] or the measurement of another physical property in time during an isothermal heat treatment. The reason for this is that these measurements are more realistic for the anticipated applications.

1.4.4 Processability

There are many different ways to attack the problem of the bad processability of thermally stable polymers. The search for new and/or better solvents is the first strategy to fight this problem. A new solvent with a strong solvent power is HMPA (Hexa methyl phosphor triamine) which was especially developed for this area. Unfortunately this solvent is very carcinogenic. It was also discovered that the addition of inorganic salts such as $CaCl_2$ or LiCl to aprotic polar solvents such as NMP, DMSO and DMAc[10] improves their solvent power for certain polymers. Despite these new solvents most thermally stable polymers will appear to be insoluble. Ultimately strong concentrated acids, such as concentrated sulfuric acid, can be used as a solvent for most thermally stable polymers. Aromatic polyamid fibers for example are prepared from solutions in concentrated sulfuric acid. Of course the use of such corrosive solvents presents additional problems.
Another, very recently discovered, approach which might be successful is the preparation of conducting polymer solutions[18] of charged conjugated polymers in strong electrolytes. For example Frommer[19] shows the preparation of polyphenylene and polypyrrone solutions by a subtle process which involves doping with AsF_5 and dissolving in AsF_3.

The main effort to improve the tractability of the polymers is a structural modification by introducing a mitigation of the requirements for optimal stability. For example the introduction of flexible groups such as ether or sulfonyl groups in the polymer backbone to increase the flexibility and thus introducing solubility and meltability. Most aromatic polymers from category D, such as the polyamids, polyesters and polysulfones already possess flexible units and are therefore much more tractable compared to the heterocyclic polymers of category E and F. Both the thermal and the chemical stability of the former category however are inferior to that of the latter categories.
Another improvement by structural modification of the polymer is the introduction of bulky side groups to the backbone. This was successfully applied to polyphenylenes[10] and polyquinoxalines[20] where the phenylated forms appeared to be more tractable. This was mainly accounted for by a decrease in crystallinity. Although the aromatic character is maintained by this modification the stability is decreased. Most heat resistant polymers that are commercially available can be considered as structural compromises between stability and processability.

An important technique to circumvent the intractability without making a compromise to the chemical structure is preparing the polymer in two or more steps through a processable prepolymer.

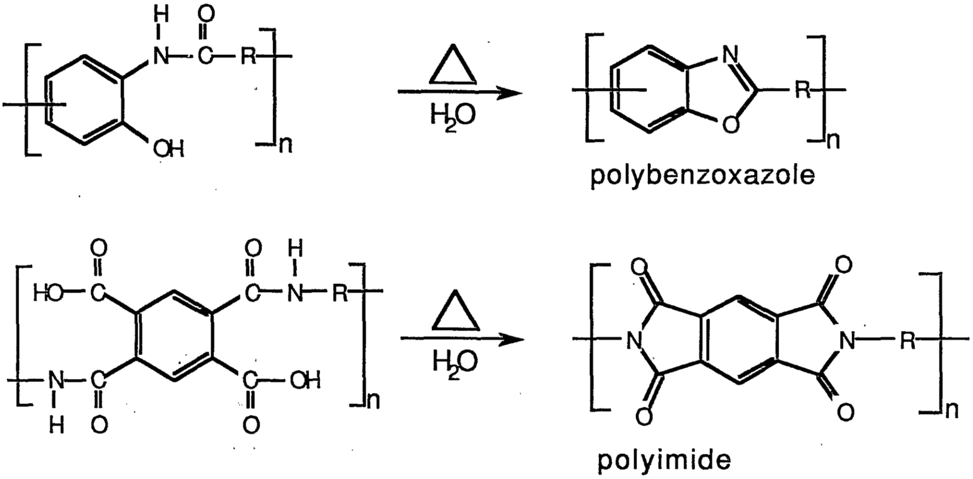
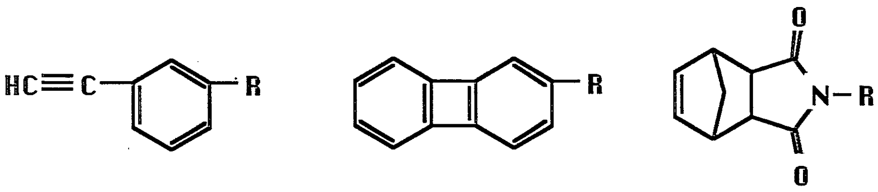


Figure 1.3: Schematic representation of the second step of the two-step preparation routes for polybenzoxazoles and polyimides through cyclodehydration of their processable prepolymers.

Once the prepolymer is processed into a desired configuration a thermal or chemical treatment introduces an internal reaction by which the prepolymer converts into the desired polymer, mostly accompanied by loss of a volatile condensation product. Many of the heterocyclic polycondensation polymers of categories E and F can be prepared in this way, like the polybenzoxazoles and the polyimides[21], schematically represented in figure 1.3.

Another two-step technique is the preparation of oligomers of the desired polymers with reactive end groups, like acetylene, norborene or biphenylene, schematically represented in figure 1.4. These end-capped oligomers are processable due to their low molecular weights. Upon a thermal treatment crosslinking reactions are set in without any volatile by-products resulting in chain extension or crosslinking into a network structure. When the oligomers have been end-capped with acetylene, thermosets are obtained upon heating.

This technique has been applied for many polymers like for example polyimides, polyquinoxalines and polysulfones[22]. Thermally curable oligomers can also be used as reactive plasticizers by blending them with their thermoplastic corresponding polymers so introducing an improved processability[23,24].



phenylethynyl (acetylene)

biphenylene

norbornene (nadimide)

Figure 1.4: Some thermally reactive end-capped oligomers R

A combination of the above mentioned techniques is the introduction of thermally reactive pendant side groups, like is represented in figure 1.5. Here the polymer, a polyquinoxaline, obtains tractability by the introduction of bulky pendant side groups and a thermal treatment introduces an intramolecular cyclo-addition reaction between the acetylenic side groups without volatile by-products to give a rigid and insoluble polymer[24]. Introduction of thermally reactive groups as pendant groups on the main chain can also provide intramolecular crosslinking possibilities for these polymers[22].

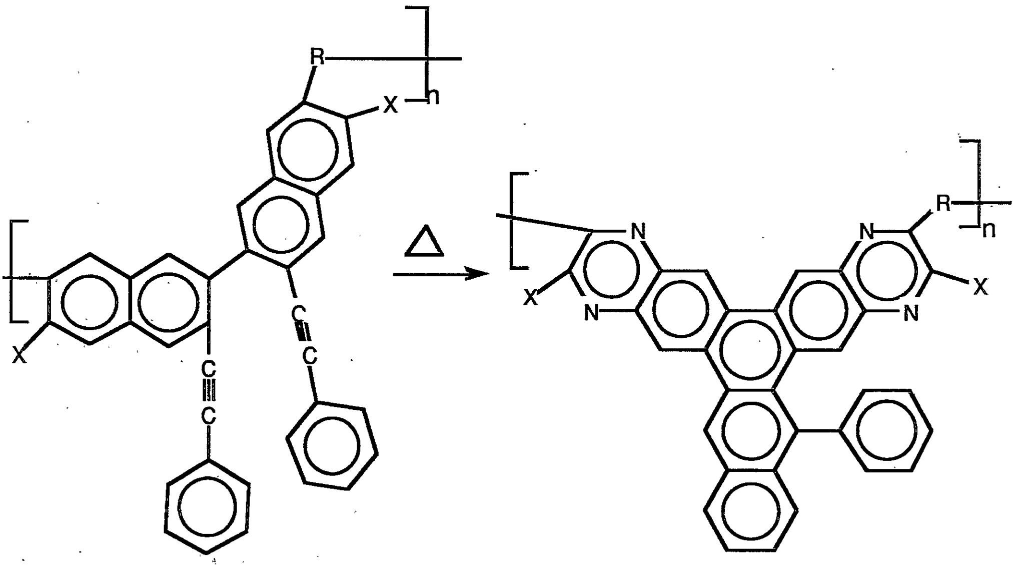


Figure 1.5: Polyquinoxaline with pendant thermally curable side groups

If the above techniques to improve the processability of a certain type of polymer are not possible or not desired a different way of processing could give a solution to the problem. Sintering of finely ground polymer powder, mentioned in section 1.2, is such another technique. This is in fact being done for PTFE[3].
A completely different approach is perhaps a preparation technique starting from the monomers but these techniques are still very much in a stage of development and still have a lot of limitations concerning the chemical structures of polymers that can be prepared. Recently neutral films of polyphenylene and polypyrrones have been prepared by electrochemical polymerization from conducting monomer solutions, where thin films were deposited on the electrodes[18,25].

1.4.5 Membranes from thermally stable polymers

The different approaches towards the processability of a polymer discussed above can also be found in literature for the preparation of membranes. The most frequently used approach is the structural modification by the introduction of flexible units in the backbone such as ether, sulfone or isopropyl groups, after which the polymers can be solved in a suitable solvent and cast or spun into a desired membrane structure. A lot of these membranes, prepared from polymer solutions, especially of polyimides and polybenzimidazoles are described in Japanese and Russian patents. Commercially available are polyimide UF membranes of the Japanese company Nitto and polybenzimidazolone membranes manufactured by the Japanese company Teijin Ltd. Sarbolouki[26] describes the preparation of UF membranes of some commercially available soluble polyimides. A review of the work done on polybenzimidazole(PBI) membranes is given by Model[27]. These membranes are made of soluble polybenzimidazoles by solution casting from DMAc with LiCl. Insoluble PBI can be prepared by a chemical modification of the polymer and crosslinking with perfluorglutaric acid. Aromatic polyamid (PA) membranes prepared by solution casting from DMAc and NMP solutions containing LiCl are described by Strathmann[28].
Membranes of insoluble polyimides can be prepared through a two-step process. This process, described by Strathmann[29], includes a thermal conversion of precursor polyamic acid membranes. The two-step method has also been applied for the preparation of polyimidazopyrrolone RO membranes, described by Scott et.al.[30] and for polyoxadiazole RO membranes, described by Klimmek and Krieger[31]. Inorganic polyphosphazene membranes are described by McCaffrey et.al[32] prepared by solution casting from 1%

polymers solutions in ethyl acetate.

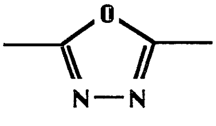
1.5 Polyoxadiazoles and polytriazoles

For the work described in this thesis two families of thermally stable polymers have been selected from the category of heterocyclic/aromatic polycondensation type of polymers: the polyoxadiazoles and the polytriazoles. For the selection of these polymers the following selection criteria have been used:

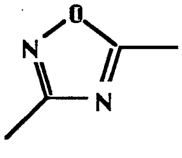
- the polymer should possess high thermal, chemical and solvent stability
- the polymers should not be commercially available and relatively new for membrane preparation, because of the innovative character of the project
- the polymer synthesis should be relatively simple, in view of a practical application, i.e. it should not consist of many consecutive steps and no excessive monomer synthesis and purification should be necessary
- the possibility of using the phase inversion method for membrane preparation

1.5.1 Polyoxadiazoles

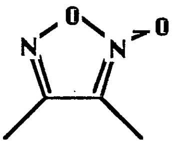
The polyoxadiazoles are characterized by their heterocyclic oxadiazole five-ring. Some of these oxadiazole rings are presented below, of which the 1,3,4-isomer is most widely known and applied[33]. When referring to the oxadiazole-ring in the context of this thesis the 1,3,4-isomer is meant.



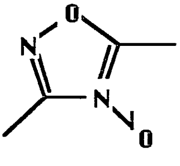
1,3,4-oxadiazole



1,2,4-oxadiazole



1,2,5-oxadiazole-N-oxide

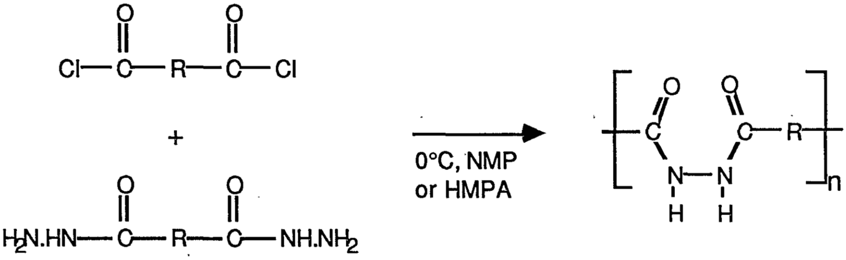


1,2,4-oxadiazole-N-oxide

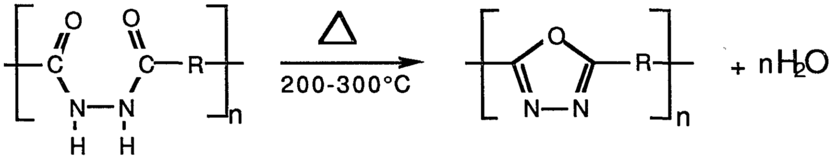
There are 5 different synthetic reaction paths, which will be briefly discussed in order of their technical importance.

Method 1: a two-step process introduced by Frazer[34,35], where in the first step a polyhydrazide is formed by a solution polycondensation reaction between a carboxylic acid dichloride and a carboxylic acid dihydrazide and in the second step the isolated polyhydrazide is thermally converted into a polyoxadiazole by a cyclodehydration reaction:

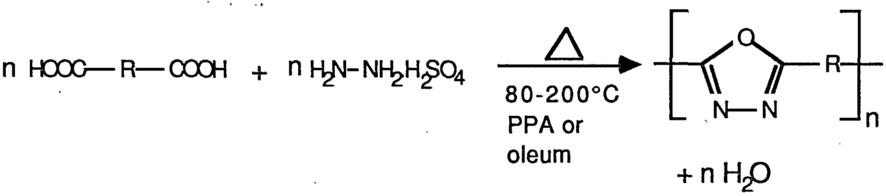
first step:



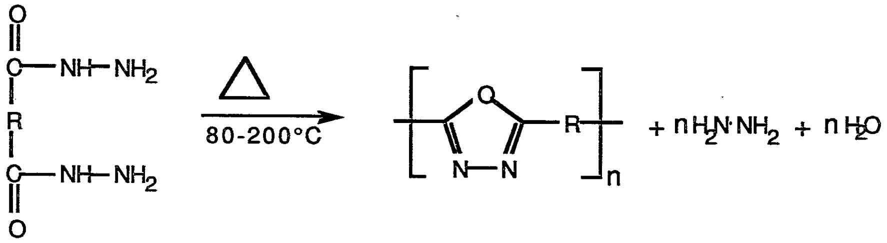
second step:



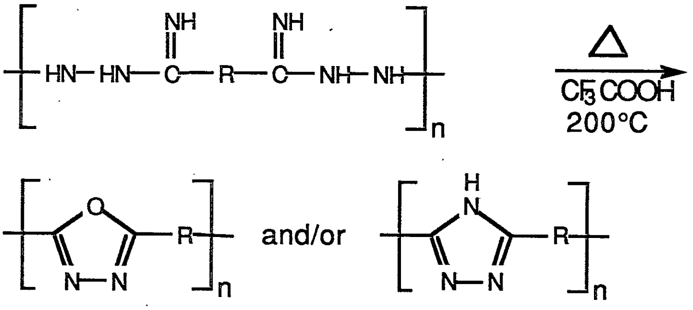
Method 2: a one-step solution polymerization in oleum or polyphosphoric acid (PPA) introduced by Iwakura[36,37]. The polymerization takes place because of a reaction between a dicarboxylic acid or a derivative with hydrazine or its salt.



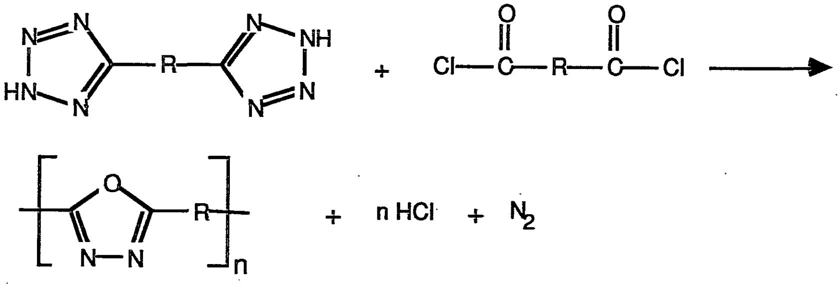
Method 3: a self-polymerisation of a dicarboxylic hydrazide in oleum or PPA also introduced by Iwakura[37]. Just like method 2 this reaction proceeds through the intermediate polyhydrazide which is not isolated but is converted in-situ into the polyoxadiazole



Method 4: a cyclo-de-ammonising of the polymer poly(N-acylhydrazidine) by heating this polymer in strong acids. Depending on the reaction conditions both oxadiazole and triazole rings can be formed. This method finds very little application[33].



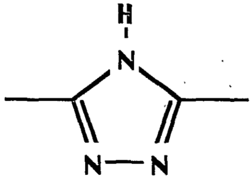
Method 5: this method is only of historical importance because it was the first important method for the polyoxadiazole preparation introduced by Abshire and Marvel[38]. It consists of a reaction between a carboxylic acid chloride and a bistetrazole



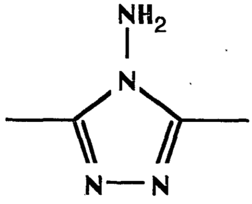
Out of these possible preparation methods method 1, the two-step process, was adopted for the membrane preparation studied in this thesis. In this two-step process membranes of the soluble polyhydrazide are prepared first followed by a thermal treatment of the solid membranes to convert them into the insoluble polyoxadiazole membranes. In this way the intractability of the desired, completely aromatic, polyoxadiazoles can be circumvented and for the preparation of the polyhydrazide membranes the versatile phase-inversion method can be applied. The aromatic polyhydrazides are soluble in aprotic polar solvents such as DMSO, NMP and DMAc. The preparation of any membrane structure therefore belongs to the possibilities. Besides the above described two-step preparation process also method 2, the one-step Iwakura process, coupled with membrane casting directly from the oleum reaction solution, has been studied but not in detail.

1.5.2 Polytriazoles

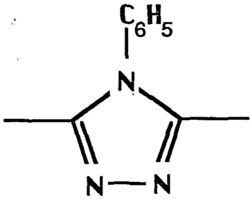
The polytriazoles are characterized by the heterocyclic triazole five ring, where one of the nitrogen atoms is substituted with hydrogen or another group like presented below. When referring to the triazole group in the context of this thesis the 4-phenyl-1,2,4-triazole group is meant.



1,2,4-triazole



4-amino-1,2,4-triazole

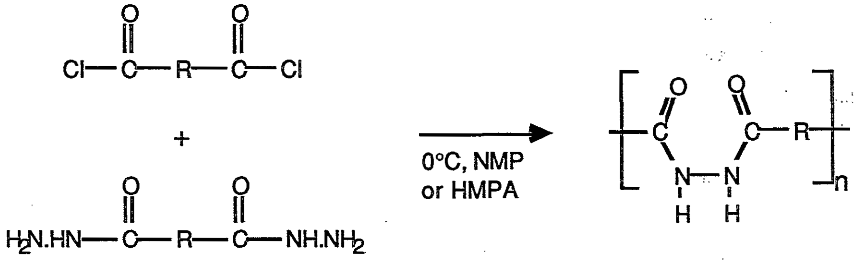


4-phenyl-1,2,4-triazole

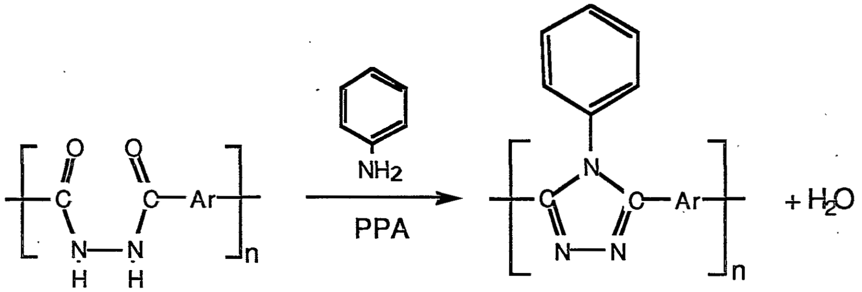
For the preparation of aromatic poly-phenyl-triazoles two methods are known:

Method 1: a chemical cyclisation reaction of a polyhydrazide with aniline in polyphosphoric acid, introduced by Holsten and Lilyquist[39-42]. This is a two-step procedure, where the first step is the preparation of a precursor polyhydrazide in the same way as in method 1 for the polyoxadiazole preparation according to Frazer[34].

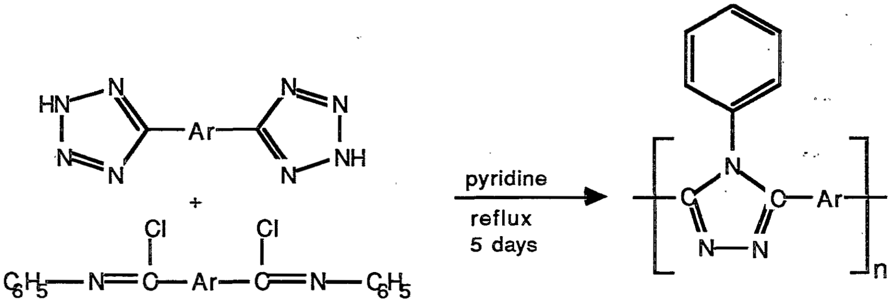
first step:



second step:



Method 2: a reaction between a bistetrazole and a bisimidoyl chloride in pyridine, introduced by Abshire and Marvel[38]



This first method, developed by Holsten and Lilyquist, was adopted for the polytriazole preparation discussed in this thesis because higher molecular weights were reported in literature for this method and it also includes the polyhydrazide preparation. The same prepolymer, an aromatic polyhydrazide, can be used for the preparation of both the polyoxadiazoles and the polytriazoles.

For the preparation of polytriazole membranes it is not necessary to prepare the membranes in two steps since the polytriazoles do possess some solubility. The polytriazoles can be considered as phenylated forms of an aromatic and heterocyclic backbone and because of this phenylation they possess an improved solubility. Formic acid and some phenol derivatives appear to be solvents for aromatic polytriazoles of which formic acid is the best solvent. Because of this good solubility membranes can be prepared directly from a formic acid solution of polytriazole by the phase-inversion process. In this way any desired membrane structure can be obtained.

1.6 Structure of this thesis

The preparation of polyoxadiazole membranes by the thermal conversion of polyhydrazide membranes in the solid state, as described in paragraph 1.5, presented some problems. The polyhydrazide precursor membranes were thermally converted by situating them in furnaces at high temperatures (260-320°C) under reduced pressure or N_2-purge gas. The problems arising with this second step were twofold, firstly high temperatures and prolonged heating times were necessary for complete conversion of the polyhydrazides and secondly the finally obtained polyoxadiazole membranes were very brittle, they desintegrated upon the slightest force applied to them. To learn more about this second conversion step the reaction mechanism of the cyclodehydration reaction in the solid state was studied by following the reaction kinetics of the conversion process using thermogravimetry (TG).

In **Chapter 2** thermogravimetry is used to follow the conversion of the polyhydrazide during a continuous heating up of the sample. For the evaluation of the kinetic parameters a method developed by Ozawa was used for which a set of TG curves recorded at different heating rates is required. Compared to the conventional isothermal experiments this method is much faster, very accurate and the kinetic parameters can be determined for every degree of conversion.

Chapter 3, in contrast to chapter 2, discusses isothermal gravimetrical experiments, which represent the anticipated conversion process of polyhydrazides. Both evaluation methods are compared and interesting agreements and differences between dynamical and isothermal conversion are found.

Chapter 4 deals with the influence of the preparation history of the polyhydrazide samples on the conversion kinetics. The preparation history seemed to be of great importance for the conversion rate which was reflected by an observed difference in conversion kinetics between powder and film of the same polymer. Also in this chapter a final model is presented for the conversion mechanism, with suggestions for the improvement of the thermal conversion.

Appendix B deals with the one-step Iwakura process for the preparation of polyoxadiazoles and the preparation of membranes directly from oleum solutions.

In **appendix C** some comments will be given concerning the brittleness of the polyoxadiazole membranes prepared through the cyclodehydration of polyhydrazide membranes.

In contrast to the polyoxadiazoles the preparation of membranes of the second group of polymers studied, the polytriazoles, presented no serieus problems. The polytriazoles prepared from the same precursor polyhydrazides appeared to be soluble in formic acid and could be processed into tough and flexible membranes. Therefore good polytriazole membranes were easily available that could be used for membrane filtration experiments. In particular homogeneous polytriazole membranes have been tested for their potential for the separation of gases.

In **chapter 5** the permeabilties for several single gases are presented not only measured at room temperature but also at temperatures up to 200°C. Special attention has been paid to the separation of CO_2/CH_4 and O_2/N_2. **Chapter 6** discusses the thermal behaviour of these polytriazole membranes at temperatures between 200°C and 500°C studied with differential scanning calorimetry (DSC). Special attention has been paid to crystallization phenomena and the influence of thermal treatments.

1.7 References

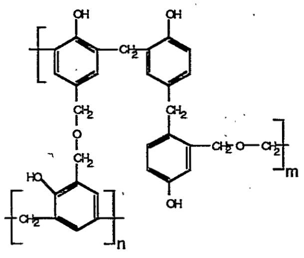
1] A.L.Lehninger, Biochemistry, sec. ed., Worth Publishers, Inc. New York(1976)
2] P.M.Bungay, H.K.Lonsdale, M.N.dePinho(ed.),Synthetic Membranes: Science, Engineering and Applications, p683-699, D.Riedel, Dordrecht(1986)
3] E.S.Perry, C.J.van Oss (Ed.),"Progress in Separation and Purification", Vol.3, Wiley-Interscience, New York, 1970
4] H.K.Londsdale, J.Membr.Sci. 10, 81-181(1982)
5] High Polymers. Vol 5,"Cellulose and Cellulose Derivatives, Part 1, Interscience Publishers, Inc., New York, 1954
6] R.E. Kesting, "Synthetic Polymer Membranes", McGraw Hill, New York, 1972
7] J.D. Ferry, Chem. Rev.,18, 373(1936)
8] U.S.Patent 4,685,940 (1987)
9] H.Strathmannn, "Trennung von molekularen Mischungen mit hilfe synthetischer Membranen",

Steinkopf Verlag, Darmstadt, 1979
10] P.E.Cassidy, Thermally Stable Polymers, Marcel Dekker, New York (1980)
11] J.G. Wijmans, Thesis, University of Twente, Enschede, The Netherlands (1984)
12] A.J.Reuvers, Thesis, University of Twente, Enschede, The Netherlands (1987)
13] R.G.Sudak, M.E.McKee, Desalination, 22, 235-242(1977)
14] P.E.Cassidy, J.Makromol.Sci.-Chem.,A15(7),1435-1460 (1981)
15] J.P.Critchley, G.J.Knight, W.W.Wright, Heat Resistant Polymers, Plenum Press, New York(1983)
16] A.H.Frazer, Polym. Rev,17,"High temperature resistant Polymers"(1969)
17] R.J.Cotter, M.Matzner, Organic Chemistry,"Ring-Forming Polymerisations, Part B,1: Heterocyclic Rings", Academic Press, New York, 1972.
18] J.Fauvarque, M.Petit, A.Digua, G.Froyer, Makromol.Chem.188,1833-39 (1987)
19] J.E.Frommer, Acc.Chem.Res.,19,2-9(1986)
20] P.M.Hergenrother, Macromol.,14(4),891-897(1981)
21] M.M.Bessonov, M.M.Koton(ed.), V.V.Kudryavtsev and L.A.Laius, "Polyimides", Consultants Bureau, New York, 1987
22] P.M.Hergenrother, Polym.Prep.,1,97(1984)
23] P.M.Hergenrother, Polym. J.,19,1,73-83(1987)
24] P.M.Hergenrother, J.Macromol.Sci.-Rev.Macromol.Chem., C19(1),1-34(1980)
25] W.Wernet. G.Wegner, Makromol.Chem.,188,1465-1475(1987)
26] M.N.Sarbolouki, J.Appl.Polym.Sci., 29, 743-753(1984)
27] F.S.Model, H.J.Davis, J.E.Poist onbekend boek, p 231-
28] P.Zschocke, H.Strathmann, Angew.Makromol.Chem, 73, 1-23(1978)
29] H.Strathmannn, Desalination, 26, 85-91(1978)
30] H.Scott, F.L.Sefarin, P.L.Kronick,Polym. Lett.,8,563-571(1970)
31] A.Klimmek, W.Krieger, Angew. Macromol.Chem.,109/110, 165(1982)
32] R.R.McCaffrey, et.al., Sep.Sci.Techn.,22(2+3), 873-887(1987)
33] P.E.Cassidy, N.C.Fawcett, J.Macromol.Sci.,Revs. Macromol.Chem., C17(2), 209-266(1979)
34] A.H.Frazer, F.T.Wallenberger, J.Polym.Sci.,A,2,1157(1964)
35] A.H.Frazer, F.T.Wallenberger, J.Polym.Sci.,A,2,1181(1964)
36] Y.Iwakura, K.Uno, S.Hara, J.Polym.Sci., A3, 45-54(1965)
37] Y.Iwakura, K.Uno, S.Hara, Makromol. Chem.,95, 248-260(1966)
48] C.H.Abshire, C.S.Marvel, Macromol.Chem.,44-46, 338(1961)
39] M.R.Lilyquist, J.R.Holsten, Belg.Patent 645,926(Monsanto Co)(1964)
40] J.R.Holsten, M.R.Lilyquist, J.Polym.Sci.,A3,3905(1966)
41] M.R.Lilyquist, J.R.Holsten, J.Polym.Sci.,C,19,77(1967)
42] M.R.Lilyquist, J.R.Holsten, U.S.Patent 3,318,728 (Monsanto Co)(1967)

Appendix A

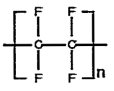
An overview of thermally stable polymers

A Thermosets



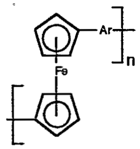
phenol-formaldehyde

B Fluor polymers

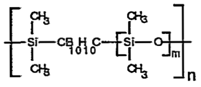


poly-
tetrafluorethylene

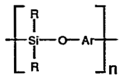
C Organo-metallic and inorganic polymers



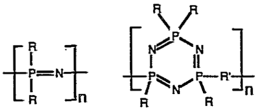
ferrocene polymers



polycarboranes



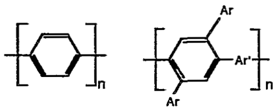
siloxanes



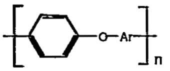
R= -O-Ar, Cl, -O-R, $-NR_2$

polyphosphazenes

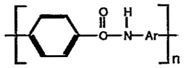
D Aromatic polymers



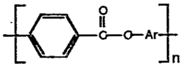
polyphenylenes



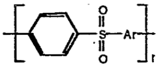
polyethers



polyamids

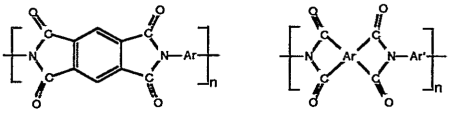


polyesters

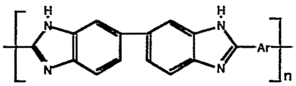


polysulphone

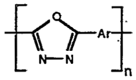
E Heterocyclic polymers



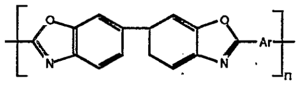
polyimides



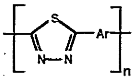
polybenzimidazoles



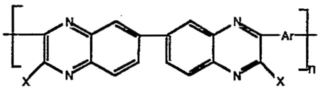
polyoxadiazoles



polybenzoxazoles

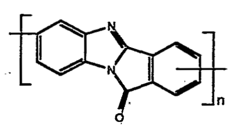


polythiadiazoles

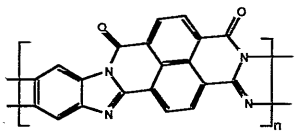


polyquinoxalines

F Ladder polymers



polypyrrone



poly(benzimidazobenzophenantroline)

Chapter 2 The cyclodehydration reaction of polyhydrazides. Part I: kinetic parameters obtained with non-isothermal thermogravimetry

B.Gebben, M.H.V.Mulder, C.A.Smolders

Summary

The thermal conversion reaction of poly-(1,3-phenyl-1,4-phenyl)-hydrazide into poly-(1,3-phenyl-1,4-phenyl)-1,3,4-oxadiazole has been studied using thermogravimetry (TG). For the evaluation of the energy of activation and other kinetic parameters of this cyclodehydration reaction a method developed by Ozawa was used, where polymer samples are heated with different constant heating rates. With this method the energy of activation can be determined accurately as a function of the degree of conversion. In this way a parallel reaction could be observed starting at the end of the non-isothermal conversion process. The polymer was used in two different morphological states, a powder and a film. A slightly higher energy of activation and a considerably higher pre-exponential factor were observed for the film indicating a dependency of the kinetics on the morphological state or on the history of the polymer sample.

2.1 Introduction

Aromatic polyhydrazides can be used as precursor polymers for the preparation of thermally stable and chemically resistant polyoxadiazoles[1,2]. When a polyhydrazide is heated, a cyclodehydration reaction of the hydrazide groups in the polymer results in a polymer with oxadiazole five-rings in the backbone. The reaction scheme is shown in figure 2.1 for poly-(1,3-phenyl-1,4-phenyl)-hydrazide (TIPH) consisting of alternating m- and p-substituted benzene rings in the polymer backbone between the hydrazide groups.

Little attention has been paid in the literature to the kinetics of this conversion reaction. Frazer[3,4] did some kinetic experiments and calculated the kinetic parameters. He performed isothermal treatments with his polymer samples at different temperatures and used oxygen analyses to follow the conversion reaction[3]. To obtain a degree of conversion of 100% it takes prolonged heating times at elevated temperatures, for example 48 hours at 280°C[4]. It is therefore very time consuming to obtain a full set of isotherms.

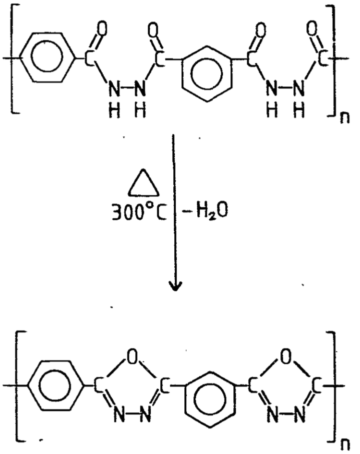


Figure 2.1: ***Reaction scheme for the thermal conversion of poly-(1,3-phenyl-1,4-phenyl)-hydrazide (TIPH) to poly- (1,3-phenyl-1,4-phenyl)-1,3,4-oxadiazole.***

In this chapter dynamical thermogravimetry (TG) is used to follow the conversion of the polyhydrazide TIPH into the corresponding polyoxadiazole. During TG a specimen is heated with a constant heating rate and weighed continuously. Besides the fact that these measurements are less time-consuming than the conventional isothermal procedures they have a further advantage over measurements at constant temperature because in the latter procedure a part of the sample may already start converting while the sample is being heated to the desired temperature. The kinetic parameters are calculated from the thermogravimetric data according to a method developed by Ozawa[5], in which non-isothermal TG experiments are conducted at a series of constant heating rates.
Also a different method, developed by Flynn[13,14] for the calculation of the initial stage energy of activation from a non-isothermal TG experiment, is applied for comparison. Both methods have the advantage over other data evaluation methods in the fact that they do not require an assumption for the rate dependency on the composition of the sample. For heterogeneous reactions like the one treated here a simple model function for this dependency is mostly inadequate in describing the process and can lead to erroneous results[6].

2.2 Theory of conversion kinetics under non-isothermal conditions

The general mathematical model to describe the kinetics of a system undergoing chemical change is

$$d\alpha/dt = f(\alpha).k(T) \qquad (1)$$

where α is the degree of conversion and t is the time.
From eq.(1) it can be seen that the rate of conversion is both a function of the degree of conversion, given by $f(\alpha)$, and a function of temperature, given by $k(T)$.
When a constant heating rate is used, β=dT/dt, eq.(1) becomes

$$d\alpha/dT = f(\alpha).k(T)/\beta \qquad (2)$$

The conversion function $f(\alpha)$ is in general extremely complicated for heterogeneous reactions and specific assumptions for $f(\alpha)$ often lead to erroneous predictions[6]. The two methods discussed below are methods which do not require a specific expression for $f(\alpha)$. Like in most kinetic studies the Arrhenius equation is used for expressing the temperature dependence of k(T). Eq.(2) now becomes

$$d\alpha/dT = f(\alpha).(A/\beta).\exp(-E/RT) \qquad (3)$$

where A is the pre-exponential factor, E is the energy of activation, R is the gas constant and T is the absolute temperature.
Eq.(3) can be written in the following integrated form

$$\int_0^{\alpha} d\alpha/f(\alpha) = (A/\beta).\int_{T_0}^{T} \exp(-E/RT).dT \qquad (4)$$

The left hand side of eq.(4) is the conversion integral $F(\alpha)$, which can not be solved because of the unknown conversion function $f(\alpha)$. The right hand side of eq.(4) contains a temperature integral which cannot be expressed in a closed form[7]. The value of the temperature integral is expressed and tabulated by Doyle[7,8,9] as the following function p :

$$\int_0^{T} \exp(-E/RT).dT = (E/R).p(E/RT) \qquad (5)$$

If the value (E/RT) is larger than 20, p(E/RT) can be approximated by the following formula[10]:

$$\log p(E/RT) = -2.315 - 0.457E/RT \qquad (6)$$

Both Ozawa[5] and Flynn and Wall[12] independently used Doyle's solution (eq.(6)) for their method of data processing, which runs as follows :
Using eq.(6) the solution of eq.(4) becomes

$$\log F(\alpha) = \log(AE/R) - \log \beta - 2.315 - 0.457E/RT \qquad (7)$$

Eq.(7) generates straight lines of slope -0.457E/R by plotting $\log\beta$ against 1/T for iso-fractional conversions and considering A and E to be independent of the applied heating rate. Eq.(7) can be written as

$$\Delta\log\beta/\Delta(T)^{-1} = -0.457E/R \quad [\alpha=\text{constant}] \qquad (8)$$

Thus it is possible to calculate from the slopes of such an Ozawa plot an energy of activation and to follow this energy during conversion.

As $\log[(AE/\beta R).p(E/RT)]$ is equal to $\log F(\alpha)$, according to eq.(7), both A and n, the order of reaction, can be determined by comparing both values for any degree of conversion. This can be done graphically by comparing the experimental master curve with the theoretical master curves for different orders of reaction. The experimental master curve can be obtained by plotting $\log[(E/\beta R).p(E/RT)]$, using the determined E, against α. The experimental master curve has to be shifted along the abscissa with a factor logA to be superposed upon one of the theoretical curves. By comparing the shape of the curves the order n can be determined. The theoretical master curves can be obtained by plotting $\log F(\alpha)$ against α. For the calculation of $\log F(\alpha)$ an expression for the conversion function is absolutely required. The most simple and most applied expression for the conversion function is[7]

$$f(\alpha) = (1-\alpha)^n \qquad (9)$$

where n is the exponential factor, also called the order of reaction.

LogF(α) then becomes respectively

$$\log F(\alpha) = \log[(1-n)^{-1}.(1 - (1-\alpha)^{(1-n)})] \qquad \text{for } n\neq 1 \qquad (10)$$

$$\log F(\alpha) = \log[-\ln(1-\alpha)] \qquad \text{for } n=1 \qquad (11)$$

Another method of calculating an energy of activation without requiring an expression for f(α) was developed by Flynn[13,14], now using the differential form of the kinetic equation. Differentiation of eq.(3) with respect to α gives[13]

$$d(d\alpha/dT)/d\alpha = E/RT^2 + f'(\alpha)/f(\alpha).d\alpha/dT \qquad (12)$$

By applying the mean value theorem, one obtains for $\alpha << 1$

$$(d/d\alpha)(T^2 d\alpha/dT) = E/R + 2T \qquad (0 < \alpha \leq 0.05) \qquad (13)$$

where T and α are values averaged over the intervals ΔT and Δα.
With this method the energy of activation of the initial stage of the reaction can be obtained from the slope of a plot in which $T^2 d\alpha/dT$ is plotted against α.

2.3 Experimental

Materials

Terephtaloylchloride was supplied by Merck and recrystallized from hexane before use. Isophtaloyldihydrazide was prepared according to Frazer[1] from isophtalic acid dimethyl ester and hydrated hydrazine, both supplied by Merck. The isophtaloyldihydrazide was recrystallized from water.
The solvents NMP and DMSO were supplied by Merck and dried with 3Å molecular sieves.

Polyhydrazide syntheses

The polyhydrazide, TIPH, was synthesized according to Frazer[1-5] from isophtaloyldihydrazide and terephtaloylchloride using a low temperature, solution polycondensation reaction in NMP. The reaction temperature was 0°C, the reaction time was 2 hours.

The reaction medium was poured in excess of water and the precipitated polymer was washed several times with water and methanol and dried in an oven at 80°C.
The inherent viscosity measured with an Ubbelohde viscometer using a 0.5 g/100ml DMSO solution at 30°C was η_{inh}=1.3 dl/g.

Sample preparation

The powder samples were taken from the washed and dried polymer and subsequently dried in a N_2-atmosphere at 200°C overnight.
A homogeneous film was cast from a 15 wt.% solution of the washed and dried polymer in DMSO and evaporated for 3 hours at 80°C in a N_2-atmosphere. Subsequently the film was dried at 200°C overnight in a N_2-atmosphere. Samples were cut from the polymer film to fit in the TG sample pans. The initial weight of all samples was about 1.0-1.5 mg.

Thermal analysis

A Perkin-Elmer TGS-2 Thermogravimetrical Analyser in combination with a System 4 Microprocessor Controller and a Model 3700 Thermal Analysis Data Station was used for the TG experiments. During all experiments a N_2-atmosphere was provided by a continuous gas flow of 85 ml/min. The applied constant heating rates were :1, 2, 5, 10, 20 and 50°C/min. Before each run every sample was held isothermally at 200°C for 20 minutes to make sure that the samples were completely freed from adsorbed water. Each run was started from 200°C.

The degree of conversion, α, can be determined from the thermogravimetric weight loss curves by

$$\alpha = (w_o - w_t)/\Delta w_{max} \qquad (14)$$

where w_o and w_t represent the sample weight at the beginning and at time t respectively. The determination of the experimental maximal weight loss from dynamic runs is obstructed by the fact that after 100% conversion no period of constant weight is reached. The maximal weight loss for completion of the reaction, Δw_{max}, was therefore calculated theoretically from the structural formula of the polymer, being 11.0% of w_o, taking into account the non-reactive endgroups.

2.4 Results and discussion

Figure 2.2 shows a complete TG curve for the polyhydrazide powder sample recorded at a heating rate of 20°C/min. Three distinct phases of weight loss can be observed. According to Frazer[3] the first one represents the loss of adsorbed water, the second one represents the loss of water caused by the cyclodehydration dehydration reaction of the hydrazide groups and the third phase of weight loss represents the loss of volatiles caused by the degradation of the polyoxadiazole formed in situ.

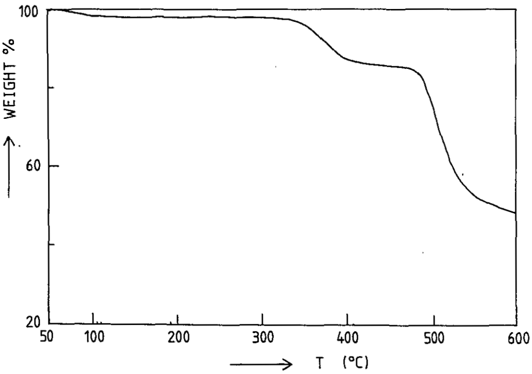


Figure 2.2: Thermo gravimetrical weight loss curve for TIPH recorded at a heating rate of 20 °C/min. in a nitrogen atmosphere.

The results of the thermogravimetry at various heating rates as they are recorded are shown in figure 2.3 and 2.4 for powder and film sample respectively.

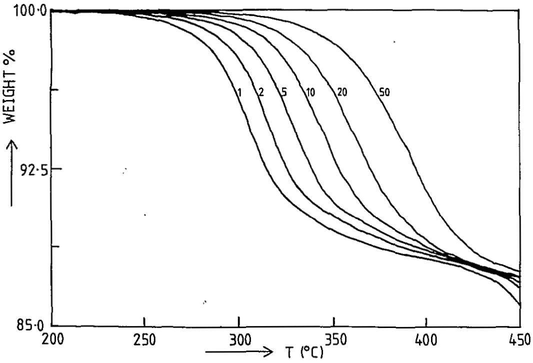


Figure 2.3: Thermogravimetric weight loss curves for a TIPH polymer powder recorded at 6 different heating rates β.

The TG curves shift to higher temperatures with increasing heating rate. Both the shape and the position of the curves in the thermograms are different for both kinds of samples. The curves of the film samples are shifted to less higher temperatures compared to the powder samples and seem to be more steep.

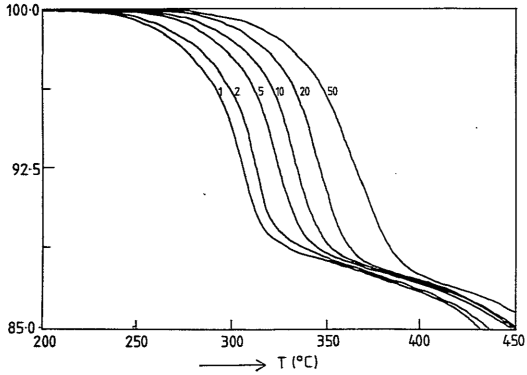


Figure 2.4: Thermogravimetric weight loss curves for a TIPH homogeneous film recorded at 6 different heating rates β.

Both samples show a slight decrease in weight after the cyclisation weight loss, which makes it difficult to distinguish both the end of the cyclisation and the beginning of the degradation process.

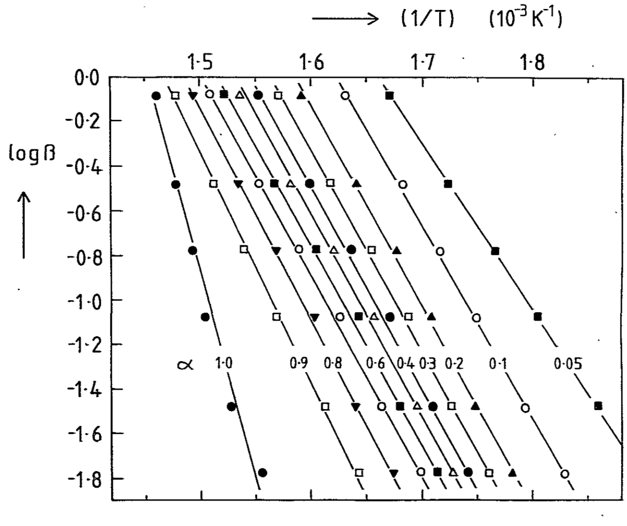


Figure 2.5: Ozawa plot for TIPH in powder form.(β in °C/min)

The Ozawa plots, according to eq.7, are given in figure 2.5 and 2.6 where the logarithms of the heating rates are plotted against the reciprocal of the absolute temperatures for iso-fractional conversions.

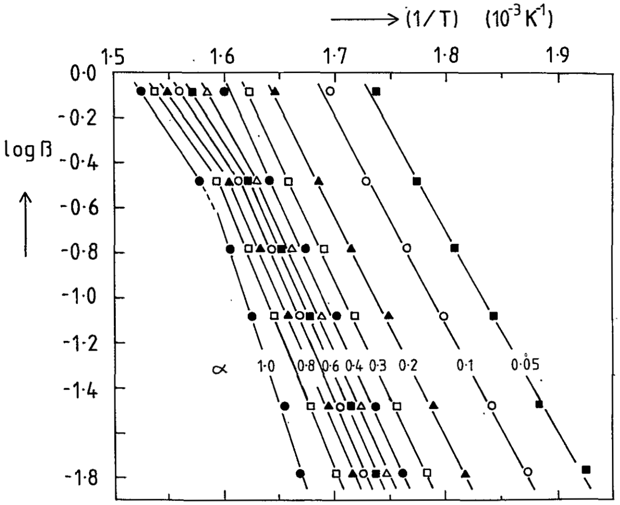


__Figure 2.6:__ Ozawa plot for TIPH in film form. (β in °C/min)

Through the iso-conversional points straight lines can be drawn by the method of least squares. Straight lines are obtained except for the top left hand corner of the film plot. A possible explanation for this deviation may be the fact that at high heating rates the heat flow to the samples can become rate determining. This was already pointed out by Flynn[12] who indicated that the upper limit of meaningful kinetic data lies somewhere between 10 and 60°C/min. depending on the design of the apparatus and the size of the sample.

From the slopes of the iso-conversional lines energies of activation are calculated using eq.8 and presented in table 2.1.The values of both the film and powder samples do agree well. After a slight increase during the first 10% of conversion a constant value is reached of about 164 kJ/mole for the powder samples. This value does not agree with the value obtained by Frazer[3] who found for the same polymer, in powder form, an energy of activation of 211.3 kJ/mol.

α	E_{akt} (kJ/mol) film	powder
0.05	142.4	147.0
0.10	152.5	160.0
0.20	165.9	166.3
0.30	172.2	165.9
0.40	181.4	165.1
0.50	183.5	163.0
0.60	183.1	163.8
0.70	177.7	167.2
0.80	179.8	178.1
0.90	177.7	210.4
1.00	185.6	303.7

Table 2.1: *Energies of activation for the conversion of the polyhydrazide, TIPH, in film and powder form, calculated with the Ozawa method.*

After 70% conversion the energy of activation of the powder sample slowly increases with increasing degree of conversion until a value of about 303.7 kJ/mole is reached at the theoretical point of complete conversion. A steady increase in the energy of activation can be caused by the occurrence of a parallel competitive or independent reaction with a higher energy of activation as was shown by Ozawa[6,15] and Flynn[13]. In this case we are inclined to think of the beginning of some kind of degradation reaction.

The pattern of the film samples is somewhat different. In the beginning a slight increase in the energy of activation from 138 till a mean constant value of 181 kJ/mole is reached at about 40% of conversion which is maintained almost until theoretical completion of the conversion. At this point an increase in the energy of activation appears.

In order to get information about the pre-exponential factor and the order of reaction a method suggested by Ozawa[5] is applied, in which the experimental master curve is compared with the theoretical master curves calculated with some model functions f(α), given by eq.(10) and (11). The method however is not valid in cases of more than one process operating at the same time, therefore only the average energy of activation belonging to the cyclisation reaction has been considered. The experimental master curves for a heating rate of 10°C/min, for both the film and the powdered samples, are compared with theoretical master curves for different orders as is shown in figure 2.7.

It is very difficult to distinguish between the different orders especially in the first part of the curves. The best fit in this case however seems to be a first order reaction although there is a considerable deviation from this curve for the film sample. The determination of the order of the process with this method is not unambiguous. This, however, applies to all other methods where a model relation is tested for linearity, because of the small differences between the values of the individual model functions[7]. Furthermore one has to consider that the function f(α) is a very simple and limited function. For example it cannot describe in general the kinetics of diffusion or nucleation and nuclei growth. Especially for heterogeneous reactions where, in contrast to homogeneous reactions, several processes can be operating at the same time the factor n has a purely empirical meaning.

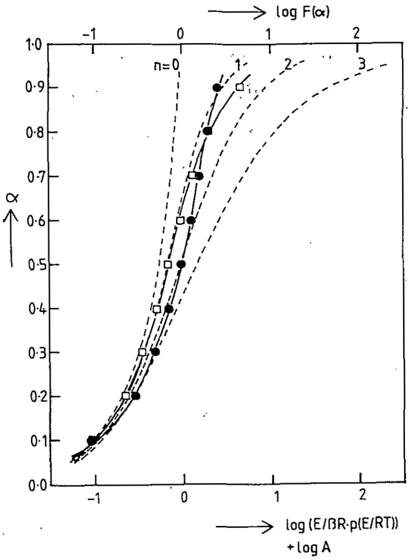


Figure 2.7: Theoretical thermogravimetric master curves (dashed lines) for 4 different reaction orders (n) compared with the experimental thermogravimetric master curves for TIPH both in film (●) and in powdered (□) form. The experimental master curve for the film has been shifted along the abscissa with a factor 13.7, the curve for the powder has been shifted with a factor 11.7.

Much more information can be gained from figure 2.7 about the pre-exponential factor. The pre-exponential factor A is of the order of 10^{12} for the powder and 10^{14} for the film sample. A higher value for the pre-exponential factor causes the TG curves to shift to lower temperatures compared to the curves with lower pre-exponential factors as was shown mathematically by Sestak[16]. This explains the position of the film sample curves compared to the powder sample curves at lower temperatures in the thermogram. Frazer[3] determined for the pre-exponential factor a value in the order of 10^{16} sec^{-1} which is considerably higher than our value. He determined an order of reaction of 1 using the same model function f(α).

The pre-exponential factor can be used in calculating the entropy of activation, $\Delta S^{\ddagger}$, using the following formula

$$A = (ekT/h).\exp(\Delta S^{\ddagger}/R) \qquad (15)$$

where k is the Boltzman constant and h the Planck constant.

Calculation of this entropy of activation leads to a value of -34.4 J/mol.K for the powder, while Frazer finds +58.8 J/mol.K. The difference in the sign of these values is very striking. Because of the positive entropy change Frazer suggested a rate controlling process that involves the breaking of some crystalline structure[3]. A negative entropy change does not allow such an explanation, but indicates a process that involves an increase in order or a decrease in flexibility. This is more likely to be the case in a process where a flexible hydrazide group is converted into a more rigid oxadiazole group.

For the polymer in film form however the entropy of activation becomes about 3.8 J/mole. Compared with the powder this could indicate a more ordered structure in the beginning of the process, so that less entropy loss occurs during the rate controlling process. As this conversion process is not a simple molecular process however, like for example most gas phase reactions, care must be taken in the interpretation of the entropies of activation.

The energies of activation of the initial stages of the reaction are also determined with a different method developed by Flynn[12,13] (eq.(13)), using the same data that was used to obtain the Ozawa plots. For determining these energies of activation the first derivatives of α with respect to the temperature had to be obtained in the first 5% of the conversion process. Because there is much experimental scatter in the thermogravimetric data in this range it is impossible to derive accurate derivatives. Therefore the data (20 points) is used for curve fitting using an exponential function of the form $y=a+b.\exp(c.x)$. The fitted function is then employed to calculate the derivatives. Plots of $T^2 d\alpha/dT$ against α are given in figure 2.8 for both powder and film samples and for some different heating rates showing straight lines in all cases. The calculated energies of activation are given in table 2.2.

β (°C/min)	E_{akt}(kJ/mole) film	 powder
1.0	139.9	118.9
10.0	142.0	112.1

Table 2.2: Initial stage energies of activation determined by the method of Flynn for $\alpha < 0.05$.

Although the accuracy of this method is less than for the Ozawa method, because of the determination of the reaction rates, the determined energies of about 113-143 kJ/mole in the first 5% of conversion agree much better with those obtained by the Ozawa method at α=0.05, being about 143-147 kJ/mole, than with those obtained by Frazer. The fact that two different mathematical methods for obtaining the energy of activation, one based on the integral form and the other based on the differential form of the rate equation, give comparable results indicates the correctness and reliability of these methods[14].

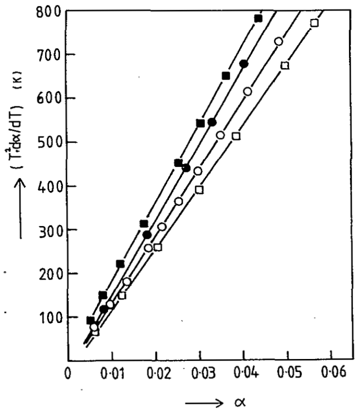


Figure 2.8: $T^2 d\alpha/dT$ plotted against α for the first 6% of conversion according to eq.(13) for the powder sample at a heating rate of 1 (○) and 10 °C/min (□) and for the film sample at a heating rate of 1 (●) and 10 °C/min.(■).

For the apparent differences between our results and Frazer's there are some possible explanations. First there is the difference in analytical technique used to follow the degree of conversion. Frazer used oxygen analysis while we used a gravimetrical technique of which the latter is in our opinion the more accurate one. A second explanation may be the question of the correctness of the mathematical treatment of the data derived from an isothermal or a dynamical process. MacCallum[16] raised the question whether kinetic parameters obtained in non-isothermal procedures are the same as those obtained by conventional isothermal methods and considers isothermal measurements absolutely necessary in evaluating the 'true' kinetic parameters. At least both methods have to be compared. A last explanation may be that the rate controlling process in the conversion of the polyhydrazide is different whether the process is performed isothermally or dynamically.

In the following chapter isothermal gravimetrical analysis with the same polymer will be described and discussed. The results will be compared with the results derived with the non-isothermal measurements given here. Attention will also be focused on both types of morphology of the polymer sample, film and powder, to investigate whether there is an essential difference in kinetics or not. From these results a mechanism for the conversion reaction will be deduced.

2.5 Conclusions

The Ozawa method for calculating the energy of activation from non-isothermal TG runs at different heating rates proves to be an accurate method for obtaining the energy of activation of the thermal conversion process of a polyhydrazide into a polyoxadiazole. The energy of activation in the initial part of the conversion process agrees well when determined with two different evaluation methods.

With the Ozawa method it is possible to follow the energy of activation during the entire conversion process. In this way the appearance of a parallel independent reaction starting at the end of the conversion process was indicated.

The determination of the pre-exponential factor and the order of reaction is less reliable as it needs a model describing the dependency of the reaction rate upon the composition of the sample.

Although the determined energies of activation for the polyhydrazide in powder form and in film form do agree the latter does have a considerable higher pre-exponential factor indicating a dependency of the kinetics on the morphological form or the history of the polymer sample.

2.6 References

1] A.H.Frazer, F.T.Wallenberger, J.Polym.Sci.,A2,1137-1156(1964)
2] A.H.Frazer, W.Sweeny, F.T.Wallenberger, J.Polym.Sci.,A2,1157-1169 (1964)
3] A.H.Frazer, I.M.Sarasohn, J.Polym.Sci.,A1,4,1649(1966)
4] A.H.Frazer, D.R.Wilson, Appl.Polym.Symp.9(1969)
5] T.Ozawa, Bull.Chem.Soc.Japan,38,1881(1965)
6] T.Ozawa, J.Therm.Anal.,7,601(1973)
7] J.Sestak, V.Savata, W.W.Wendland, Thermochim.Acta,7,333-556(1973)
8] C.D.Doyle, J.Appl.Polym.Sci.,5,285(1961)
9] M.Szako, J.Phys.Chem.,72,2406(1968)
10] C.D.Doyle, J.Appl.Polym.Sci.,6,639(1962)
11] J.R.MacCallum, J.Tanner, Nature,vol 225,1127(1970)
12] J.H.Flynn, L.A.Wall, J.Polym.Sci.,B4,323(1966)
13] J.H.Flynn, W.J.Plummer, L.E.Smith, ACS Polym.Prep.,18.1.757(1977)
14] J.H.Flynn, L.A.Wall, Polym.Lett.,5,191(I967)
15] T.Ozawa, J.Therm.Anal.,9,217(1976)
16] J.H.Flynn, Thermochim.Acta, 37,225-238(1980)
17] J.Sestak, Talanta,13(1966)567

Chapter 3 The cyclodehydration reaction of polyhydrazides. Part II: kinetic parameters obtained from isothermal thermogravimetry

B.Gebben, M.H.V.Mulder, C.A.Smolders

Summary

The kinetics of the thermal conversion reaction of poly-(1,3-phenyl-1,4-phenyl)-hydrazide into poly-(1,3-phenyl-1,4-phenyl)-1,3,4-oxadiazole have been studied with isothermal thermogravimetry in continuation of a study with non-isothermal thermogravimetry described in the previous chapter. Although the isothermal measurements are much more time consuming they provide some new information and insight about the cyclo dehydration reaction of the polyhydrazide. The physical state of the sample, rubbery or glassy, seems to influence the kinetics considerably. The kinetic parameters determined with the isothermal method for the polymer in its glassy state agree well with the parameters derived from the previously reported non-isothermal measurements, while the kinetic parameters for the expected rubbery state differ considerably.
The morphological state or the history of the polymer has also a considerable influence on the kinetics of the isothermal conversion process. The powder form of the polymer has a much lower isothermal conversion rate than the film form.

3.1 Introduction

In the previous chapter the kinetics of the cyclisation reaction of polyhydrazides to polyoxadiazoles was studied with non-isothermal thermogravimetry. Subject to the study was terephtaloyl-isophtaloyl- polyhydrazide (TIPH) consisting of alternating m- and p-substituted benzene rings in the polymer backbone between the hydrazide groups.
The kinetic parameters obtained did not agree with results Frazer[2] obtained with some isothermal measurements. One of the possible reasons for these deviations is that the difference is caused by the method of evaluation. MacCallum started a discussion about this point[3] and stated that isothermal measurements were necessary for obtaining the real kinetic parameters. In general it should be advisable to use more than one method for evaluating the kinetic parameters[4] especially for the more complex reactions.
A disadvantage of isothermal measurements is that they are very time consuming because it

takes long periods of time to obtain a full set of isotherms. Especially for the thermal conversion of the polyhydrazide used this takes a long time[5,6]. Frazer did perform some isothermal thermogravimetrical measurements to determine the order of the reaction but he did not use the data any further for a kinetic evaluation[7].

In the reported non-isothermal measurements a slight difference was observed between the polymer in powder form and the polymer in film form. The energy of activation was in the same order of magnitude, 164 kJ/mole for the powder and 181 kJ/mole for the film sample but the pre-exponential factor differed by a factor of 100. The polymer in film form had a much higher pre-exponential factor resulting in thermogravimetrical curves positioned at lower temperatures compared with the corresponding polymer in powder form.

In this chapter isothermal thermogravimetry experiments will be discussed employing the same polymer that was used during the non-isothermal experiments, the above mentioned polyhydrazide TIPH. Two morphologies of the polymer will be considered, the powder form, this is the washed and dried polymerization product, and a homogeneous film obtained from a TIPH solution in DMSO by evaporating the solvent.

3.2 Experimental

Materials and sample preparation

Materials and sample preparation were described in the previous chapter (Part I)[1]. For both the isothermal and non-isothermal experiments the samples were taken from the same batch to be sure that the samples had the same history. Before the measurements the samples were dried at 200°C overnight.

Thermogravimetric analysis

A Perkin-Elmer TGS-2 Thermogravimetric Analyser in combination with a System 4 Microprocessor Controller and a Kipp recorder was used for the isothermal thermogravimetry. During all experiments a nitrogen atmosphere was provided by a continuous flow of nitrogen gas of 85 ml/min. All the samples were held isothermally at 200°C for 20 minutes to remove adsorbed water. Then the sample was heated with a heating rate of 200°C/min. to the desired temperature. The point t=0 was taken at the moment where the first weight loss was observed. From measurements of the exact

temperature value near the samples a time interval of about 2 minutes was observed after t=0 before the temperature reached its final constant value.
For calculation of the degree of conversion from the thermogravimetric data the theoretical value for the maximum weight loss was used, being 11.0 % of the initial dry weight.

Differential scanning calorimetry
A Perkin Elmer DSC Differential Scanning Calorimeter in combination with a System 4 Microprocessor Controller and a Thermal Analysis Data Station Model 3700 was used for DSC measurements. A nitrogen purge gas and a heating rate of 20°C/min. was used.

3.3 Evaluation of the kinetic data

For the evaluation of the kinetic data the following rate equation is used

$$r = d\alpha/dt = k(T)\cdot f(\alpha) \qquad (1)$$

where the reaction rate r is described by k(T), the rate constant which is a function of temperature only, and $f(\alpha)$, which is a function of the degree of conversion α only.
Upon integration eq.(1) yields

$$\int_0^{\alpha} d\alpha/f(\alpha) = g(\alpha) = k(T)\cdot t \qquad (2)$$

The linear dependence of $g(\alpha)$ on time t makes it possible to find by way of trial and error the function which best fits the experimental data and to determine the rate constant k(T).
For investigation of the mechanism of conversion we use a model relation for the conversion function $f(\alpha)$ in the most simple form:

$$f(\alpha) = (1 - \alpha)^n \qquad (3)$$

where n is the exponential factor, sometimes called the order of reaction. Although this is a very simplified model relation it may serve well as preliminary information to the reaction kinetics and furthermore it is suitable for observing changes in the kinetic process[4]. The following functions $g(\alpha)$ are obtained for n being respectively 0, 1, 2 and 3:

$$g(\alpha) = \alpha \qquad [n=0] \qquad (4)$$

$$g(\alpha) = -\ln(1-\alpha) \qquad [n=1] \qquad (5)$$

$$g(\alpha) = 1/(1-\alpha) - 1 \qquad [n=2] \qquad (6)$$

$$g(\alpha) = 0.5\cdot(1-\alpha)^{-2} - 0.5 \qquad [n=3] \qquad (7)$$

For k(T) the Arrhenius relation is used:

$$k(T) = A\exp(-E/RT) \qquad (8)$$

Both the pre-exponential factor A and the energy of activation E can be determined by plotting ln k(T) against the reciprocal absolute temperature (1/T).

3.4 Results and discussion

Figure 3.1 shows some isotherms in a zero order plot for both the polymer powder and the film.

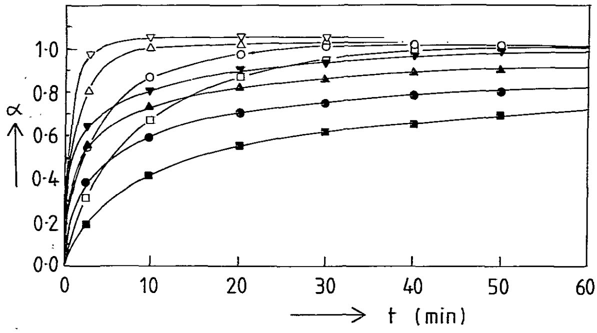


Figure 3.1: Zero order plot for the thermal conversion reaction of the polyhydrazide TIPH in powder form with the following isortherms: 268.8 °C (■), 278.5 °C (●), 282.8 °C (▲), 290.0 °C (▼) and in film form with the following isotherms 259.5 °C (□), 274.3 °C (○), 282.6 °C (△) and 290.2 °C (▽).

The plot indicates the prolonged heating times needed to obtain completion of the conversion and a striking difference can be observed between both morphologies of the polymer samples. The conversion rate of the homogeneous films is much higher than that of the powder and also the shape of the isotherms is different. Especially the shape of the powder isotherms is remarkable in its dependency on the temperature. After a high initial rate of conversion it drops suddenly to a much lower rate at a moment that seems to be depending on the temperature. The film isotherms show a more gradual decrease in the conversion rate.

First and second order plots of the data for the polymer in the powdered form are presented in the figures 3.2 and 3.3 to test the different functions g(α) for linearity with time.

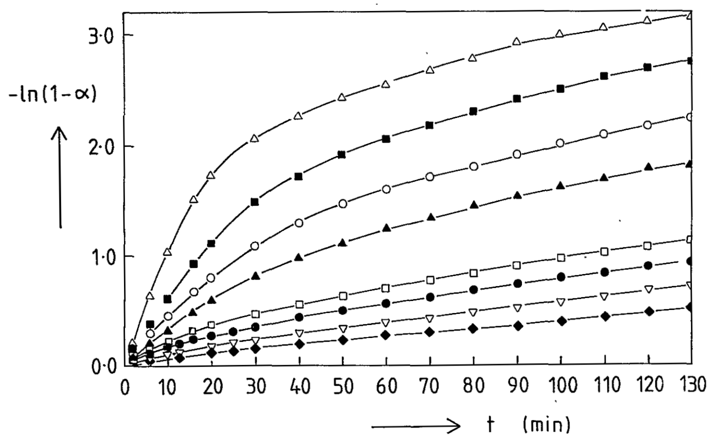


Figure 3.2: *First order plot for the polyhydrazide in powder form with the following isotherms: 306.7 ℃ (Δ). 299.8 ℃ (■), 290.0 ℃ (o), 282.8 ℃ (▲), 278.5 ℃ (□), 272.7 ℃(●), 268.8 ℃ (∇), 265.0 ℃ (♦)*

Only the first 130 minutes of the conversion process are considered in these figures since this period represents the most interesting part of the isotherms.

Although it is difficult to discriminate between both orders the best linearity is obtained for second order plots, except for the break in the slopes of the isotherms. Frazer[7] also found the best fit for the second order function but he did not observe a break in his isotherms. Frazer plotted his isotherms for a much more expanded time scale so that a possible break-point or curvature may have disappeared in the inaccuracy of the plot. Very accurate measurements and precise plotting of the data in our case shows a break-point in the isotherms from high slopes/high reaction rates to smaller slopes/lower reaction rates.

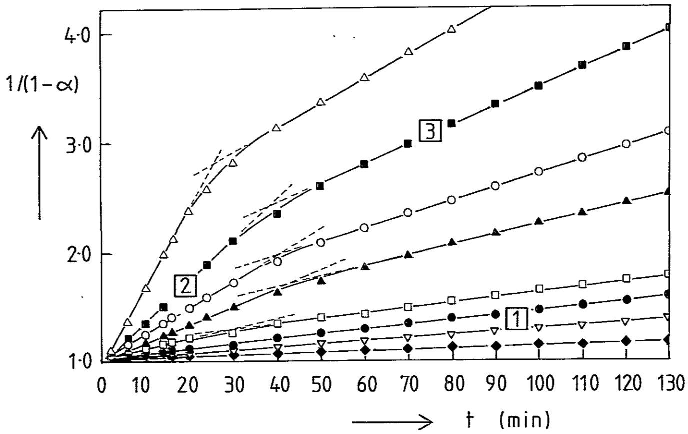


Figure 3.3: Second order plot for the polyhydrazide in powder form with the following isotherms: 306.7 °C (Δ), 299.8 °C (■), 290.0 °C (o), 282.8 °C (▲), 278.5 °C (□), 272.7 °C(●), 268.8 °C(∇), 265.0 °C (◆).

The position of the points of intersection of the slopes composing each isotherm is represented in figure 3.4 where the degree of conversion at the break-point is plotted against the temperature. This figure shows that the higher the conversion temperature the higher the degree of conversion where the break-point occurs.

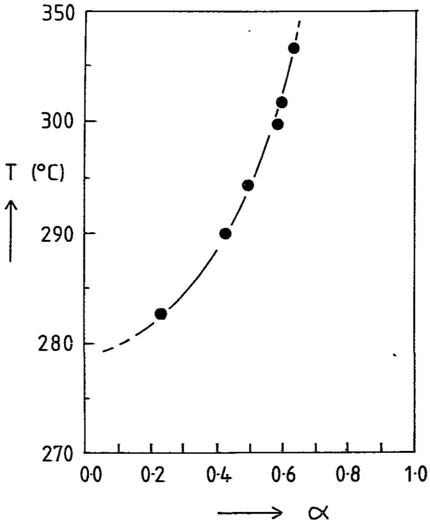


Figure 3.4: Temperature plotted against the degree of conversion belonging to the points of intersection of the second order isotherms belonging to the powder

Both facts, change of slope from high to low values and break-point dependent on the conversion temperature, lead to the assumption that the break-point represents a kind of transition in the polymer sample, possibly the rubber-glass transition. The conversion starts at a temperature above the T_g of the initial polyhydrazide, in the rubbery state, with a high conversion rate. Then due to the conversion of the flexible hydrazide groups into the more rigid oxadiazole rings the T_g increases and at a given moment it becomes higher than the applied isothermal temperature. The polymer sample thus undergoes a rubber-glass transition and attains its glassy state, where the conversion rate is slowed down.

If this assumption is correct figure 3.4 can be considered to represent the glass transition temperature as a function of the degree of conversion of the initial polyhydrazide. Extrapolation of this curve to $\alpha=0$ gives a value of about 278°C for the T_g of the initial polyhydrazide, extrapolation to $\alpha=1$ gives the T_g of the corresponding polyoxadiazole being higher than 400°C.

Figure 3.5 shows the DSC thermograms for the polyhydrazide powder and film and for their corresponding polyoxadiazoles recorded at a heating rate of 20°C/min.

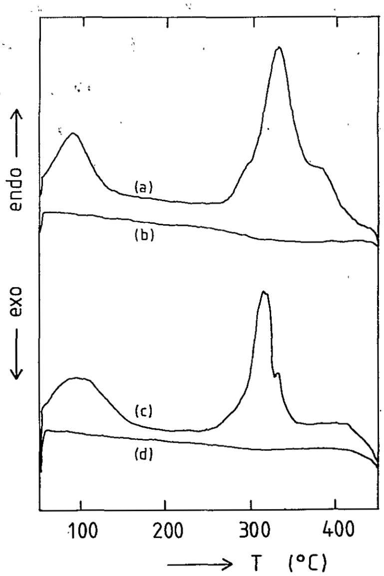


Figure 3.5: DSC thermograms for the polyhydrazide, TIPH, as a powder (a) and its corresponding polyoxadiazole (b) and for the polymer as a homogeneous film (c) and its corresponding polyoxadiazole film (d).

In the powder thermogram two endothermic peaks can be observed, the first one at about

100°C most likely represents the loss of absorbed water, the second one from about 300°C to 400°C represents the conversion process. There seems to be a shoulder on the left-hand branch of this conversion peak which might represent a glass transition but a glass transition is not clearly observed possibly because it coincides with the broad endothermic peak or it is not there at all. Also a shoulder or a peak at the right-hand branch of the conversion peak is observed, which possibly represents the parallel reaction, also observed with the Ozawa method (chapter 2), starting at the end of the non-isothermal conversion process.

Also for the polyoxadiazole one does not observe a glass transition in a DSC thermogram before the polymer starts to decompose at about 450°C. This is in agreement with the literature[2,6]. Because all the usual techniques used for T_g determination require a temperature program, the measurement will always be disturbed by the conversion reaction. These isothermal measurements could possibly represent a method to determine the glass transition temperature despite the disturbing conversion process.

If the isothermal conversion temperature is programmed below the T_g of the initial polyhydrazide the polymer is bound to stay in the glassy state throughout the process and no glass transition should occur. As can be seen in figure 3.3 such a break is not observed in the isotherms below 280°C. Figure 3.3 can now be divided in 3 different areas, where area 1 represents the isotherms below the expected initial T_g, areas 2 and 3 the isotherms above the initial T_g respectively before and after the glass transition point.

Table 3.1 represents the kinetic parameters calculated from the isothermal data for the different areas. For the conversion of the powder the energy of activation in area 2, the rubbery state, being 244 kJ/mole is higher than the energy of activation in areas 3 and 1, the expected glassy states, being respectively 172 and 160 kJ/mole. The latter values agree well with that obtained from the non-isothermal method, being 165.1 kJ/mole. Also the determined pre-exponential factor in area 3 agrees much better with the previously determined value obtained with the non-isothermal method, although the difference is still a factor in the order of 10.

The question now is raised about the physical state (rubber or glass) of the polymer samples during the non-isothermal measurements presented in chapter 2. Comparing the energies of activation, if they are reliable, one would assume the polymer to be in the glassy state when performing non-isothermal conversions.

Isothermal method:			powder			film		
area	conversion temperature	expected state	n	E	A	n	E	A
1	T < 278 °C	glassy	3	160	$2*10^{10}$	3	193	$2*10^{17}$
2	T > 278 °C	rubbery	2	244	$2*10^{18}$	2	244	$2*10^{19}$
3	T > 278 °C	glassy	2	172	$2*10^{11}$	1	294	$8*10^{23}$
Non-isothermal Ozawa method:				165.0	$5*10^{11}$		182.3	$5*10^{13}$

Table 3.1: *Kinetic parameters for the conversion of the polyhydrazide TIPH, in powder and film form, determined with isothermal thermogravimetric measurements. E in kJ/mole, A in sec*$^{-1}$.

At the start of a non-isothermal run at a temperature of 200°C the polymer is almost certainly in its glassy state. At the end of the run at a temperature of 450°C the converted polymer is also in its glassy state. During the non-isothermal conversion process no sudden changes in the energy of activation were observed in the Ozawa plots, using heating rates from 1 till 50°C/min. For these reasons it is reasonable to assume the polymer to be in the glassy state throughout the whole non-isothermal conversion process. This also means that during heating rates up to 50°C/min the rate of increase in T_g is the same or higher than the heating rate. It is likely that the sample is continuously just below its glass transition temperature in a transition state, where the movements of the polymer chain segments do not contribute to a glass-rubber transition but result in a conversion of a hydrazide group.

Applying a heating rate of 200°C/min. however, which is done in the present chapter to reach the isothermal temperatures as fast as possible, it is assumed that the polymer undergoes a glass-rubber transition so that the polymer is in its rubbery state when the isothermal process starts. According to this point of view somewhere between heating rates of 50 and 200°C/min. a glass-rubber transition should be present during non-isothermal methods.

Now changing to the other morphological state of the polymer, the film, first and second order reaction plots of the film samples are represented in figures 3.6 and 3.7 respectively.

Both the orders and the shapes of the isotherms are quite different compared to the powder samples. Instead of a break-point in the second order isotherms the curves show a better linearity in a first order plot from a certain point. Although the second order plot here differs from the plot for the powder the same subdivision into three areas has been made analogous to the powder case.

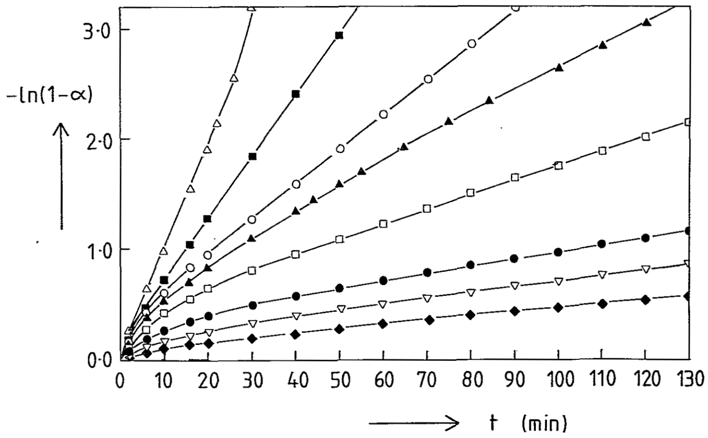


Figure 3.6: First order plot for the polyhydrazide in film form with the following isotherms: 305.2 ℃ (Δ), 300.1 ℃ (■), 290.2 ℃ (o), 282.6 ℃ (▲), 278.6 ℃ ( ), 270.0 ℃ (●), 260.2 ℃ (∇), 255.2 ℃ (♦).

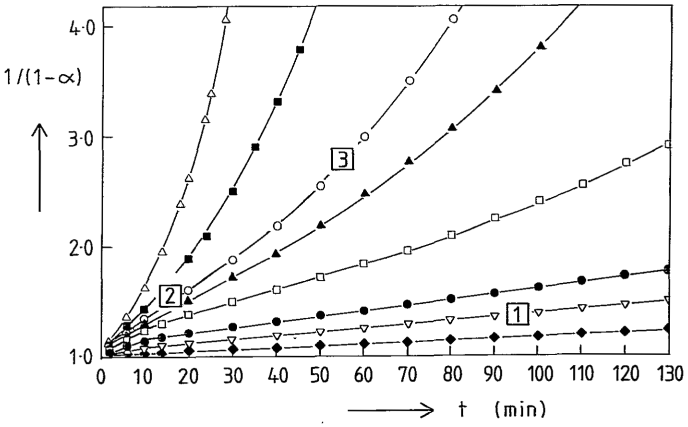


Figure 3.7: Second order plot for the polyhydrazide in film form with the following isotherms: 305.2 ℃ (Δ), 300.1 ℃ (■), 290.2 ℃ (o), 282.6 ℃ (▲), 278.6 ℃ (□), 270.0 ℃ (●), 260.2 ℃ (∇), 255.2 ℃ (♦).

The calculated kinetic parameters are also given in table 3.1. For the areas 1 and 2 there is a more or less good agreement with the powder, except for the pre-exponential factor of the film in area 1. The kinetic parameters in area 3 however deviate strongly from the parameters determined for the powder and also from the non-isothermal measurements. Both the energy of activation and the pre-exponential factor for area 3 are considerably higher than the previously obtained values. Although these parameter calculations from the isothermal data are not so accurate as compared to those from the non-isothermal method, it looks as if some totally different process is controlling the conversion rate in the polyhydrazide film samples during an isothermal conversion after the glass transition has occurred. This implies that the history and/or the morphological state of the polymer sample determines the kinetics of the conversion process.

Looking more closely at the isotherms of area 1, for both powder and film, it seems that the best linearity is even obtained with a third order. Figures 3.8 and 3.9 represent the third order plots for the isotherms below the expected glass transition temperature.

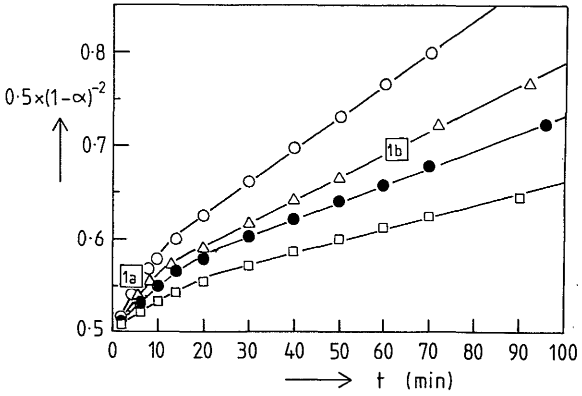


Figure 3.8: Third order plot for the polyhydrazide in powder form with the following isotherms: 260.4 °C (□), 264.7 °C (●), 269.9 °C (Δ), 274.5 °C (o)

It can be seen from these plots that during the first 10-20 min (area 1a) the slopes are somewhat higher than after this period (area 1b) when a good linear behaviour is obtained. This break-point however represents a different transition than the transition from area 2 to 3 in figure 3.3 because the energies of activation before this break-point are in the order of 118 kJ/mole, which is much lower than the energy of activation found for area 2, the rubber area. The value of 118 kJ/mole however agrees well with the energy of activation determined during the first 5% of the non-isothermal conversion. This slightly lower energy of activation in the very beginning of the conversion process is possibly caused by a simultaneous loss of traces of solvent from the polymer matrix as was already pointed out in part I.

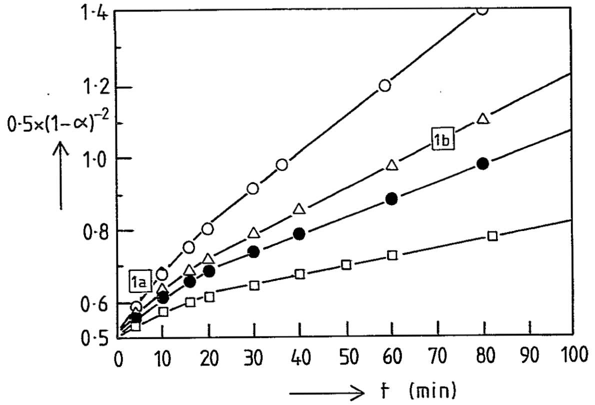


Figure 3.9: *Third order plot for the polyhydrazide in film form with the following isotherms: 254.6 ℃ (□), 259.5 ℃ (●), 264.6 ℃ (Δ), 269.7 ℃ (o)*

It seems that the determined order of the reaction decreases during the conversion process. In the beginning the order is high, being 3 or 2, and then it decreases until it has become almost zero at the end of the conversion process as can be seen from figure 3.1. One has to be careful not to give too much significance to the determined orders of reaction because for complicated heterogeneous reactions, like the one we are dealing with here, in contrast with most homogeneous reactions a simplified model relation like eq.(3) is mostly inadequate to describe the process. In literature for example for other processes even negative orders have been observed[4]. Frazer[7] tried to explain the second order by some kind of interaction between two reacting hydrazide groups. He suggested hydrogen bonding. This suggestion fitted well with his earlier assumption that the rate controlling process was the breaking out of some crystalline order[2].

In contrast to Frazer's approach we would like to propose an alternative mechanism. Another explanation for an order higher than 1 can be the fact that the hydrazide groups have a mutual interaction because they are part of the same polymer chain. Looking at the polymer structure more closely it can be seen that the conformation of the hydrazide group does not have to be in the "folded" conformation, where the carbonyl oxygen groups are opposite each other ,which is mostly presented in literature[5,6] (see chapter 2, figure 2.1). In fact there are many different conformations possible. One of them is illustrated in figure 3.10, which is called the "extended" conformation[6], where the carbonyl oxygen groups of the hydrazide group are turned away from each other. For a ring closure reaction the folded conformation seems favourable and can be attained from the extended conformation by a rotation of the chain round the N-N-axis of the hydrazide group. Such a rotation from the extended to the folded conformation implies the rest of the chain to translate or rotate as well, sometimes to a great extent. As figure 3.10 illustrates such a rotation can bring two hydrazide groups, because of their interaction, in the favourable conformation for ring closure with a kind of crankshaft movement.

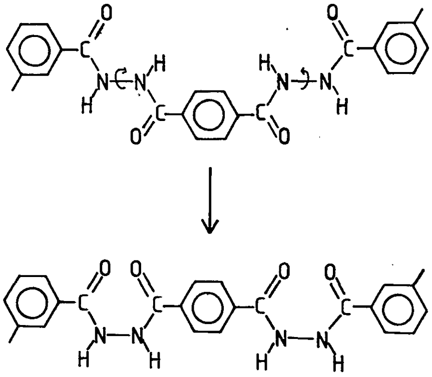


Figure 3.10: Schematic representation of a part from the main chain of the polyhydrazide TIPH. The arrows represent a coupled rotation around the N-N axes.

The proposed rate controlling mechanism for the conversion process derived from this is a rotation or movement of polyhydrazide chain segments. With this mechanism the differences between the reaction rates in the rubbery and glassy state can be explained. Also the differences between the two morphological states can, to some extent, be explained with a difference in polymer conformation. This difference is probably caused by the history of the polymer sample. It is not unreasonable to assume that the different preparation processes of the samples induce different conformations of the polymer chains with respect to the required conversion. Further research is necessary to explain these differences. In the following chapter this will be discussed in more detail.

3.5 Conclusion

In addition to the non-isothermal measurements, given in chapter 2, the isothermal measurements described in this chapter provide some new information and insight about the reaction kinetics of the thermal cyclisation reaction of a polyhydrazide. For example the physical state of the polymer, rubbery or glassy, seems to be relevant. A considerable difference in the determined kinetic parameters is observed between both expected physical states, with a distinct transition at the expected glass transition temperature of the polymer. The kinetic parameters determined with the isothermal method for the polymer in its glassy state agree well with the parameters derived from the non-isothermal measurements.

The difference in the observed kinetics between the polymer in powder and in film form is much more pronounced with these isothermal conversions as it was with the previously reported non-isothermal conversions. The powder form of the polymer has a much lower isothermal conversion rate than a homogeneous film of the same polymer, showing a dependency of the kinetics on the morphological state or the history of the polymer sample. As a mechanism for the rate controlling process in the cyclodehydration process of the polyhydrazide a rotation of segments in the polyhydrazide chain is proposed.

3.6 References

1] B.Gebben, M.H.V.Mulder, C.A.Smolders, J.Polym. Sci., 26 (1988)
2] A.H.Frazer, I.M.Sarasohn, J.Polym.Sci.,A1,4,1649(1966)
3] J.R.MacCallum, J.Tanner, Nature, vol 225, 1127(1970)
4] J.Sestak, V.Savata, W.W.Wendland, Thermochim.Acta, 7, 333-556(1973)
5] A.H.Frazer, F.T.Wallenberger, J.Polym.Sci.,A2,1137-1156(1964)
6] A.H.Frazer, W.Sweeny, F.T.Wallenberger, J.polym.Sci.,A2,1157-1169(1964)
7] A.H.Frazer, D.R.Wilson, Appl.Polym.Symp.9(1969)

Chapter 4 The cyclodehydration reaction of polyhydrazides. Part III: Influence of the sample history.

B.Gebben, E.Rolevink, M.H.V.Mulder, C.A.Smolders

Summary

The influence of preparation history upon the thermal cyclodehydration reaction of polyhydrazide samples has been investigated. Solid polyhydrazide samples were prepared from DMSO solutions using the phase-inversion technique. Significant differences in conversion rates were observed between samples prepared by non-solvent immersion precipitation and by evaporation of solvent. It appeared that contact with the non-solvent water during the sample preparation process has considerable influence on the conversion rate. Not only does the immersion in and washing with water lead to a better removal of the solvent also the pH of the water determines the rate of conversion. A distinct change in the conversion rate is found for washing water at a pH of 7. Basic washing solutions showing lower conversion rates than acid ones. A mechanism explaining these phenomena is proposed.

4.1 Introduction

In the previous chapters the kinetics of the thermal cyclodehydration reaction of polyhydrazide in the solid state has been studied using both non-isothermal and isothermal thermogravimetry. One of the results from these studies was the dependence of the reaction kinetics on the history of the polyhydrazide sample. A striking difference was observed between the kinetics of the powder, being the washed and dried polycondensation product, and a homogeneous film prepared from the same polymer. The film, prepared from the powder by solution casting and evaporation of the solvent, showed considerably higher conversion rates than the original powder. From the kinetics determined for the cyclodehydration reaction it was previously concluded that the rate determining step in the whole process was an internal rotation of chain segments towards more favourable chain conformations for the ring closure reaction. The expected reaction scheme for a hydrazide group is presented in figure 4.1.

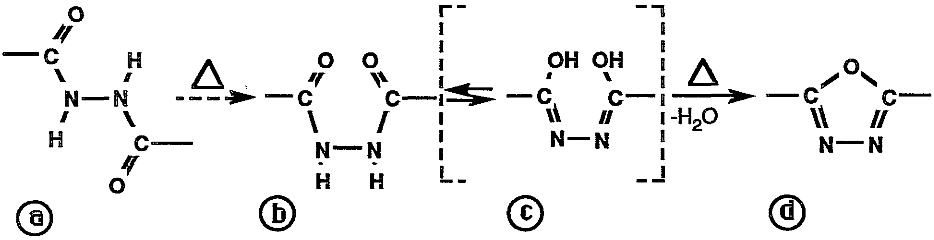


Figure 4.1: The expected reaction scheme for the thermal cyclodehydration reaction of the hydrazide group

The transition of the extended form **a** to the folded form **b**, being rotational isomers, is proposed to be the rate determining step, unless the initial conformation is already in the folded form. However the folded conformation is believed to be less favourable because of the expected oxygen repulsion. Many different conformations are possible by rotation of the hydrazide group round the N-N axis, form **a** and **b** being the extreme conformations. The transition from structure **b** to **c**, being the keto-enol tautomers, is suggested by Korshak[2]. This transition is believed to be necessary for the final dehydration reaction because this reaction very probably proceeds through a transition state close to the structure of the enol form (form **c**).

In the context of the rate determining **a** to **b** transition the observed difference in kinetics between powder and film was explained in terms of a difference in initial chain conformation. Both Frazer[1] and Korshak[2] noticed a considerable influence of orientation upon the subsequent conversion rate of their polyhydrazide fibers. The extended conformation (isomer **a**) is believed to be present preferentially in the more oriented (drawn) fibers, causing a slower conversion rate of these fibers compared to the less oriented fibers. These observations therefore strongly support the proposed reaction mechanism.

A possible difference in initial chain conformation between powder and film should be related with the process by which the solid polymer samples are prepared. Both samples are prepared from solution using a phase-inversion technique. Several factors within this process can be determining, for example the composition of the starting polymer solution, possible orientation during shaping and/or solidification, the kind of phase-inversion process, the use of a non-solvent or not, the kind of non-solvent and the rate at which the phase-inversion process proceeds.

In this chapter the determining factor or factors in the sample preparation process will be elucidated using isothermal thermogravimetry on polymer samples prepared in different ways. For comparison of the kinetics isothermal conversions at a temperature of 290°C over a period of 1 hour were followed. The polyhydrazide used for these experiments was poly-(1,3-phenyl-1,4-phenyl)-hydrazide (TIPH) as in the previous chapters. The results are used to further unravel the conversion mechanism.

4.2 Experimental

Materials

Materials and polymer preparation were described in chapter 2. Three new batches of poly-(1,3-phenyl-1,4-phenyl)-hydrazide (TIPH), TIPH1, 2 and 3 respectively were used for the experiments described in this chapter. (TIPH1: η_{inh}=1.16 dl/g, TIPH2: η_{inh}=0.92 dl/g and TIPH3: η_{inh}= 1.00 dl/g)

Water of a high purity was obtained by hyperfiltration of demineralized water using hollosep membranes (Toyobo). Methanol, analysis grade, was obtained by Merck and used as received.

Sample preparation

The original powder samples were prepared by pouring the polycondensation reaction mixture (NMP with LiCl) in a large excess of water under continuous stirring after which the precipitated polymer was washed several times with water and dried.

Films were prepared from a 6-15 wt.% solution of the polymer in DMSO by casting the solution on a glass plate using a casting knife with a slit-height of 0.20 mm. Homogeneous films were obtained by evaporation of the solvent in a N_2-atmosphere at room temperature for at least 12 hours followed by an additional drying procedure at 150°C and reduced pressure for 16 hours. Asymmetric, porous membranes were obtained by immersing the casted films in a water bath at room temperature, after which the films received the same washing treatment as the powder samples.

Additional washing treatments were performed by soaking the samples in a large excess of the washing medium for 2 days. The pH value of the washing water was measured using a glass electrode at the moment before the polymer sample was removed from the water.

Thermogravimetric analysis

A Perkin-Elmer TGS-2 Thermogravimetric Analyser in combination with a system 4 Microprocessor Controller and a Thermal analysis Data Station Model 3700 was used for the isothermal thermogravimetry. During these experiments a nitrogen atmosphere was provided by a continuous flow of nitrogen gas through the sample holder of 85 ml/min. All samples were held isothermally at 200°C for 20 minutes to remove adsorbed water till a constant weight was reached. Then the sample was heated with a heating rate of 200°C/min. to 290°C and kept at that temperature. The actual value, measured with a thermocouple near the sample was 290.3 ± 0.2°C for all samples. The point t=0 was taken at the moment where the first weight loss was observed. From measurements of the exact temperature value near the samples a time interval of about 2 minutes was observed after t=0 before the temperature reached its final constant value.

For calculation of the degree of conversion from the thermogravimetric data the theoretical value for the maximum weight loss was used, analogous to the procedure in previous chapters, being 11.0% of the initial dry weight which was calculated from the structural unit formula taking into account the non-reactive endgroups. Some of the samples were heated at 290°C over an extended period of 2 days to determine the experimental maximal weight loss and to calculate the final degree of conversion.

NMR spectroscopy

A Nicolet NT200, 200 MHz. FT-NMR spectrometer was used for obtaining the 1H-NMR spectra of TIPH solutions in deuterated DMSO (99.96%)

4.3 Results and discussion

Figure 4.2 shows one hour isotherms for several samples of TIPH1 prepared in different ways. All samples were prepared from the same DMSO solution but with different post-treatments. Some of the solutions also contained LiCl to check the influence of this salt, because LiCl is always present in the polycondensation reaction mixture from which the original powders are prepared. Some of the films were obtained by pouring instead of casting the solution on the glass plate in order to prevent possible orientation of the polymer molecules by casting. To investigate the influence of washing some of the films prepared by evaporation were also extensively washed afterwards, just as it is done with the powders.

In agreement with the results presented in the previous chapters this figure again shows the distinct difference in conversion rate between the powders prepared by immersion precipitation and the films prepared by evaporation.

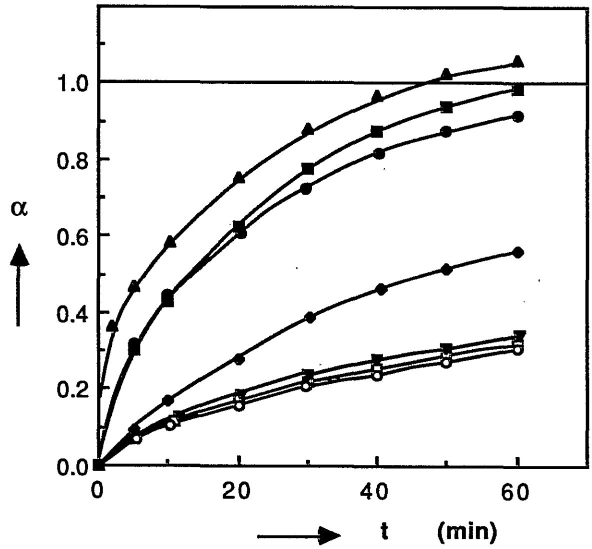


Figure 4.2: Isotherms for TIPH1 samples prepared from the same DMSO solution: homogeneous film casted (▲), homogeneous film poured (■), homogeneous film washed (◆) and powder (○); from the same DMSO solution now containing LiCl: homogeneous film (●), homogeneous film washed (▼) and powder (□)

The composition of the polymer solution does not seem to be an important factor as samples prepared from exactly the same polymer solution still show considerable differences. The addition of LiCl to the DMSO solution hardly has any influence on the kinetics and there is also no significant difference in conversion rate between films casted or poured on the glass plate. However, if the films are given the same washing treatment as is the case with the powders the conversion rates clearly decrease towards the rates normally found for the powders. From this set of varied parameters the contact with the non-solvent seems to be a decisive factor for the conversion rate.

For an explanation of these differences in the observed kinetics the extent of solvent removal comes to mind as a first possibility. The non-washed films possibly contain some residual solvent because it was observed that the final degrees of conversion of the films exceed the theoretical maximum of 1.0, while the other samples approach this value fairly well. An incorrect degree of conversion will result from the additional weight loss of solvent. Furthermore traces of residual solvent present in the polymer matrix may act as plasticizer and enhance the mobility of the chain segments, thus influencing the conversion kinetics.

The influence of washing and the nature of the non-solvent used for washing treatments is further examined. In figure 4.3 the isotherms for a homogeneous film of TIPH2 are presented before and after additional washing with tap water or with hyperfiltrated water. In this figure also the final degrees of conversion are presented. In agreement with figure 4.2 it can be seen that as a result of washing a decrease in conversion rate and a better approach of the final theoretical value for conversion is observed, probably indicating a better removal of residual solvent.

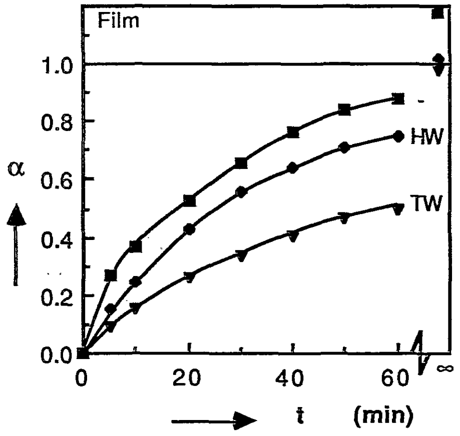


Figure 4.3: Isotherms for TIP H2 homogeneous films before (■) and after washing with tap water(TW) (▼) or hyperfiltrated water(HW) (●)

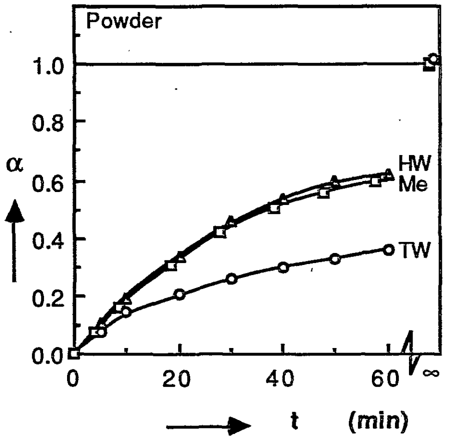


Figure 4.4: Isotherms for TIP H1 powder prepared from a 6% solution in DMSO by non-solvent precipitation and washing in tap water(TW) (○), in hyperfiltrated water(HW)(▲) or in methanol(Me)(□)

Looking at the shape of the isotherms it seems that loss of residual solvent takes place at the very beginning of the process. This is in good agreement with the observed lower energies of activation found for the process in its early stage in the previous two chapters. Additional evidence for the presence and removal of residual DMSO in the non-washed films can be obtained by sulfur analysis of a TIPH1 film before (2.2 ± 0.2% S) and after washing (0.3 ± 0.2% S). A reduction in sulfur content of about 90% can be observed after washing.

Above this effect of solvent removal also the nature of the non-solvent used for the washing treatment seems to influence the rate of conversion. The use of tap water clearly results in much lower conversion rates than the use of hyperfiltrated water. Figure 4.4 presents the isotherms for powders prepared from a DMSO solution by non-solvent precipitation in three different non-solvents, being tap water, hyperfiltrated water and methanol, followed by washing with the same medium. Again it seems that the nature of the non-solvent, used for precipitation and washing, influences the conversion rate. The conversion of the original powders can be accelerated using hyperfiltrated water or methanol instead of tap water.

An even better illustration of the influence of the nature of the non-solvent can be observed in the preparation of asymmetric porous membranes which are made by casting the polymer solution on a glass plate (comparable to the homogeneous film preparation) followed by immersion precipitation in a non-solvent (comparable to the powder preparation).

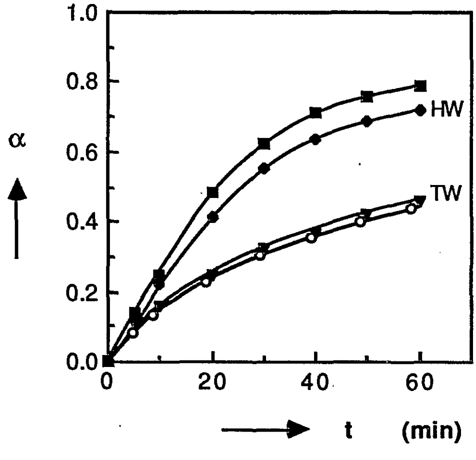


Figure 4.5: Isotherms for immersion precipitated TIPH2 films in tap water (TW)(▼) and ultra-pure water (UW) (●) compared with evaporated homogeneous film (UW washed) (■) and the original TIPH2 powder (○)

These isotherms are presented in figure 4.5 showing that the use of tap water during immersion precipitation results in asymmetric membranes with conversion rates comparable to the rates found for the original powder (also prepared using tap water) while the use of hyperfiltrated water leads to conversion rates approaching the rates found for the evaporated film.

All washed samples finally reach their theoretical weight loss indicating that washing with all three media has been effective. A difference in washing power between the three non-solvents therefore may not be expected. Besides a better removal of residual solvent by washing these experiments have also indicated an influence of the nature of the non-solvent upon the rate of conversion. Especially the difference between tap water and hyperfiltrated water is striking. Contact with tap water in all cases leads to considerably lower conversion rates than with the other media.

One of the differences between tap water and hyperfiltrated water is the presence of low molecular weight substances and ions in the former. Another point is a small difference in the pH value, the tap water in our laboratories being slightly more basic (pH=7.5-8.0) compared to the hyperfiltrated water used (pH=6.7).

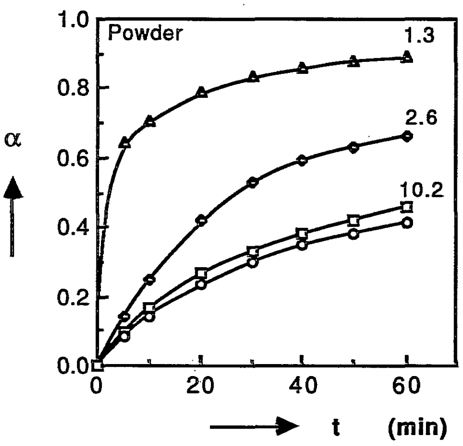


Figure 4.6: Isotherms for TIPH3 powder, before (○) and after additional washing with hyperfiltrated water given different pH values, 1.3 (▲), 2.6 (◆) and 10.2 (□)

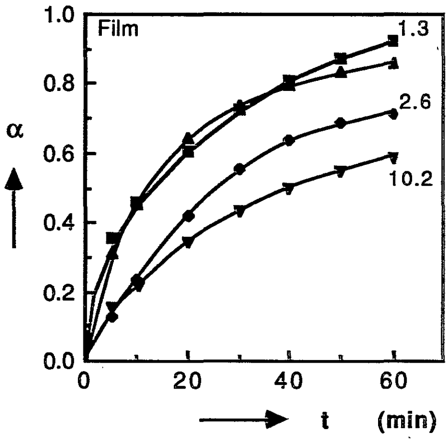


Figure 4.7: Isotherms for TIPH3 homogeneous films, before (■) and after additional washing with hyperfiltrated water given different pH values, 1.3 (▲), 2.6 (◆) and 10.2 (▼)

In order to test the influence of the pH of the water, film and powder samples of TIPH3 were given an additional washing treatment with hyperfiltrated water, to avoid the presence of ions, which was given different pH values by addition of sulfuric acid or sodium hydroxide. From figure 4.6 and 4.7, showing the isotherms of the washed films and powders respectively, a clear pH influence can be observed: higher conversion rates are obtained for pH values lower than 7, while lower conversion rates are obtained after washing at pH higher than 7.

The conversion rate for the powder can be accelerated and that for the film can be slowed down by controlling the pH of the water. Water with a pH value of 1.3 does result in an enormous increase in conversion rate for the powder. It has become so fast that already during the fast heating up towards the isothermal temperature of 290°C there is a considerable amount of conversion. Basic water on the contrary does not seem to decrease the rate in comparison with that for to the original powder.

Looking more extensively at the pH influence figure 4.8 shows the relation between the observed degree of conversion obtained after one hour at 290°C for TIPH3 powders and the pH value of the washing water. An interesting step-wise pattern can be observed.

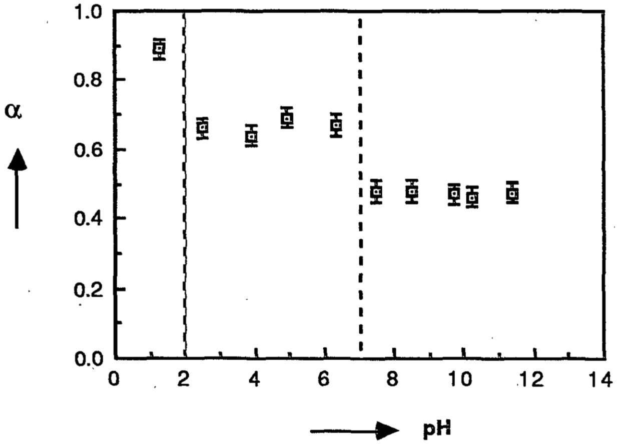


Figure 4.8: The degree of conversion reached after one hour at 290 °C for TIPH3 powders as a function of the pH of the washing water.

A distinct change in the conversion kinetics can be observed around a pH value of 7: above pH=7 a constant low degree of conversion is obtained comparable to the original powder values and below pH=7 a constant but higher degree of conversion is observed. The same trend in pH dependency can be observed when tap water is used instead of hyperfiltrated water for the above presented washing treatments. Below pH=2 increasingly higher degrees of conversion are found but it was noticed that in this acidic region, below pH=2, the maximal experimental weight loss exceeds the theoretical value markedly and simultaneous degradation has to be feared. Viscosity measurements have shown that the inherent viscosity of powders washed with water of a pH value below 2 has decreased considerably while the inherent viscosity remains unchanged after washing above pH=2.

Apart from an effect on the conversion rate the pH also has an effect on the colour of the dried polymer sample: from yellow after washing at high pH values to white after washing at low pH values. It is believed that polyhydrazides are tautomeric and that the hydrazide group can exist in the enol and the keto form. Frazer[3] reported that in an acidic environment the hydrazide groups are expected to be preferentially in the keto form (form a and b in figure 4.1), resulting in a white coloured polymer, while in a basic environment the enol form (form c) is more favourable, resulting in a yellow coloured polymer. He gave no further evidence of the coexistence of the tautomers.

When the dehydration reaction proceeds through the enol form of the hydrazide group, as some authors believe, the enol form would be expected to be the more favourable one for the conversion reaction[2,3]. Nevertheless the contrary is observed, in the above described experiments there is an inhibition of the reaction when the polymer has been in a basic environment. This can be explained however in terms of chain mobility.

Figure 4.9 shows the possible keto-enol tautomerisation equilibria for a polyhydrazide segment, where all the hydrazide groups are in the extended conformation. Except for the extreme all-ketonic form (I) and the all-enolic form (III) figure 4.9 also shows an intermediate form where one hydrazide group contains both a keto and an enol form of the amid group (II). This is a likely conformation because of the possibility of stabilization by an internal hydrogen bond between the hydroxyl group and the carbonyl oxygen of the same hydrazide group. Besides this keto-enol tautomerism figure 4.9 also shows the possibility for the enol form to have a resonance possibility (III + IV) by which the enol form is stabilized. For TIPH this form IV however is less stable than form III because of the charge separation. It can be seen that on going from form I to III, this means shifting the equilibrium to the enol side, the conjugation of the system increases and the axes of free internal rotation, the -N-N-, the -C-N- and -C-C- bonds, become more and more blocked for rotation. For hydrazide groups in the extended conformation, as is shown in figure 4.9, rotation towards the more favourable folded form will be more difficult when these hydrazide groups are mainly in the enol form.

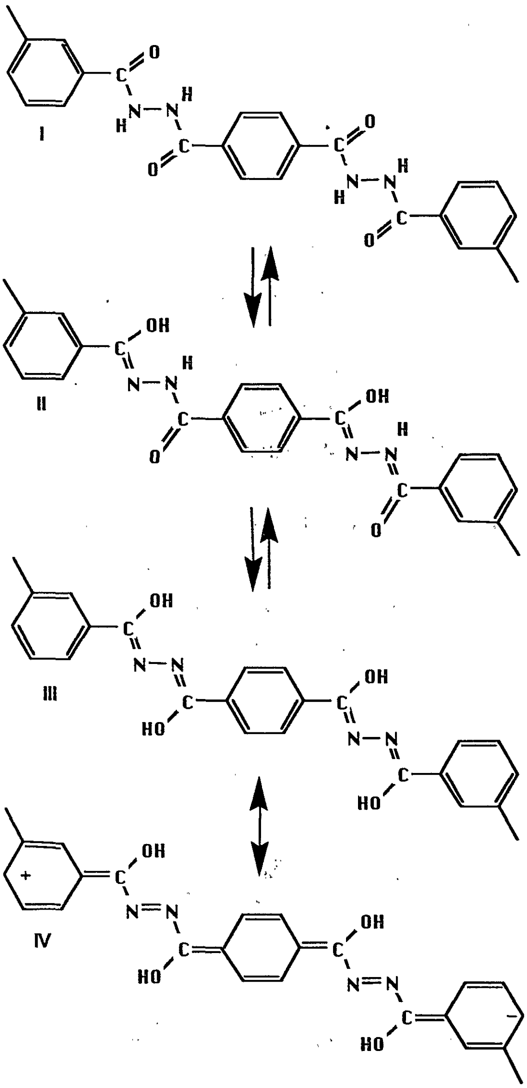


Figure 4.9: Schematic representation of the keto-enol tautomerism for an extended TIPH chain segment

The position of these equilibria is expected to be very sensitive to the polymer environment. A solvent dependency of the keto/enol fraction has been observed for other tautomers in literature[4,5]. The equilibrium seems to depend on the polarity, the hydrogen bond donor and acceptor capacity of the solvents as well as on the concentration of the solute. In addition to these factors one might expect the possibility for intermolecular hydrogen bonding between neighbouring chains as well as the possibility for intramolecular hydrogen bonding to be factors influencing the keto-enol equilibrium. In this way the chain conformation can influence the position of the keto-enol equilibrium and perhaps vice versa.

The coupling of this keto-enol equilibrium with the mobility/flexibility of the polyhydrazide chains may be the explanation for the observed environmental influence in the case of the conversion of polyhydrazides. Apparently the equilibrium position of this keto-enol transition is rather sensitive to acidic or basic conditions around pH=7. Therefore the observed difference in effect on conversion between tap water (pH=7.6) and hyperfiltrated water (pH=6.7) might be caused by a subtle difference in pH value.

It is known from literature that certain anions such as Li^+ and Ca^{2+} can interact with peptide groups[6,7] and, more specifically, Frazer found that polyhydrazides are known to form chelates at high concentrations of metal ions such as Cu^{2+}, Co^{2+} and others[8]. Both types of interactions are schematically shown in figure 4.10.

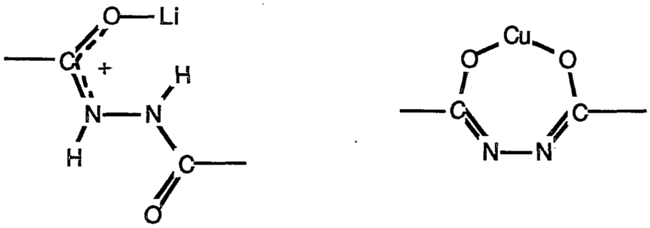


Figure 4.10: Schematic representation of possible cation interactions with the hydrazide group.

Deliberately introducing metal ions (Cu^{2+} and Li^+) to hyperfiltrated water did not have a noticeable influence on the conversion rate except that in agreement with a statement by Frazer[7] a simultaneous degradation during conversion upon the addition of copper ions was observed. The direct influence of cations on the chemical structure and the consequences for the conversion rate remain unknown and have not been examined further.

It is known from work of Frazer[8] that the thermal cyclisation reaction of polyhydrazides in the solid state is catalyzed by acids. He tested several acids and observed that the strength of the catalyst was dependent on the pK_a of the acid, from which he concluded that protonation of the hydrazide group was a major step in the catalysis mechanism. He did not include chain mobility in his explanation for the catalytic effect of acids. We think that the above proposed keto-enol transition is a significant factor for the chain mobility and that making use of this fact can help to explain the acid catalysis qualitatively.

Films of polyhydrazide are prepared from solutions in DMSO which is an aprotic polar solvent. There is absolutely no way in which the hydrazide groups could be protonated when prepared from DMSO but still the reaction proceeds much faster than for the powders. In this case it is certainly not a protonation which makes the conversion fast but possibly the polarity of the surrounding medium of the polymer which contributes to its initial configuration and chain mobility. It is clearly shown in figure 4.2 and 4.4 that the conversion for films can be slowed down by washing with tap water, giving a reduction which can not be assigned only to removal of solvent. A considerable change in conformation of the solid polyhydrazide sample upon contact with water is not very likely as this would imply a considerable movement of the chains. A shift in the keto-enol equilibrium of the polymer from the keto to the enol side of this equilibrium therefore seems to be the best explanation. The extent of this shift being dependent on the pH value of the water used.

Apart from the visible colour difference ($pH<7$: white or colourless and $pH>7$: yellow) it is difficult to evidence the existence of the keto and enol form. Infrared analysis using colourless and yellow homogeneous films (acid and base washed respectively) showed no difference in spectra. Both films showed equally strong and broad carbonyl stretching peaks at $1650 cm^{-1}$. Other analyses were performed with dilute solutions in DMSO. Ultraviolet spectra could not be made properly using DMSO solutions because DMSO itself shows considerable absorbence in the ultraviolet range. In the visible range however the differences are obvious because of the colour difference. The yellow solution showed an absorption at λ_{max}= 390nm. Also ^1H-NMR spectra (presented in figure 4.11) are identical although the dilute DMSO-d6 solutions were markedly different in colour.

The ^{1}H-NMR spectrum does give us some clue concerning the conformation of the hydrazide groups in solution. The signal at δ=8.13 ppm is assigned to the aromatic protons, the other signal at δ=10.77 ppm must represent the hydrazide protons. The fact that only one singlet is observed indicates that these protons belong either to an extreme side of the keto-enol equilibrium or to the average position of the transition which is possible when the transition is much faster than the time constant of the NMR-measurement. Apart from this the considerable shift of these protons indicates acidic protons or a structure were the protons are involved in hydrogen bonds. The colour difference can be explained by a difference in degree of conjugation.

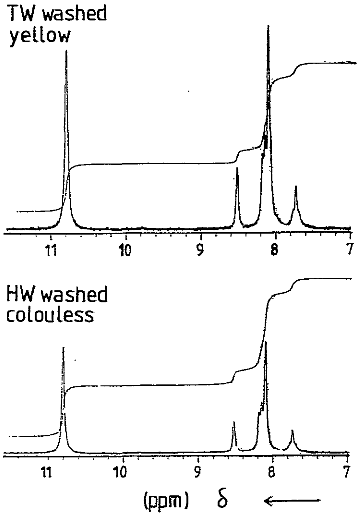


Figure 4.11: ^{1}H-NMR spectra in DMSO-d6 of TIPH3, washed with tap water(TW) to give a yellow coloured polymer solution and with hyperfiltrated water(HW) to give a colourless solution.

In figure 4.12 the most probable conformation is presented, an extended conformation with internal hydrogen bonds. This conformation allows for a very fast keto-enol transition, the presence of internal hydrogen bonds and a difference in degree of conjugation.

The above given evidence for the extended conformation of course represents the conformation in dilute solution. It is not allowed to extend this evidence to conformations existing in the solid state where also intermolecular hydrogen bonds will influence the type of conformation and where quite different structures can be expected. It does give us an indication that these conformations are possible.

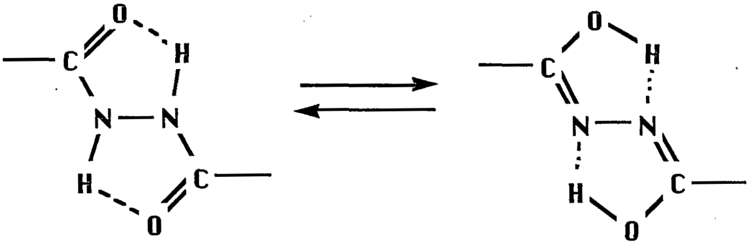


Figure 4.12: Proposed hydrazide conformation in solution according to NMR interpretation

The experiments described in this chapter have shown that the cyclodehydration reaction kinetics of a polyhydrazide is very responsive to its history. The effect of polymer orientation was already known from literature[2,3]. Orientation probably changes the conformation of the chains, it will increase the extended to folded ratio. Now it has been shown that also the nature of the environment can influence the kinetics considerably, probably by an effect on the tautomerism of the hydrazide groups. It is this phenômenon which is believed to contribute largely to the differences between powders and films observed in the previous two chapters.

4.4 Conclusions

The history dependence observed in the previous chapters of the thermal cyclodehydration reaction of polyhydrazide in the solid state is caused by the phase inversion process. If the polymer sample has been prepared by non-solvent precipitation and has been in contact with tap water the rate of conversion is much lower compared to polymers prepared by evaporation of solvent. Besides a more complete removal of solvent by immersion precipitation an additional influence of the nature of the non-solvent is observed. Asymmetric membranes prepared by non-solvent precipitation showed much higher rates of conversion when hyperfiltrated water was used instead of tap water. The pH of the water used has a considerable influence. A distinct change in conversion rate is observed at a pH value of about 7. Below pH=7 higher rates of conversion have been observed. This pH dependency is explained by the sensitivity of the keto-enol tautomerisation equilibrium of the hydrazide groups for the environment and the effect of the tautomeric forms and their degree of conjugation on chain mobility. Apart from a possible difference in initial chain conformation also a difference in the position of the keto-enol equilibrium of the hydrazide groups determine the conversion rate of solid polyhydrazides into polyoxadiazoles.

4.5 References

1] A.H.Frazer, F.T.Wallenberger, J.Polym.Sci.,A2,1137-1156(1964)
2] V.V.Korshak, Vysokomol. Soyed.,A16,8, 1745-1722(1974) Eng.translation.
3] A.H.Frazer, W.Sweeny, F.T.Wallenberger, J.Polym.Sci.,A2,1157-1169(1964)
4] S.Masusa, M.Tanaka, T.Ota, Makromol.Chem.,187, 1087-1095(1986)
5] S.Masusa, M.Tanaka, T.Ota, J.Polym.Sci.,C,Polym.Lett.,24,529-532(1986)
6] D.Balasubramanian, R.Shaikh, Biopolymers, 12, 1639-1650(1973)
7] D.Balasubramanian, B.C.Misra, Biopolymers, 14, 1019-1026(1975)
8] A.H.Frazer, F.T.Wallenberger, J.Polym.Sci., A,2,1825-1832(1964)
9] A.H.Frazer, D.R.Wilson, Appl.Polym.Symp.9(1969)
10] A.H.Frazer, W.P.Fitzgerald Jr., J.Polym.Sci.,C,19,95-101(1967)

Appendix B

Polyoxadiazole membranes using the one-step Iwakura process

Instead of the two-step preparation process developed by Frazer, and described in detail in the previous chapters, Iwakura developed a process in which aromatic polyoxadiazoles are prepared in a one-step polycondensation procedure. With this method high molecular weights and the formation of tough films and fibers have been reported in literature[1]. Polyoxadiazoles have been prepared, according to Iwakura, by a polycondensation reaction between phtalic acid and hydrazine sulfate (about 5% excess hydrazine to equimolarity) in oleum. A schematic representation is given in figure B.1, showing that the meta and para substituted phenylene groups can only be incorporated randomly.

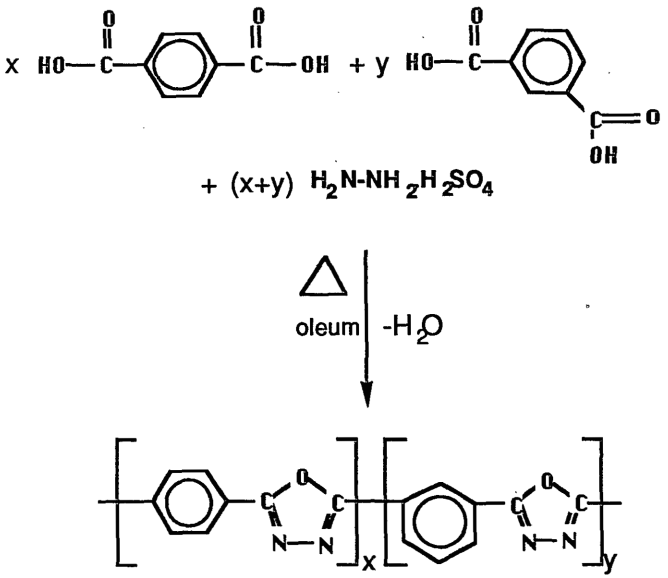


Figure B.1: Schematic representation of the one-step polyoxadiazole preparation according to Iwakura[1]

For the membrane preparation a patent by Sekiguchi was followed, describing the preparation of RO and UF membranes of water-swollen polyoxadiazoles[2]. Membranes or films were prepared by casting the oleum reaction solutions directly on a glass plate using a stainless steel casting knive of slit-height 0.20 mm. The films were gelled by immersing them in a water bath containing 50% by weight sulfuric acid, followed by a 100% water bath. Progressively more diluted aqueous sulfuric acid baths were also suggested in another patent by Iwakura and Sekiguchi to prevent hydrolysis[3]. After additional washing with water the films were dried. Some of the films, especially of the polyoxadiazoles containing a high para-fraction, appeared to be tough and flexible, while the others shrank and became brittle upon drying. Table B.1 shows the results of the syntheses and the film properties.

nr.	para content (%)	η_{inh} (a) (dl/g)	film(b)
1	0	-	+-
2	50	-	+-
3	75	-	+-
4	85	-	+-
5	100	3.22	++
6	100	2.83	++
7	100	2.94	++
8	100	3.04	++

a) 0.5g/100ml concentrated sulfuric acid (96%) at 30°C
b) +-: shrinkage and brittle films after drying at room temperature
++: tough film

Table B1: Results of the one-step polyoxadiazole syntheses with different ratios of para- and meta substituted phtalic acid

The 100% para reactions resulted in oleum solutions of very high viscosity which were difficult to manufacture into thin films because of the high viscosity. The membranes obtained after coagulation were very thin and had the appearance of opaque homogeneous membranes. Correspondingly these polymers had high inherent viscosities, around 3.0 dl/g, when measured in sulfuric acid, in agreement with values found in literature[2,4], indicating high molecular weights. Compared to the inherent viscosities of the polyoxadiazoles obtained with the two-step procedure, presented in table C.2 (Appendix C), which were found to be in the range of 0.4 to 0.7 dl/g, the polyoxadiazoles obtained with the one-step method show considerably higher inherent viscosities. Since we are dealing with polymers with different molecular structures one has to be very careful in comparing inherent viscosities with respect to the molecular weights.

The determination of the molecular weight of poly-p-phenylene-oxadiazole using light scattering was obstructed by the fact that possibly micro-gel formation in the dilute sulfuric acid solutions had occurred. Figure B.2 shows the Zimm-plot of polyoxadiazole (sample nr.5 from table B.1): the curved (and dashed) lines in the lower angle region represent the experimental curves and indicate the presence of larger particles in the solution, possibly micro-gels.

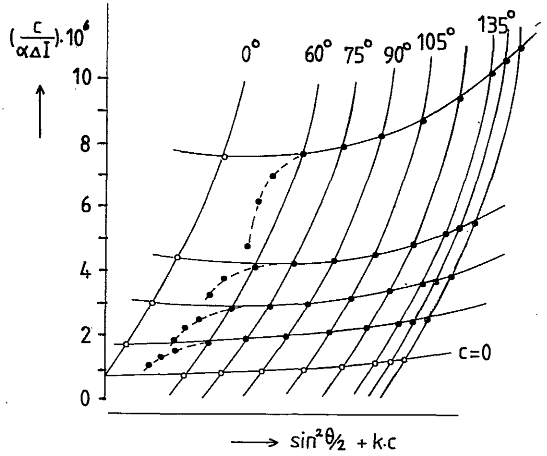


Figure B.2: Zimm-plot of poly-p-phenylene-oxadiazole determined using static light scattering with dilute solutions of the polymer in sulfuric acid (96%)

These deviations at small angles have also been observed by Leibnitz et.al.[4]. They even observed inherent viscosities up to 5 dl/g. When the lower angle data in the Zimm-plot are not considered the M_w value obtained from this plot amounts to ±120.000, in agreement with values presented by Leibnitz[4]. This value however is not very reliable due to the possible micro-gel formation.

Using Mark-Houwink relations, derived by Tsetkov et.al.[5] for poly-p-phenylene -oxadiazoles, and estimating the intrinsic viscosities from the determined inherent viscosities given in table B.1, these viscosities correspond with molecular weights higher than 50.000, which is outside the reliability range of the derived Mark-Houwink relations.

$[\eta]=K_\eta.M^a$ $\quad$ $K_\eta=1.268.10^{-3}$ and $a=1.23$ $\quad$ for $1 < M < 5.5.10^3$

$K_\eta=4.116.10^{-2}$ and $a=0.825$ $\quad$ for $5.5 < M < 50.10^3$

Following the same procedure with the inherent viscosities found for the polyoxadiazoles obtained by the two-step method the molecular weights are found to be in the range of 6,000 to 8,000. These molecular weights however are only very rough estimates not only because different polymers are being compared and the intrinsic viscosities have been estimated but also regarding the uncertainty in the reliability of the Mark-Houwink relations used.

The inherent viscosities, presented in table B.1, of polyoxadiazole in sulfuric acid solutions decreased in time, especially the viscosities of the polyoxadiazoles containing a higher meta-fraction, indicating a slow degradation in this medium possibly caused by residual, not converted hydrazide groups. The reaction products obtained with increasing isophtaloyl acid content contained relatively more hydrazide groups than when terephtaloyl acids were used and consequently the former degradated more. The presence of residual hydrazide groups was evidenced using infrared spectroscopy by the presence of a weak carbonyl oxygen band at 1640 cm^{-1}. Furthermore these polyoxadiazoles showed a weight loss in the temperature range between 200 and 400°C. This weight loss might represent the cyclodehydration of residual hydrazide groups but an acid catalyzed decomposition or loss of residual solvent may also contribute to this weight loss.

Removal of residual sulfuric acid from the final polyoxadiazole membranes is another problem that has been reported in literature[2]. This removal is very important because otherwise the membranes are destructed by the residual acid upon heating. The obtained tough poly-p-phenylene membranes became brittle after 15 hr. exposure at 170°C. This thermal treatment reduced the inherent viscosity of polyoxadiazole sample nr.5 from 3.22 to 0.10 dl/g. An additional washing cycle using water with 1% methanolamine or another base is suggested in a patent[6] for a better removal of sulfuric acid.

Only limited attention has been paid to this one-step polyoxadiazole preparation. Summarizing, the problems encountered with this one-step polyoxadiazole membrane preparation are mainly caused by the solvent sulfuric acid. Apart from the fact that the use of this solvent requires special attention because of its corrosiveness it also appears to be very difficult to remove completely from the final membrane causing degradation at elevated temperatures. Furthermore sulfuric acid is not such a convenient solvent to use in the phase-inversion method for the preparation of membranes because it does not allow much variation in the preparation parameters. The inherent viscosities of the so obtained polyoxadiazoles indicate the formation of high molecular weights compared to the polyoxadiazoles obtained with the two-step procedure. Some of the one-step polyoxadiazoles could be processed into tough films, whereas the two-step polyoxadiazoles resulted in brittle films only.

References

1] Y.Iwakura, K.Uno, S.Hara,J.Polym.Sci., part A, 3, 45-54(1965)
2] U.S.Patent 4,067,804 (1978)
3] Japan Kokai 7429,298 (1974); Chem. Abstr., 82,74068t (1975)
4] E. Leibnitz, et.al., Faserforschung und Textiltechnik, 27, 507-11(1976)
5] V.N. Tsvetkov et.al.,Vysokomol.Soedin, 1,133-142(1980) (Russ.)
6] Japan. Kokai 77,117,285 (1977); Chem. Abstr., 88, 122337c (1978)

Appendix C

Some comments on the brittleness of polyoxadiazole membranes

Introduction

Polyoxadiazole membranes prepared with the two-step method through the cyclodehydration of polyhydrazide membranes, as discussed in the previous chapters, appear to be extremely brittle at high degrees of conversion. They disintegrate upon handling, which makes the application of completely converted polyoxadiazole membranes impossible.

There is no exact definition of brittleness and toughness. But generally a material that breaks after only small deformation is called brittle. The best measure for brittleness is the area under a stress-strain curve. By increasing this area the material becomes more tough especially when there is a yield drop in the curve. All thermally stable polymers, because of their stiff aromatic and heterocyclic structure can be considered to be brittle. In order to break a polymeric product the force that has to be applied has to overcome the forces that hold the molecules and atoms together. The polymer chain interaction is caused by physical and chemical interactions. The physical intermolecular forces are dipole-dipole interactions (Keesom forces), dipole-induced dipole interactions (Debye forces), dispersion forces due to induced dipoles (London-v.d.Waals forces) and hydrogen bonding. The chemical intermolecular forces are due to intermolecular chemical crosslinking.

The polyoxadiazole membranes were so brittle that they disintegrated upon the slightest force applied on them. Some of the possible factors causing this mechanical behaviour will be discussed below.

1. The molecular weight

The relation between the molecular weight of a polymer and its tensile strength is represented schematically in figure C.1. A critical molecular weight, M_c, can be distinguished below which the tensile strength drops to very low values resulting in a brittle polymer[1]. Tough films can only be obtained if the molecular weight of the polymer exceeds this critical molecular weight.

The polyhydrazides are expected to posses stronger intermolecular forces than the corresponding polyoxadiazoles due to the hydrogen bonding capacity of the former. Upon conversion from polyhydrazide to polyoxadiazole the hydrogen bonding capacity will decrease. The σ,M_w-curve of the polyoxadiazoles therefore is expected to be shifted to higher M_w's compared to the polyhydrazide curve. This is schematically shown in figure C.2.

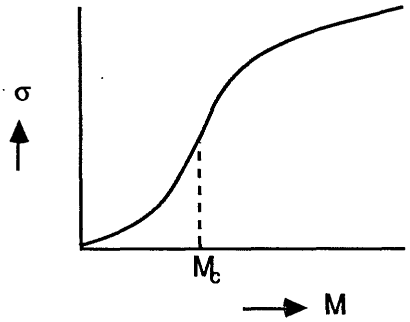


Figure C.1: Schematical drawing of the tensile strength as function of the molecular weight of a polymer

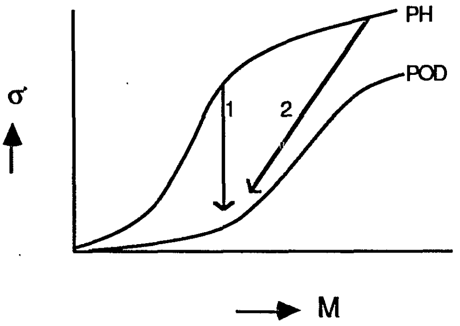


Figure C.2: Schematical drawing of expected σ,M_w*-curves for polyhydrazide (PH) and polyoxadiazole (POD) with possible conversion routes*

In table C.1 the molecular weights of some TIPH polyhydrazide samples of different inherent viscosites are presented which have been determined using static light scattering. A molecular weight of 14,000 appears to be sufficient for non-brittle films of the polyhydrazide. A molecular weight of about 30,000 could reproducibly be obtained but appeared to be the upper limit for the discussed polyhydrazide preparation method (Chapter 2, paragraph 2.2). None of the 60 different syntheses that have been carried out resulted in a viscosity higher than 1.4 dl/g. A higher molecular weight however could be expected when the polycondensation reaction is performed with monomers of the highest purity, with distilled solvents and the rigorous exclusion of water during all stages of the reaction.

η_{inh} (dl/g)	M_w	film appearance
0.30	5,200	brittle*
0.69	14,000	tough
0.74	14,000	tough
1.33	30,000	tough

*breaking upon folding

Table C.1: Molecular weights of TIPH determined using light scattering with diluted DMSO solutions and film properties of homogeneous membranes prepared by evaporation from DMSO solutions

After conversion of the above mentioned TIPH membranes the corresponding polyoxadiazole membranes were brittle. Thermal conversion was accomplished by placing the membranes in furnaces under N_2 atmosphere at isothermal temperatures between 250 and 320°C.
When discussing the appearance of brittleness in terms of a too low molecular weight two possible causes can be mentioned. Figure C.2 illustrates these two possibilities:

1] The molecular weight does not change during conversion but it is too low for polyoxadiazoles to give a tough film (route 1)
2] The molecular weight decreases during conversion because of simultaneous degradation (route 2).

The occurrence of a simultaneous degradation reaction towards the end of the conversion process at high degrees of conversion and at high temperatures has been suggested in chapter 2. Possibly this means a decomposition of the very last not yet converted hydrazide groups, being less stable than the aromatic or heterocyclic rings. Some conformations of the hydrazide group, like the one presented in figure C.4, will be very hard to bring to cyclisation because of steric hindrance, especially in the glassy state and at high oxadiazole content. Because of this conformation the chain is bended, and rotation around one of the C-N axes is necessary to obtain a more favourable conformation. This rotation will involve an enormous transition of the whole chain and instead of cyclisation this group might decompose resulting in chain cleavage.

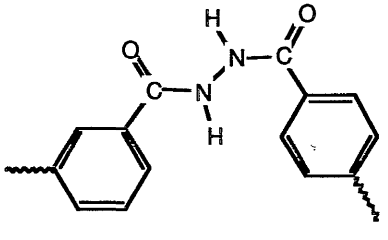


Figure C.4: Schematical representation of an unfavourable hydrazide conformation for cyclisation

A study by Ballestreri[2] of the thermal decomposition processes taking place in totally aromatic polyhydrazides, using direct pyrolysis mass spectroscopy (DPMS), revealed a quantitative loss of only water up to a temperature of 440°C which was accounted fully to the oxadiazole formation. Although this may be an argument against degradation, a severe degradation is still possible when only one chain cleavage per chain is assumed to be accompanied by no loss of any volatile component at all. (note that only one chain cleavage per chain is enough to reduce the molecular weight by a factor of 2)

The determination of the molecular weights of the polyoxadiazoles is very difficult because of their insolubility. Sulfuric acid has to be used as solvent. For light scattering measurements this is not an ideal solvent. The sulfuric acid used appeared to have abnormal behaviour (an asymmetry in scattering intensity around 90°) possibly caused by contaminations and/or water. Furthermore the sulfuric acid solutions appeared very difficult to be filtered. Besides this solvent problem the Zimm-plot obtained showed strong deviations at small angles indicating the presence of bigger particles, possibly micro-gels. See figure B.2, appendix B. This observation is in agreement with that of Leibnitz et.al. who studied poly-p-phenylene-oxadiazoles in sulfuric acid[3]. Therefore no reliable molecular weights of the polyoxadiazoles have been obtained.

TIPH$^{(a)}$	Conversion cycles		TIPOD$^{(b)}$	ref.
η_{inh} (dl/g)	t (hr)	T (°C)	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	
Literature:				
0.22	34	310	0.23	[5]
1.5	24	280	0.5	[6]
1.7	24/24/24	280/300/320	0.93	[4]
1.9	24/24/24	280/300/320	1.04	[4]

(a) 0.5 g/100ml DMSO
(b) 0.5 g/100ml sulfuric acid (96%)

Table C.2: *Inherent viscosities of TIPH powders before and after thermal conversion compared to literature data on TIPH fibers*

Inherent viscosities have been obtained for some polyoxadiazoles in diluted sulfuric acid solutions (0.5 g/dl), which were found to be all in the range of 0.3 to 0.7 dl/g. In table C.1 the polyoxadiazole viscosities are presented showing a proportional relation with the original polyhydrazide values.

These viscosity values can be used in comparison with literature values for the same polymers. Frazer[4] reported for completely converted TIPH fibers inherent viscosities in the range of 0.7 to 1.0 dl/g. These polyoxadiazole fibers, upon conversion, were all described as tough. In an earlier stage he reported values in the range of 0.1 to 0.6 dl/g[5]. Korshak did not report inherent viscosities higher than 0.5 dl/g[6]. In a patent of Sekiguchi (Furukawa Electric Company) describing polyoxadiazole membranes prepared using the one-step method an inherent viscosity of 1.5 dl/g is mentioned as a lower limit for film preparation[7]. Although this statement is not supported by data and care must be taken in referring to patent literature it might be an indication that the molecular weights obtained through the two-step method are too low for film forming polyoxadiazoles. Polyoxadiazole membranes prepared according to the one-step method have been discussed in appendix B. These polyoxadiazoles showed considerably higher inherent viscosities compared to the above presented polyoxadiazoles prepared by the two-step procedure.

2 Intermolecular forces

Apart from the molecular weight influence, discussed in section 1, also the nature and the strength of the individual forces are important for the mechanical properties. In general the strength of the London-vanderWaals dispersion forces show a reciprocal exponential dependence on the intermolecular distance. A high packing density or a high degree of orientation therefore is favourable for toughness.

In literature[4] tough polyoxadiazole fibers are described prepared by the two-step method. Aromatic polyoxadiazole fibers prepared through the thermal conversion of polyhydrazide fibers, which have been oriented by drawing, show good mechanical properties, even with polyhydrazide inherent viscosities in the relatively modest range of 1.0-1.5 dl/g. The good mechanical behaviour of these fibers might be caused by their orientation. Using X-ray scattering measurements no signs of orientation could be observed for homogeneous TIPH membranes described in this thesis. The lack of orientation in the films may therefore be a reason for brittleness.

Another type of intermolecular forces are chemical crosslinks which might occur between two neighbouring polyhydrazide molecules by an intermolecular dehydration reaction. While a low degree of crosslinking probably enhances the toughness, a too high crosslinking density can lead to brittleness[8]. Several observations, like the solubility in sulfuric acid of the final polyoxadiazole, the agreement between experimental and theoretical conversion weight loss and the infrared data do not indicate crosslinking, at least not to a large extent.

3 Crystallinity

The effect of crystallinity on the mechanical properties is dependent on the degree of crystallization and the size of the crystallites. For the same crystalline fraction many small crystallites are considered to be preferable for mechanical behaviour above a few big ones[1]. Internal stresses caused by density differences between the crystalline and the amorphous regions may cause the brittleness of the polymer[9].

X-ray diffraction (WAXS) has been performed on finely ground powder samples. Three different aromatic polyhydrazides were prepared according to the method described in chapter 2, paragraph 2.2 using terephtaloyl and isophtaloyl monomers in different ratios. Besides the polymer studied in the previous chapters, with alternating meta and para phenylene groups (TIPH), also an all-para (TPH) and an all-meta polyhydrazide (IPH) were investigated. The polymer specifications are given in table C.3 and the corresponding powder diffractograms are presented in figure C.3.

polymer	para content (%)	sample code	conversion conditions(a) time (hr)	temp. (°C)	degree(b) of conversion
IPH	0	1a	-	-	0.00
		1b	16	273	0.75
		1c	16/16	273/291	1.00
TIPH	50	2a	-	-	0.00
		2b	62/100/20	280/300/350	1.00
TPH	100	3a	-	-	0.00
		3b	48	320	0.99

(a) isothermal heating cycles
(b) determined by thermogravimetry from weight loss between 250 and 450°C

Table C.3: Overview of different polyhydrazide samples used for WAXS

These X-ray investigations indicate a change in crystallinity or orientation upon conversion from polyhydrazide to polyoxadiazole. The diffractograms show amorphous behaviour for the initial polyhydrazides before thermal conversion while after conversion the occurrence of some crystallinity can be observed. This change in crystallinity of the polymer during conversion might cause internal stresses. Comparing the X-ray diffractograms of the three different polymers qualitatively the all-para polymer seems to show a higher crystallinity both in the polyhydrazide and the polyoxadiazole state. This is probably caused by its regular and more linear structure.

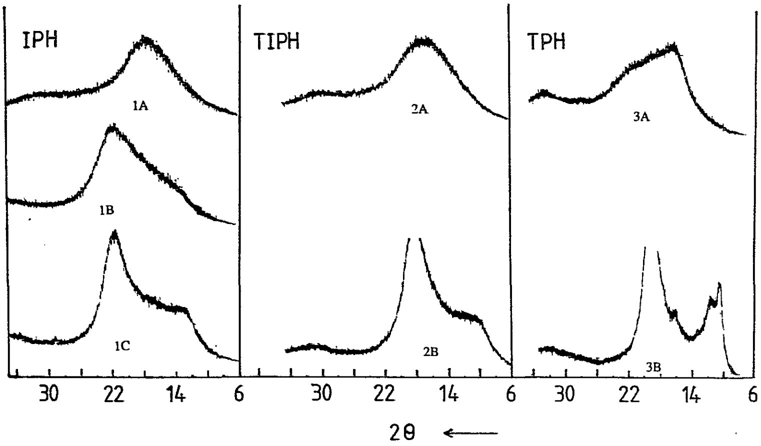


Figure C.4 : X-ray diffractograms of polyhydrazide powders, specified in table C.3

4 Chain structure

Because of the rigid chain structure of polyoxadiazoles a high chain flexibility can not be expected. The problem of brittleness is often encountered with these types of thermally stable polymers and is more or less inherent to the chemical structure[10]. During the conversion the flexibility of the polyhydrazide chains will be greatly reduced because of the conversion of flexible hydrazide units into rigid oxadiazole rings. Chemical modification by incorporation of flexible units in the polymer backbone generally improves the mechanical behaviour. In general meta-substituted benzene rings compared to para-substituted rings in the main chain show slightly lower glass transitions and a higher chain flexibility can be expected. This structure influence is probably also reflected in the conversion rate where the conversion rate of the polyhydrazide increases considerably with the meta content. This effect is shown in figure C.5. However at room temperature the differences in flexibility of the films are expected to be negligibly small.

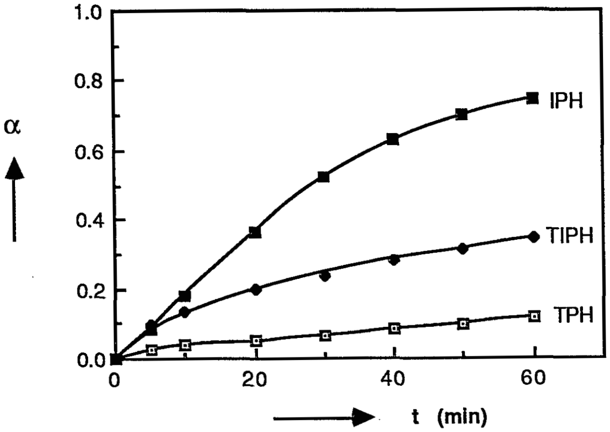


Figure C.5: *290 °C isotherms for the isothermal conversion of three different polyhydrazides with different para/meta ratios, 100% para (TPH), 50% para (TIPH) and 100% meta (IPH)*

All membranes prepared from TIPH and IPH (the all-meta polymer) appeared to be brittle after thermal treatment. Membranes of TPH, the all-para polymer, could not be prepared because of the insolubility of this polyhydrazide. However all-para polyoxadiazoles prepared through the one-step process developed by Iwakura, discussed in appendix B, could be processed into tough films, in agreement with literature[4,11], showing that despite the rigid chain structure tough products are possible.

5 Glass-rubber transition during isothermal conversion

In chapter 3 it is shown that during isothermal conversions at temperatures above 280°C the sample can undergo a rubber-glass transition when the sample is initially in the rubbery state. This transition from the rubbery to the glassy state can introduce internal stresses because of the distinct change in thermal expansion coefficient above and below T_g. It is dependent on the rate of the transition process whether these stresses can be released by relaxation or not. This rubber-glass transition during conversion can be prevented either by using a conversion temperature below the T_g of the initial polyhydrazide or by continuously or stepwise raising the conversion temperature to keep it above the T_g of the copolymer. A disadvantage of this latter method is that by raising the temperature the degradation temperature of the polyhydrazides may be passed causing simultaneous degradation.

6 Chain shrinkage

During the cyclodehydration reaction the polyhydrazide chains become shorter because of the reduced distance between the carbon atoms of the hydrazide group in the extended form and in the folded or final oxadiazole form. This is schematically shown in figure C.6.

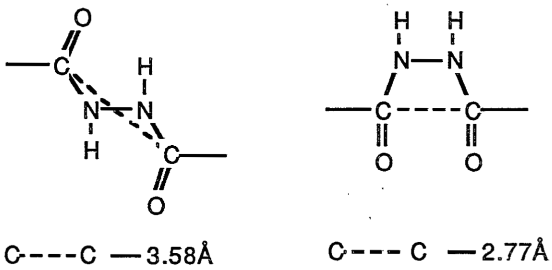


Figure C.6: C-C distance in extended and folded conformation of a hydrazide group, from V.V.Korshak[12]

Because of the expected oxygen repulsion the hydrazide group will always be in a conformation where the C-C distance is larger than the distance in the oxadiazole ring. The chain movement and shrinkage of the chain during the cyclisation process could lead to the build up of internal stresses. To overcome this the conversion should take place completely in the rubbery state or the conversion should take place in intervals to assure the possibility of relaxation. Another possibility is to take care that the initial conformation of the hydrazide groups is close to the intermediate folded conformation thus reducing the shrinkage effect. Orientation of the molecules in the initial polyhydrazide membranes therefore should be prevented as much as possible as it is believed that orientation results in the extended hydrazide conformation. A possibility is perhaps a chemical modification of the hydrazide group by a substitution on the nitrogen atom in such a way that the hydrazide group is forced into its folded conformation.

7 Wet-dry irreversibility in case of porous membranes

Wet-dry irreversibility is a problem encountered only with porous membranes. It is therefore not the factor causing the brittleness of the non-porous homogeneous membranes. Porous membranes with pore radii in the range of a few nm's can deform and become brittle when they are being dried from a fluid which wets them. This is a problem often encountered for example with Reverse Osmosis (RO) cellulose acetate membranes[13]. For this destruction very high capillary forces in the pores are responsible caused by the pressure differences over the curved interface surfaces of the wetting fluid in the pores and air. To illustrate the enormous pressure differences table C.4 presents some pressure differences, ΔP, as function of the pore radius calculated from the Laplace equation. The pressure differences caused by the various pores of different pore radii can cause the pore walls to collapse.

r_c (nm)	ΔP (atm)
100	14.6
10	146
1	1460

Table C.4: Calculated pressure differences, using the Laplace equation, $\Delta P=2\gamma\cos\theta/r_c$, over the water-air interface in a pore of pore radius r_c. $\gamma_{water}=73.10^{-3}$N/m. θ, the contact angle is assumed 0° for ideal wetting in these calculations.

Most of the asymmetric porous membranes prepared from TIPH, as described in chapter 4, section 4.2, became brittle and deformed upon drying from water at mild temperatures. Also the brittleness of some of the one-step polyoxadiazoles, discussed in appendix B, upon drying might be caused by this phenomenon. It will depend on the membrane formation parameters whether pores of a critical pore size will be formed. Starting the thermal conversion with an already brittle film will lead to a brittle end-product. To overcome this wet-dry irreversibility, water in the membranes should be exchanged by a non-solvent with a low surface tension or the membranes should be dried above the critical point of water (T_{cr}=374°C, P_{cr}=218atm). The latter method has the disadvantage that simultaneous conversion and possible degradation will occur. The exchange of water by hexane (using ethanol as intermediate non-solvent which mixes with both) proved to be very successful for the drying of tough porous polyhydrazide membranes. Thermal conversion of these dry membranes however still resulted in brittle polyoxadiazole membranes.

Conclusions

The possible causes of brittleness of the investigated polyoxadiazole membranes, prepared with the two-step process, can be divided into two categories: a too low molecular weight and the build up of internal stresses. A too low molecular weight may be caused by a too low molecular weight of the precursor polyhydrazide or by a degradation of the polymer during the thermal treatment. The possible causes for the build up of internal stresses can be largely contributed to the thermal cyclisation process.

When comparing the studied two-step procedure with the one-step procedure it appears that the latter procedure results in polyoxadiazoles with considerably higher inherent viscosities indicating higher molecular weights. Furthermore it can be expected that contributions to the build up of internal stresses caused by the thermal conversion process will be absent when polyoxadiazoles are prepared by the one-step procedure.

References:

1] L.H.Sperling,"Introduction to physical polymer science", Wiley Interscience, New York,1986
2] A.Ballistreri et.al., Polymer, 28,139-146(1987)
3] E.Leibnitz et.al., Faserforschung und textiltechnik 27, 507-511(1976)
4] A.H.Frazer, D.R.Wilson, Appl.Polym.Symp., 9,89-106(1969)
5] A.H.Frazer, W.Sweeny, F.T.Wallenberger, J.Polym.Sci., part A, 2,1157-1169(1964)
6] V.V.Korshak, E.S.Krongauz, A.L.Rusanov, J.Polym.Sci., C, 16, 2635-2647(1967)
7] U.S.Patent 4,067,804 (1978)
8] I.M.Ward,"Mechanical Properties of Solid Polymers",Wiley Interscience, Chichester (1971)
9] Y.Iwakura, K.Uno, and S.Hara, Ibid.,3,45 (1965)
10] P.E.Cassidy, "Thermally Stable Polymers",Marcel Dekker, New York (1980)
11] Y.Iwakura, K.Uno, S.Hara, J.Polym.Sci., part A, 3, 89-106(1965)
12] V.V.Korshak et.al.,Vysokomol. Soyed.,A16, 8, 1714-1722(1974)
13] K.Vaserhelyi, J.A.Ronner, M.H.V.Mulder and C.A.Smolders, J.Membr.Sci., 34, 45(1987)

Chapter 5 Gas separation properties of a thermally stable and chemically resistant polytriazole membrane

B.Gebben, M.H.V.Mulder, C.A.Smolders

Summary

The polymer poly(1,3-phenyl-1,4-phenyl)-4-phenyl-1,3,4-triazole has been investigated for its gas separation properties. This thermally stable and chemically resistant polymer can be processed into membranes by the phase-inversion technique because of its unexpectedly good solubility in formic acid.

Homogeneous membranes have been tested with respect to their permeability for several gases and the influence of time and temperature upon permeation has been investigated. The polymer shows reasonable permeabilities for several gases and excellent selectivities. After a conditioning time of several days in which the permeability of the faster gases increases with a factor of about 2, the permeation properties of the polymer remain constant for at least two months. A thermal treatment at 295°C, just above the glass transition temperature, can reduce the conditioning time and can prevent the film from shrinkage at high permeation temperatures without affecting the permeation properties.

5.1 Introduction

Today synthetic membranes are used in a wide range of applications. However most of these membranes show poor thermal and chemical resistance. Membranes with higher stabilities could open up new fields of applications and prolong the life time of membranes already used for separation problems.

A reasonably large research effort has been invested already in this field and some thermally stable and chemically resistant polymer membranes have become commercially available; for example membranes from polyimides, polybenzimidazoles and polybenzimidazolones[1-6] are now on the market.

The largest problem in the preparation of membranes from stable polymers is the difficulty in processing due to the fact that these polymers have a low solubility and can often not be molten. These unfavourable properties, however, are inherent to their high stability. Improvement of the processability, for example by introducing flexible units in the polymer backbone[7], inevitably leads to reduction in stability. The commercially available high temperature polymers often seem to be compromises between processability and stability.

In our effort to prepare stable polymer membranes we have tried to obtain the maximum in stability without changing the chemical structure of the polymer. Generally speaking[7] the structure should be all aromatic and/or heterocyclic without so called 'weak' spots such as hydrogen or oxygen, bonded to aliphatic groups, which can easily be attacked.

The poly(1,3-phenyl-1,4-phenyl)-4-phenyl-1,2,4-triazole, which will be investigated in this paper, is an example of such a polymer. Due to its aromatic and heterocyclic character the polymer has an outstanding resistance against oxidative, hydrolytic or chlorine mediated degradation in combination with a high temperature resistance[8-10]. Furthermore, the polymer has the advantage that it is easily processable because of its surprisingly good solubility in formic acid.

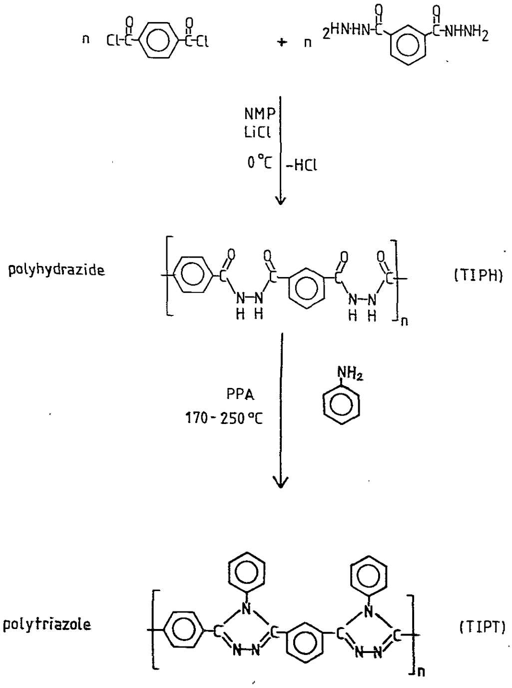


Figure 5.1: ***Reaction scheme for the two-stage preparation of poly(1,3-phenyl-1,4-phenyl)-4-phenyl-1,2,4-triazole***

In this paper the gas permeation properties of poly(1,3-phenyl-1,4-phenyl)-4-phenyl-1,2,4-triazole will be discussed. The polymer has been prepared by a method described by Holsten and Lilyquist[8] in a two stage process by first preparing an aromatic polyhydrazide followed by a reaction with aniline in polyphosphoric acid. A general reaction scheme is given in figure 5.1.

Homogeneous membranes of this polymer have been used for gas permeation and gas separation experiments. Attention has been focussed to the separation of CO_2/ CH_4, O_2/N_2 and of He/N_2. The influence of time and temperature on membrane performance has been investigated. Because of the high temperature resistance of this polymer the permeability properties have been measured at temperatures up to 200°C.

5.2 Experimental

materials

Terephtaloyl chloride was supplied by Merck and was recrystallized from hexane prior to use.

Isophtaloyl hydrazide was prepared according to Frazer[11] from isophtaloyl methyl ester and hydrazine hydrate (100%) both supplied by Merck. The isophtaloyl hydrazide was recrystallized from water, washed with methanol and dried prior to use.

Aniline was supplied by Merck and was used as received.

The solvents PPA (poly phosphoric acid), NMP and formic acid (98%) were supplied by Merck. The NMP was dried over molecular sieves of 3 Å.

polymer preparation

The prepolymer, poly(1,3-phenyl-1,4-phenyl)hydrazide, was prepared according to Frazer[11] from terephtaloyl chloride and isophtaloyl hydrazide using a low temperature solution polycondensation reaction in NMP. Polymers were obtained with inherent viscosities of 1.4 dl/g measured in DMSO.

The polytriazole was prepared from the polyhydrazide by reacting this polymer with a mixture of aniline in PPA according to Holsten and Lilyquist[8]. Temperatures of 179-190°C and reaction times ranging from 2-5 days were used. Polymers were obtained with inherent viscosities of 1.2-1.4 dl/g measured in formic acid.

The structural formula of the polymer could not be confirmed to satisfaction using elemental analysis, infrared analysis and thermogravimetry. There is a possibility that some different structure elements are present in the chains like oxadiazole rings, open triazole rings or even some unreacted hydrazide groups.

The elemental analysis gave: N: 18.57% (theor. 19.2%), C: 72.88% (theor. 76.7%), H: 4.23% (theor. 4.1%), rest 4.32% (theor. 0%).

Using infrared analysis it can be observed that the carbonyl stretching band at 1650 cm^{-1}, present in the initial polyhydrazide, has almost completely disappeared and that a C=N band has appeared at 1580 cm^{-1}.

The thermogravimetric weight loss of the product recorded at temperatures between 200 and 400°C due to possible cyclization of unreacted hydrazide groups[11] is less than one percent indicating that at least 90% of the initial hydrazide groups have reacted either to triazole rings or oxadiazole rings[8].

membrane preparation

Polymer solutions of the polytriazole were made by dissolving the polymer in formic acid at room temperature. The concentrations varied from 15 - 25 % polymer by weight. The solutions were filtered over 5 μm filters to remove inhomogeneities. Thin films were cast on a glass plate using a casting knife of 0.15 mm slit height. Homogeneous films were obtained by evaporating the solvent at 80°C in a nitrogen atmosphere. The films were removed from the glass plate with a little water. Finally the membranes were dried in a vacuum oven at 150°C for at least 24 hours. The thickness of the films varied between 20 and 30 μm.

chemical stability

Small pieces of homogeneous films were exposed for a period of 30 days to the following conditions: hot air at 275°C, boiling water, pH-range of 1-13 and a chlorine solution of 10%. The effect of these exposures upon the films was studied both visually and using infrared analysis.

gas permeation experiments

The flat sheet membranes were placed in Millipore dead-end filtration cells sealed with Viton rubber rings. The cells were put in an oven . The cells could be fed with pure gases at pressures not exceeding 7 bar. The permeate flow was measured with soap film capillaries with capillary radius of 0.5 mm. A schematic representation of the experimental

set-up is given in figure 5.2.
The following pure gases were used: O_2, N_2, CO_2, CH_4 and He. The temperature of the oven could be raised till 200 °C and its course was registrated with a thermocouple.

The permeability P is calculated using the following formula:

$$P_i = Q_i.l/(A.\Delta p) \qquad (1)$$

were Q_i is the measured flow of gas i (cm^3/sec), l is the thickness of the film (cm), A is the membrane surface area (cm^2) and Δp is the pressure difference across the membrane (cmHg). The ideal selectivity is defined as the ratio of the pure component permeabilities:

$$\alpha_{id} = P_i/P_j \qquad (2)$$

CO_2/CH_4- separation measurements
On a different type of equipment membranes could be tested using gas mixtures of CO_2 and CH_4. A schematic representation of this installation is given in figure 5.3.

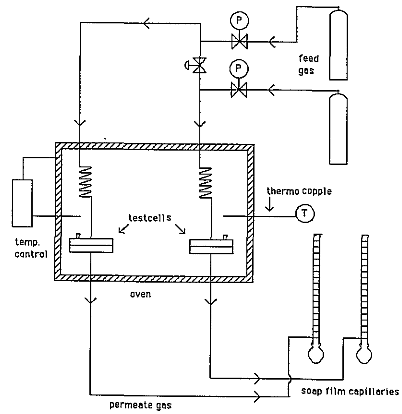


Figure 5.2: Equipment for the permeation measurements of single gases

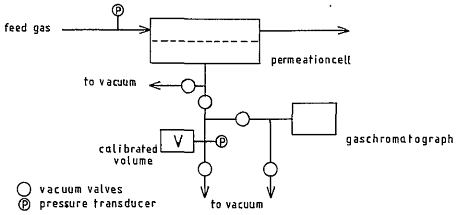


Figure 5.3: Equipment for the gas separation measurements of CO_2/CH_4 gas mixtures

The flux is determined by evacuating the downstream side of the membrane cell and accurately measuring the pressure increase with time in a calibrated volume. The permeability P_i is calculated using the following formula:

$$P_i = ((\Delta p/t).V.x_{i,p})/(A.p.x_{i,f}) \qquad (3)$$

where $\Delta p/t$ (cmHg/sec) is the pressure increase per unit of time in the permeate chamber, V the calibrated volume (cm^3), A the membrane surface area (cm^2), p the feed pressure (cmHg) and $x_{i,f}$ and $x_{i,p}$ are the partial molarities of component i in the feed and in the permeate respectively.

The selectivity is determined using gas chromatography and it is defined as the quotient of the molar ratios in permeate and feed respectively:

$$\alpha = (x_i/x_j)_p / (x_i/x_j)_f \qquad (4)$$

The films were tested at 3 bar pressure difference, at room temperature and with gas mixtures containing 20% CO_2 and 80% CH_4 (molar ratios).

5.3 Results and discussion

influence of time

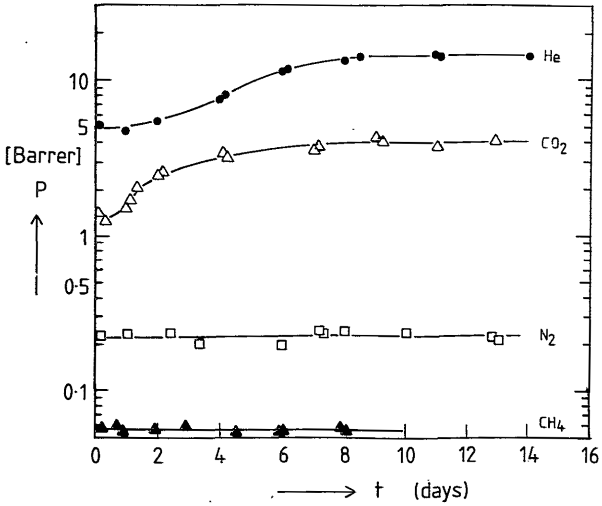


Figure 5.4: *Pure gas permeabilities for several gases each measured with a freshly prepared polytriazole membrane as a function of time, at 50 °C and 6 bar pressure difference.*
1 Barrer = 10^{-10} cm^3(STP).cm.cm^{-2}.s^{-1}.cm Hg^{-1}

In figure 5.4 the permeabilities of He, CO_2, CH_4 and N_2 are presented as a function of time using freshly prepared membranes. During the first days of the experiment an increase in permeability by more than a factor 2 is observed for the faster permeating gases, He and CO_2. The increase in permeability of the slowly permeating gases, CH_4 and N_2 ,is almost nil in a period of fourteen days. After this initial conditioning period the permeabilities become constant and remain constant for at least two months as figure 5.5 illustrates; here the permeabilities for several pure gases are shown measured with the same membrane at a temperature of 41 °C.

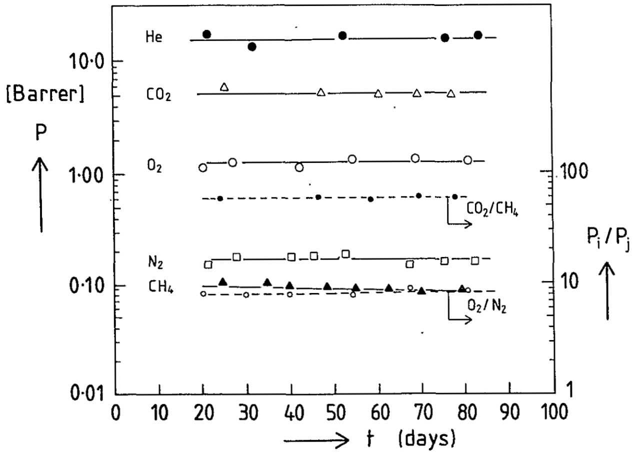


Figure 5.5: *Pure gas permeabilities for several gases all measured with the same membrane after a conditioning period of fourteen days as a function of time, at 41 °C and 6.0 bar pressure difference*

This initial increase in permeability can be explained either by a slow replacement of solvent or water molecules present in the initial film by the fast permeating gas molecules or by a relaxation phenomenon of the polymer or a combination of both. The influence of a thermal treatment at a high temperature on this initial behaviour of the membrane permeabilities will be discussed below.

influence of temperature

Figure 5.6 shows the influence of the temperature on the permeabilities and the ideal selectivity of He and N_2.

Increasing the temperature up to 200°C leads to a considerable increase in the permeability and a decrease in the ideal selectivity from about 120 at room temperature to about 25 at

200°C. The same type of behaviour is presented for O_2 and N_2 in figure 5.7. The ideal selectivity for the O_2/N_2 separation at room temperature, being about 10 is rather high compared with other polymers[15] but it decreases to about 3 at 200°C, which is still reasonable considering the higher permeabilities.

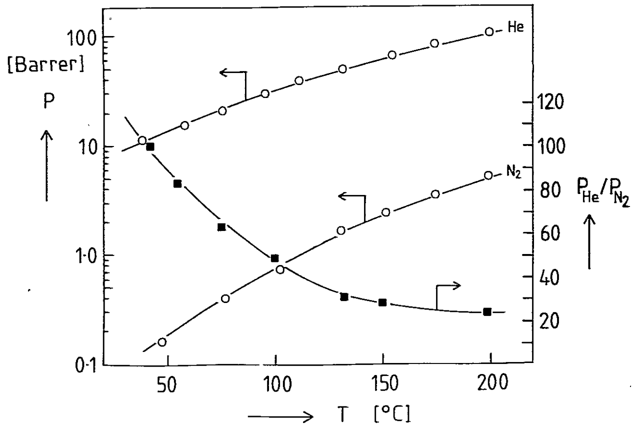


Figure 5.6: *He and N_2 permeabilities and the ideal selectivity measured with a conditioned polytriazole membrane as a function of temperature*

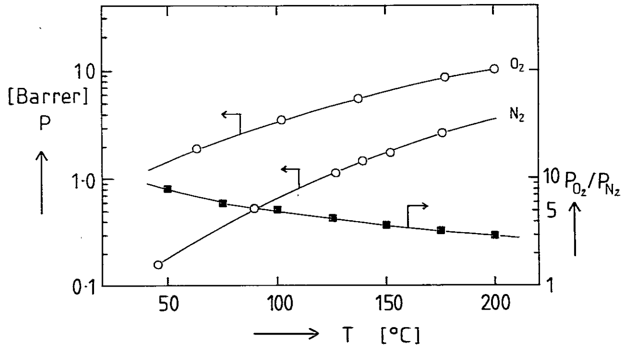


Figure 5.7: *O_2 and N_2 permeabilities and the ideal selectivity measured with a conditioned polytriazole membrane as a function of temperature*

From the permeation vs. temperature data Arrhenius plots can be derived. In figure 5.8 the Arrhenius plots are presented showing straight lines with high correlation coefficients for the three gases studied indicating that the pure gas permeation of He, O_2 and N_2 follows an

Arrhenius behaviour.

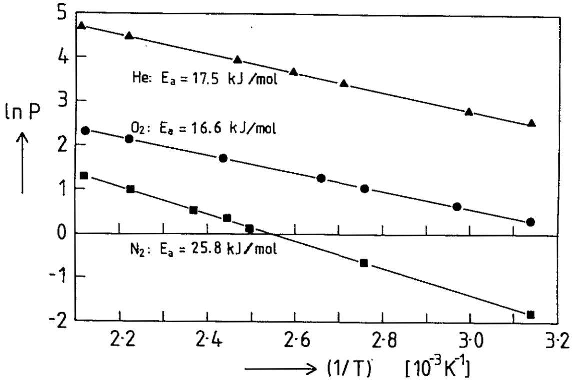


Figure 5.8: Arrhenius plots for He, O_2 and N_2 permeabilities measured with conditioned polytriazole membranes.

The energies of activation for the He, O_2 and N_2 permeation calculated from the slopes are 17.5, 16.6 and 25.8 kJ/mole respectively, which values are in the same order of magnitude as the energies of activation for diffusion in amorphous polymers[12].

CO_2/CH_4- separation

Figure 5.9 gives a selectivity-permeability-plot for homogeneous films of the following commercial polymers: Polysulfone (P3500, Udel), Polyethersulfone (Victrex, ICI), Polyphenyleneoxide (General Electric) and Polyetherimide (Ultem, General Electric), all measured using the same CO_2/CH_4-separation equipment and under the same conditions[13]. The values for Kapton polyimide are obtained from literature[14].

The results for the polytriazole films are presented in the shaded rectangle. Compared to the above mentioned polymers the polytriazole membrane possesses an excellent selectivity and a reasonable CO_2-permeability. Especially if we compare the CO_2-permeability with that of Kapton which is also a thermally stable and chemically resistant polymer the difference is striking. Although the reproducibility of the selectivity was good the measured permeabilities sometimes differed by a factor 2. These variations might be caused by an effect of CO_2-conditioning since the films that had first been tested on the single permeability equipment showed higher CO_2-gas fluxes while freshly prepared films showed lower fluxes. Besides this conditioning reproducibility of the permeability it can be observed that the measured CO_2 permeabilities using this CO_2/CH_4-separation equipment are at least a factor 2 higher than the measured permeabilities using the single gas permeation equipment. We believe this to be caused by the difference in the permeate pressure and/or the experimental technique of measuring the permeate fluxes.

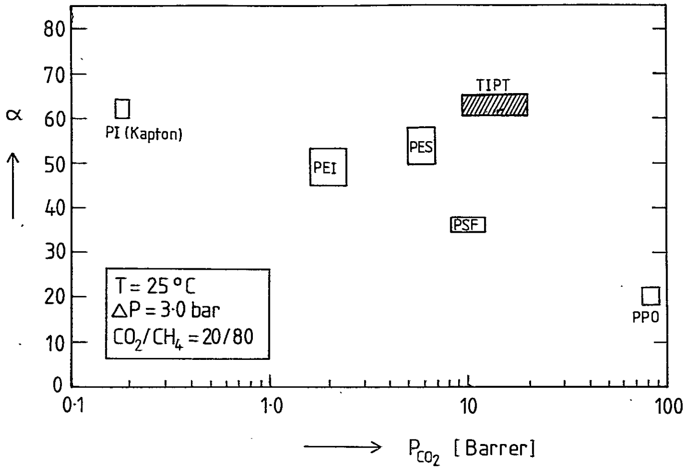


Figure 5.9: *Permeability-selectivity plot for the separation of CO_2/CH_4 mixtures (20/80) measured with flat sheet homogeneous membranes for several different polymers, at 25°C and 3.0 bar pressure difference.*

Thermal treatment of the films

After permeation measurements at 200°C some shrinkage of the membranes was noticed which sometimes lead to leakage of the membranes at the edges. In order to prevent this the films were pre-shrunk by giving them a thermal treatment of one hour at 295°C following Holsten and Lilyquist[9] who performed such a treatment to their polytriazole fibers. Another motivation for giving the membranes a thermal treatment is the completion of possibly unfinished ringclosure reactions. Since we are dealing with a thermally stable and chemically resistant polymer it is important for the final stability that all the hydrazide groups present in the initial polyhydrazide have been closed to a ring, either a triazole or an oxadiazole ring. It is questionable however if such a short thermal treatment is sufficient to finish these very last ring closures considering the prolonged heating times and elevated temperatures reported in the chapters 2 to 4 for completion of the polyhydrazide conversion.

In table 5.1 the effects of the thermal treatment on some film properties are represented. It is very striking to notice the enormous shrinkage of the film by about 20%. This shrinkage however does not seem to affect the gas permeability values. Almost the same values are obtained for membranes with or without a thermal treatment.

Property	before	after
volume(a)	Vo	$0.8V_o \pm 0.08V_o$
weight(b)	w_o	$0.9w_o \pm 0.04w_o$
density(c) (g.cm-3)	1.243	1.234
Tg (°C) (d)	270.4	275.6
P(He)(e)	14.0	14.5 Barrer
$P(N_2)$	0.2	0.2 "
$P(CO_2)$(f)	8.9	9.2 "
α (CO_2/CH_4)	62.5	60.5 "

(a):determined by measuring the dimensions
(b):determined by thermo gravimetrical analysis
(c):determined using a density gradient column of tetrachloro-methane and 2-ethyl-isohexanol
(d):determined by differential scanning calorimetry at 20°C/min.
(e):determined on the gas permeation equipment at 50°C and 6 bar after conditioning
(f):determined on the CO_2/CH_4 separation equipment at 3 bar pressure difference

Table 5.1: *Properties of a homogeneous polytriazole film before and after a heat treatment at 295 °C for one hour.*

The effect of the heat treatment on the initial permeability values is illustrated in figure 5.10 where it can be seen that the membranes which have had the thermal treatment show a considerable shorter conditioning time and a final constant permeability value which is equal to the value of the conditioned membranes without the heat treatment. The question now is raised about the nature of both the conditioning process and the thermal treatment.

In figure 5.11 DSC curves of the film before (curve b) and after (curve c) the thermal treatment and after a conditioning experiment with CO_2 gas permeation (curve d) are represented. Comparison of curves c and d shows clearly that there is a difference between these two treatments.

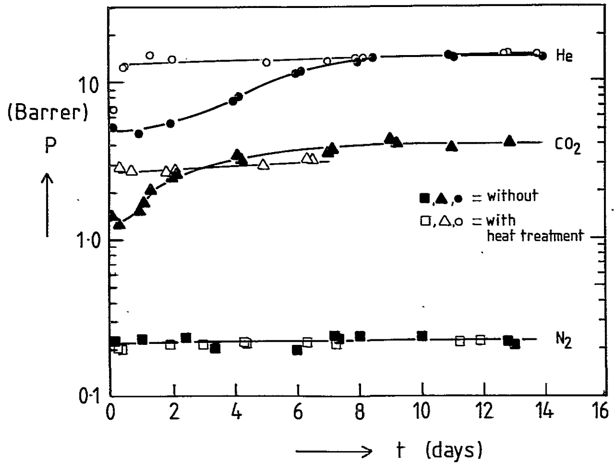


Figure 5.10: *Pure gas permeabilities for several gases each measured with a freshly prepared polytriazole membrane with(filled figures) and without(open figures) a thermal treatment at 295°C as a function of permeation time, at 50°C and 6 bar pressure difference.*

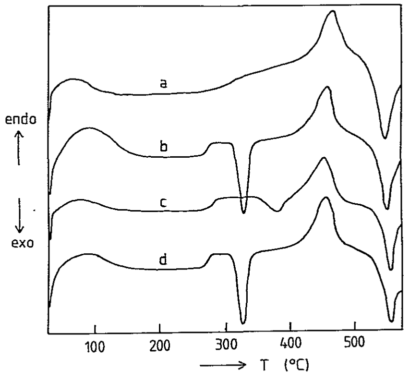


Figure 5.11: *DSC thermograms for the polytriazole powder (a), for a homogeneous polytriazole film before (b) and after (c) a heat treatment at 295°C and for a homogeneous film after CO_2 permeation during fourteen days(d)*

Compared with the thermogram of a polytriazole powder (curve a, the washed and dried reaction product) the thermograms of the films are different in two respects. Firstly the glass transition temperature of the films (~270°C) are about 25°C lower than the T_g for the powder (~295°C) and secondly the non heat-treated film does exhibit a sharp exothermic peak just after the glass transition which is not observed at all in the powder thermogram. This DSC behaviour of the film will be discussed in more detail in chapter 6 of this thesis.

After the thermal treatment of the film the sharp exotherm has shifted to higher temperatures and it has decreased in size. An explanation for this phenomenon might be that during the thermal treatment of the polymer film there has been some crystalline ordering in the polymer which is responsible for the decrease and shift of the exothermic peak during the subsequent DSC run. In this context the endothermic peak starting at about 400°C, which is present in all the DSC curves, possibly represents the crystalline melting. The powder does not show the exothermic peak when it already possesses crystallinity. With X-ray diffraction (WAXS ,wide angle X-ray scattering) indeed some small degree of crystallinity or ordering could be observed in the TIPT powder (see chapter 6).

While a thermal treatment probably causes some crystallinity in the polymer the CO_2 permeation obviously does not. It is not unreasonable to assume that the presence of traces of solvent and/or water plays some role in these phenomena. More research however is needed to fully understand the exact nature of this thermal treatment effect and of the nature of the conditioning process. A more detailed thermal analysis study of these polytriazoles will be discussed in chapter 6.

chemical stability

Table 5.2 shows the results from the chemical stability test performed with homogeneous films of the polytriazole studied.

Condition	Effect	
	visual	IR
Boiling water	no	no
275°C in air	no	no
pH range 1 - 13	no	no
chlorine solution(10%)	no	no
conc. HCl	brittle	bigger C=O peak at 1680 cm^{-1}

Table 5.2: Effect on a homogeneous polytriazole film after exposure to several severely agressive conditions

The effect on the films after exposure to several severely conditions was studied with infrared analysis (IR) and by observing the films visually. After a period of 30 days the films are only affected by the concentrated hydro chloric acid which clearly makes the films brittle.

5.4 Conclusion

The investigated polytriazole polymer combines good thermal stability and chemical resistance with processability. This polytriazole seems to be a promising polymer for gas separation, not only at ambient temperatures but also at elevated temperatures. High separation factors were found for CO_2/CH_4- and for O_2/N_2-separation with reasonable permeabilities compared to other thermally stable polymers. Increase in the temperature at which the permeation experiments are being performed leads to an increase in permeability and a decrease in selectivity. The permeabilities of the pure gases follow Arrhenius behaviour.

Newly prepared membranes show an initial increase in membrane performance when they are permeated with CO_2 and He in a dead-end permeation cell and atmospheric pressure at the permeate side. After this initial conditioning period the performance of the membranes can be maintained for a period of at least two months. An additional heat treatment for newly prepared membranes of 1 hour at 295°C makes the membranes shrink by about 20%, shortens the conditioning time but does not affect their final separation properties.

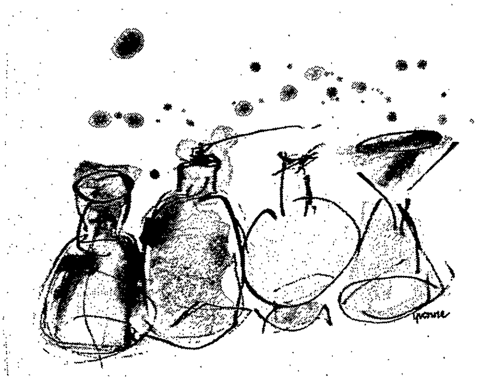
5.5 References

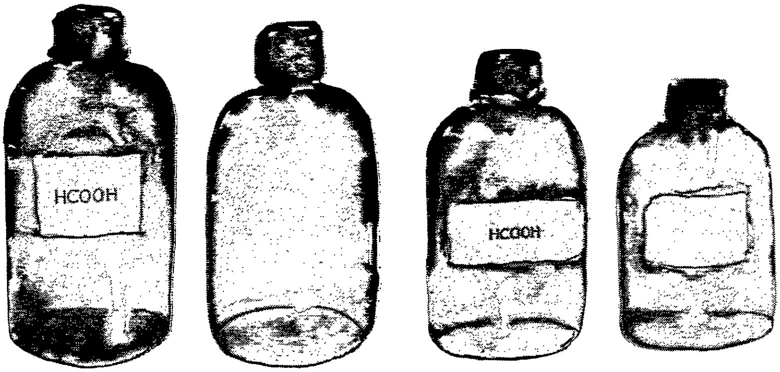
1] H. Strathmann, Desalination, 26 (1978) 85-91
2]. A. Iwama, Y. Kazuse, J.Membr.Sci. 11 (1982) 297-309
3] M.N.Sarbolouki, J.Appl.Polym.Sci., 29 (1984) 743-753
4] F.S. Model, H.J.Jones, J.E. Proust, in: S. Sourirajan (Ed.), Reverse Osmosis and Synthetic membranes, National Research Council Canada, 1977
5] L.C. Sawyer, R.S. Jones, J.Membr.Sci., 20 (1984) 147-166
6] R.L. Goldsmith, B.A. Wechsler, S. Hara, Desalination, 22 (1977) 311-333
7] P.E.Cassidy,' Thermally Stable Polymers: Synthesis and Properties',M.Dekker, New York 1980
8] J.R. Holsten, R.M. Lilyquist, J.Polym.Sci., A3 (1966) 3905
9] R.M. Lilyquist, J.R. Holsten, J.Polym.Sci., C19 (1967) 77
10] U.S.Patent 3,318,728 (Monsanto Co.)(1967)
11] A.H. Frazer, F.T. Wallenberger, J.Polym.Sci.,A2 (1964) 1137
12] J. Crank, G.S.Park (Eds.),"Diffusion in Polymers", Academic Press, London 1968

13] P.Kamps, internal report, University of Twente (1987)

14] R.T.Chern, W.J.Koros, H.B.Hopfenberg, V.T.Stannet in "Material Science of Synthetic Polymer Membranes" Ed. D.R.Lloyd, A.C.S. Symp. Ser. 269 (1985) p25

15] O.J.Sweeting (Ed.): 'The Science and Technology of Polymer Films',Vol.2, Wiley, New York 1971




HCOOH
HCOOH

Chapter 6 Thermal behaviour of polytriazole films. A thermal analysis study

B.Gebben, M.H.V.Mulder, C.A.Smolders

Summary

The thermal behaviour of poly(1,3-phenyl-1,4-phenyl)-4-phenyl-1,2,4-triazole has been investigated using differential scanning calorimetry (DSC) and thermogravimetry (TG). Processes are studied for this thermally stable polymer that take place between 200 and 500°C. While the polycondensation reaction product in powder form appeared to be partially crystalline, films prepared by casting from a formic acid solution appeared to be completely amorphous. A thermal treatment between T_g (~270°C) and T_m (~430°C) can introduce crystallinity in the films because of the polymer's ability to cold crystallinity. The cold crystallization temperature T_c seems to be dependent on the preparation history of the solid polymer phase. Thermal annealing of the films just below T_g does not introduce crystallinity but inhibits subsequent cold crystallization at higher temperatures. crystallization upon cooling from the crystalline melt has not been observed either. At temperatures just above the crystalline melting point the polymer starts to decompose in an exothermic reaction.

6.1 Introduction

Aromatic poly-4-phenyl-1,2,4-triazoles form a group of polymers known for their thermal and chemical stability[1,2]. The polymers are known since the early sixties and can be prepared in different ways[3-5]. The most successful preparation route was developed by Holsten and Lilyquist[6,7]. They developed a two stage preparation route which involves the preparation of a prepolymer, an aromatic polyhydrazide, followed by a cyclization reaction of this prepolymer with aniline in polyphosphoric acid.

The preparation of fibers, films and coatings of polytriazoles have been reported in literature and patents[8,9]. Very recently the authors have successfully applied poly(1,3-phenyl-1,4-phenyl)-4-phenyl-1,2,4-triazole (TIPT) for the preparation of gas separation membranes with outstanding performance, described in the previous chapter.

Little attention has been paid in literature to the high temperature behaviour of these polytriazoles[7]. In this chapter a thermal analyses study of the behaviour of poly(1,3-phenyl-1,4-phenyl)-4-phenyl-1,2,4-triazole (TIPT) above 200°C is described. The polymer preparation is described in the previous chapter according to the reaction scheme represented in figure 5.1. Different batches of the same polymer are prepared and used for the investigations. The techniques used are differential scanning calorimetry (DSC) and thermogravimetry (TG). A discrimination will be made between the behaviour of the polymer in powder and in membrane/film form and special attention will be paid to the effect of thermal history on the DSC behaviour of the films.

6.2 Experimental

materials

Terephtaloyl chloride was supplied by Merck and was recrystallized from hexane prior to use.

Isophtaloyl hydrazide was prepared according to Frazer[10] from isophtaloyl methyl ester and hydrazine hydrate (100%) both supplied by Merck. The isophtaloyl hydrazide was recrystallized from water, washed with methanol and dried prior to use.

Aniline was supplied by Merck and was used as received.

The solvents PPA (polyphosphoric acid), NMP and formic acid (98%) were supplied by Merck. The NMP was dried over molecular sieves of 3 Å.

polymer preparation

The prepolymer, poly(1,3-phenyl-1,4-phenyl)hydrazide (TIPH), was prepared according to Frazer[10] from terephtaloyl chloride and isophtaloyl hydrazide using a low temperature solution polycondensation reaction in NMP. A polymer was obtained with an inherent viscosity of 1.2 dl/g measured with a 0.5 g/dl. solution in DMSO.

The polytriazole was prepared from the polyhydrazide by reacting this polymer with aniline in PPA according to Holsten and Lilyquist[7]. Temperatures between 170 and180°C and reaction times of 2 to 5 days were used. The viscous reaction solution was poured in an excess of water and washed in a sodium hydroxide solution till neutrality. The precipitated polymer was extracted with ethanol using a Soxhlet extraction technique and afterwards dried in a stove at reduced pressure. Reaction conditions and specifications of the polymers used are given in table 6.1.

batch	T (°C)	t (hr)	η_{inh}^(a)^ (dl/g)	C/N^(b)^	C/H^(b)^	Δw^(c)^ (%)
TIPT1	175	160	1.2	4.06	17.63	1.38
TIPT2	180	48	0.9	4.16	17.62	0.57
TIPT3	172.5	180	1.3	4.03	18.30	0.58

(a) determined with a 0.5 g/100ml formic acid solution at 25°C
(b) determined using elemental analyses. Theoretical: C/N=3.99 and C/H=18.71
(c) weight loss determined using thermogravimetry at 20°C/min between 200 and 400°C

Table 6.1: Reaction conditions and specifications of the polytriazole TIPT batches used for the experiments.

Using infrared analysis it can be observed for all polymers that the carbonyl stretching band at 1650 cm^{-1} and the N-H band at 3350 cm^{-1}, present in the initial polyhydrazide, have almost completely disappeared and that a C=N band has appeared at 1580 cm^{-1}.

film preparation

Polymer solutions of the polytriazole were made by dissolving 15% polymer by weight in formic acid at room temperature. The solutions were filtered over filter paper and pressed through a 5 μm filter to remove inhomogeneities. Thin films were cast on a glass plate using a casting knife of 0.15 mm. slit height. Homogeneous films were obtained by evaporating the solvent at room temperature in a nitrogen atmosphere. The films were removed from the glass plate with a little water. Asymmetric porous membranes, were obtained by immersing the cast films into a water bath followed by washing. Finally all films were dried in a vacuum oven at 150°C for at least 24 hours. The thickness of the homogeneous films varied between 20 and 30 μm. Homogeneous films prepared from batch TIPT1 were used for the investigations on gas separation reported in the previous chapter.

Differential scanning calorimetry

A Perkin Elmer DSC Differential Scanning Calorimeter in combination with a System 4 microprocessor Controller and a Model 3700 Thermal Analysis Data Station (TADS) was used for DSC measurements. Nitrogen purge gas was purged through the sample

chambers at all times. The polymer samples were placed in aluminium sample pans which were sealed with perforated covers. Before each scan and before the weight determination the polymer sample was held isothermally at 200°C for 10 min. to remove adsorbed moisture. The runs were started from 200°C and, unless stated differently in the text, a heating rate of 20°C/min. and a cooling rate of 320°C/min. were used.
Peak enthalpies were calculated by the TADS system, and the T_g was defined as the midpoint temperature of the secundary transition.
The system was calibrated using Indium and Lead.

Thermogravimetry
A Perkin-Elmer TGS-2 Thermogravimetrical Analyser in combination with a System 4 Microprocessor Controller and a model 3700 Thermal Analysis Data Station were used for the TG experiments. During all experiments a nitrogen atmosphere was provided by a continuous gas flow of 85 ml/min. The scan rates are equal to the ones used for the DSC experiments.

6.3 Results and discussion

In figure 6.1 both the TG and the DSC curve are presented for polytriazole, in powder form, in the temperature range of 50 to 500°C. Below 100°C the first weight loss is observed which corresponds to a broad endothermic peak in the DSC curve representing the loss of adsorbed water. After this first weight loss the weight seems to be constant till about 450°C above which temperature a rapid and considerable weight loss sets in. This latter weight loss corresponds to an exothermic peak in the DSC curve and represents the thermal decomposition of the polymer.

In the temperature region in between these two weight losses the DSC curve reveals two further processes which do not seem to be coupled to simultaneous weight losses. A second order transition is observed at about 300°C and an endothermic peak at about 430°C just before the decomposition process sets in. The second order transition most probably represents the rubber-glass transition, the endothermic peak will be explained below.

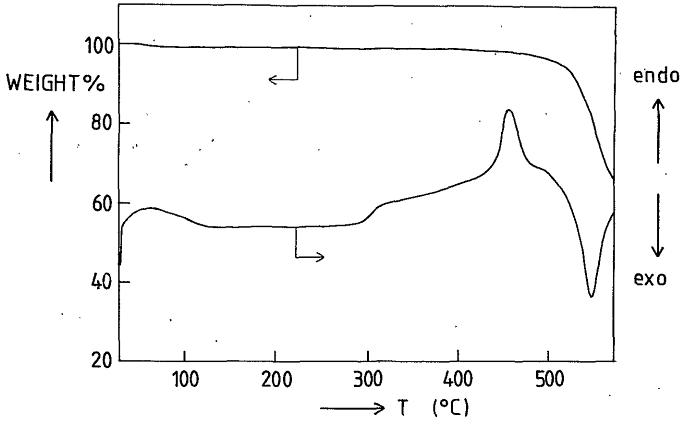


Figure 6.1: *TG and DSC curves for the polytriazole TIPT1 in powder form recorded at a heating rate of* 20°C/min.

Figure 6.2 compares the DSC curves for powder and homogeneous film in the temperature range between 240 and 460°C. A striking difference can be observed between both morphological forms concerning the glass transition and the occurrence of an exothermic peak for the film at 360°C.

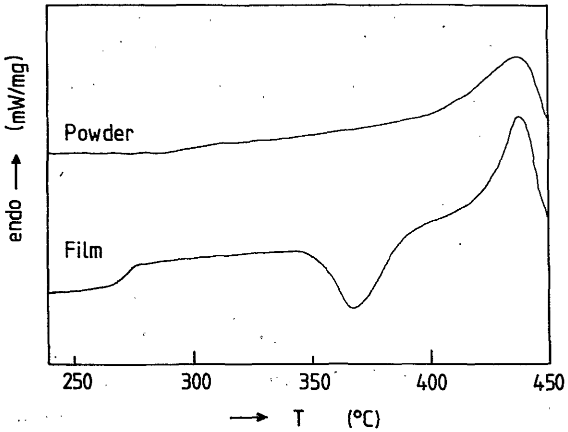


Figure 6.2: *DSC curves for TIPT2 in powder and in film form recorded at a heating rate of 20 °C/min.*

Compared to the polytriazole film possesses a much more distinct glass transition with a larger change in specific heat. Furthermore the film shows an exothermic peak at about 360°C which is completely absent in the powder curve. There is agreement however in the presence of an endothermic peak at about 430°C which can be found in both the powder and film curves. The same trend is observed for all investigated TIPT batches except for the exact temperature positions of the peaks, especially the exothermic peak. Temperatures and peak enthalpies found for the homogeneous films of the three batches are represented in table 6.2.

Batch	T_g (°C)	ΔC_p (J/g.K)	T_{exo} [(a)] (°C)	$-\Delta H_{exo}$ (J/g)	T_{endo} [(b)] (°C)	ΔH_{endo} (J/g)
TIPT1	269	0.155	333	26.0	427	27.7
TIPT2	271	0.189	368	17.6	422	18.9
TIPT3	268	0.164	328	23.9	422	23.1

(a) minimum temperature
(b) onset temperature

Table 6.2: Calorimetric properties of homogeneous films prepared from three TIPT batches determined using DSC

The DSC curve of the polytriazole film shows resemblance to DSC curves of polymers which undergo cold crystallization, like for example poly(ether-ether-ketone)[11]. In this context the exothermic peak represents the cold crystallization and the endothermic peak represents the crystalline melting.

With two simple DSC experiments this hypothesis of crystallization can be verified. The first experiment is to observe the dependency of the exothermic process on the applied heating rate. It is expected that the cold crystallization, which is a kinetic process, is strongly dependent on the scanning rate. Figure 6.3 shows a set of DSC curves for the TIPT1 film scanned at different heating rates, ranging from 10 to 80°C/min, from which a shift of the exothermic peak to higher temperatures with increasing heating rate can be observed. This shift is much stronger than is the case with the other processes which also show a slight shift to higher temperatures. This temperature shift is observed for all batches. For TIPT2, besides a shift, also a decrease in the peak enthalpies is observed. In figure 6.4 the enthalpies of the corresponding peaks for TIPT2 films are presented showing a considerable decrease in enthalpy with increasing heating rate.

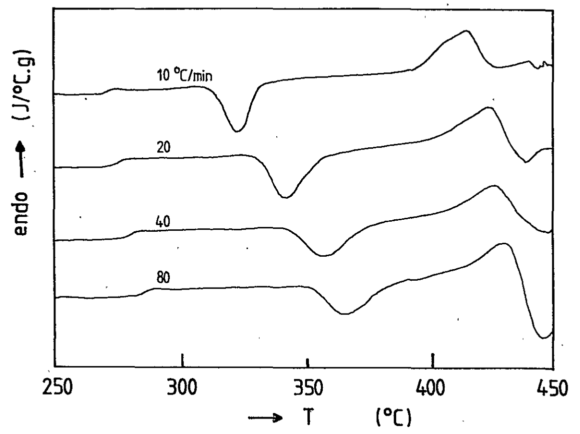


Figure 6.3: *DSC curves for TIPT1 film recorded at different heating rates.*

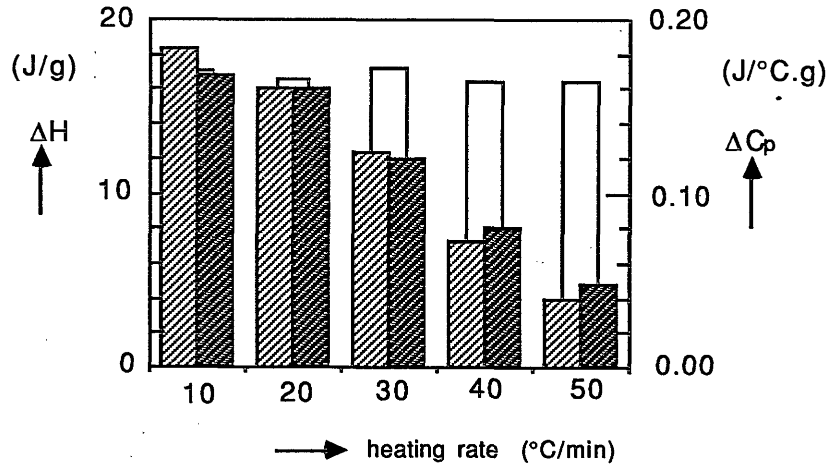


Figure 6.4: *Block diagram giving enthalpies of the exothermic (▨) and endothermic(▩) processes as well as the change in specific heat, ΔCp, at Tg (☐) determined for TIPT2 film using DSC at different heating rates*

The enthalpies of the exothermic and endothermic peaks follow the same trend and are more or less of the same decreasing value. The endothermic process therefore seems to be related to the exothermic process. The step change in specific heat at T_g, ΔC_p, is also presented in figure 6.4 and is not dependent on these heating rates.

Another experiment to investigate the possible crystallization phenomenon is to observe the glass-rubber transition, especially the magnitude of the step change in specific heat at T_g. This step change in specific heat is proportional to the mobile amorphous fraction of the polymer[12]. In figure 6.5 two consecutive runs are shown for TIPT2 powder. Just after the endothermic peak of the first run the sample is cooled very quickly to 200°C and run again. If the endothermic peak represents crystalline melting and no crystallization takes place upon rapid cooling then the amorphous fraction of the polymer sample should have been increased and consequently a larger step change in specific heat at T_g should be observed. This is indeed the case as figure 6.5 clearly illustrates. Further it can be observed that run 2 for the powder now shows an exothermic peak at 360°C analogous to the film curves.

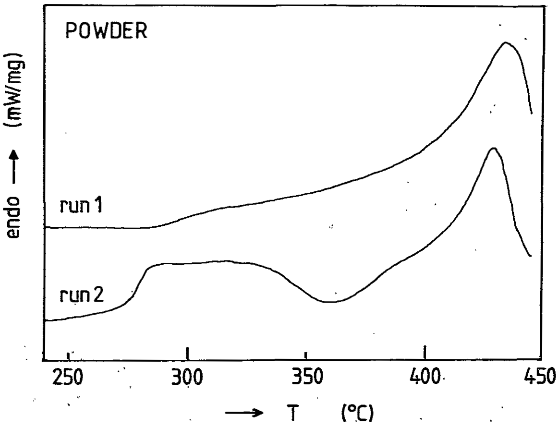


Figure 6.5: DSC curves of two consecutive heating runs for TIPT2 powder.

Figure 6.6 shows two consecutive heating runs for a film sample where run 1 is stopped just after the exothermic peak upon which the sample is cooled again. Now run 2 shows a smaller step change at T_g indicating that the amorphous fraction has decreased because of the exothermic process in run 1.

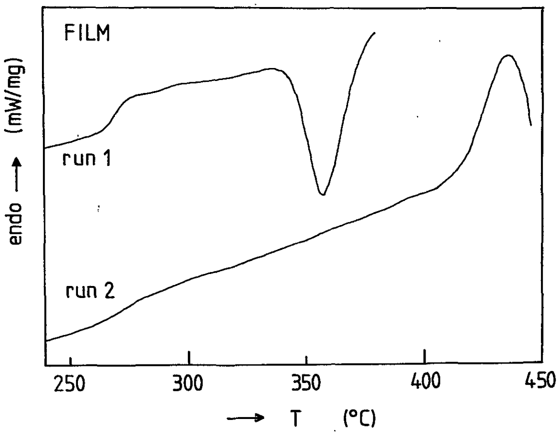


Figure 6.6: DSC curves of two consecutive heating runs for TIPT2 film

Both these observations and the heating rate dependency strongly confirm the crystallization behaviour. Quantitative data are collected in table 6.3.

Sample (TIPT2)	run nr.	T_g (°C)	ΔC_p (J/g.K)	x_a (%)	T_c (°C)	$-\Delta H_{exo}$ (J/g)	ΔH_{endo} (J/g)
Powder	1	291	0.046	24	-	0.0	21.0
	2	275	0.189	100	361	9.7	9.7
Film	1*	271	0.189	100	368	17.6	-
	2	271	0.059	31	348	0.0	18.1

*run till 390°C

Table 6.3: Calorimetric properties of TIPT2 powder and a homogeneous TIPT2 film determined using DSC for two subsequent heating runs from 200 till 445°C with a heating rate of 20°C/min.; x_a is the fraction amorphous polymer.

These DSC observations indicate that the original powder form of the polymer is partly crystalline whereas the films seem to be amorphous. The occurrence of crystallinity in the powder samples can be confirmed using X-ray diffraction. Figure 6.7 shows the diffraction spectra for TIPT1 powder and film, showing qualitatively the existence of crystalline regions in the powder whereas no crystallinity can be observed for the film.

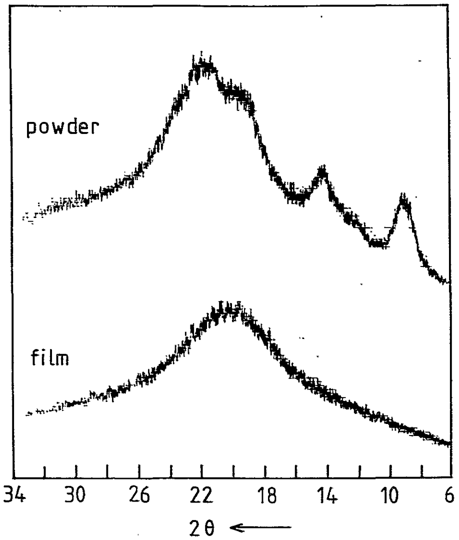


Figure 6.7: X-ray diffractograms of TIPT1 powder and film

From the step change in specific heat at the glass-rubber transition, ΔC_p, the amorphous fraction, x_a, can be calculated using the ΔC_p value of 0.189 J/g.K of the amorphous material[12]. These results are also presented in table 6.3. It is disputable to calculate the fraction of crystalline material from the heat capacity jump since most semi-crystalline polymers can not simply be considered to be composed of crystalline and amorphous regions[12]. The so called rigid amorphous phase, which does not exhibit a distinct change at T_g, has also to be taken into consideration. This rigid amorphous phase can form a considerable fraction in the polymer and can even be higher than the mobile amorphous fraction, which causes the jump in specific heat at T_g[12]. The crystalline fraction therefore can not be calculated from ΔC_p but it must be smaller than $(1-x_a)$.

Since melting and crystallization are reversible processes they are expected to reappear if the heating cycles are repeated. Figure 6.8 shows that the consecutive heating runs 2, 3 and 4 of TIPT2 powder all show both the exothermic and the endothermic peak. The surface area under the peaks, which is proportional to the polymer fraction involved in the process, has decreased with every run. Obviously the ability to crystallize or the fraction that is able to crystallize decreases after repeated melting. The same behaviour is observed for the film samples and is valid for all batches.

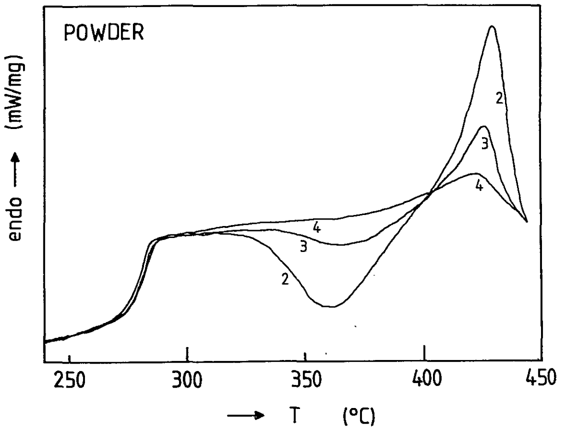


Figure 6.8: DSC curves of 3 consecutive heating runs for TIPT2 powder, respectively run numbers 2, 3 and 4

If we take a closer look at the endothermic peaks e.g. in figures 6.1, 6.2 and 6.8 it appears that just after the peak maximum the heat capacity drops strongly towards the exothermic side so that it seems that an exothermic process is starting just after the melting process. As pointed out before this might be the start of a decomposition process. This process might influence the kinetics of the cold crystallization in such a way that after repeated melting the fraction that crystallizes becomes less. Nevertheless this repeated melting obviously does not affect the glass-rubber transition temperature, as can be seen in figure 6.8. Hence no severe degradation may be expected.

Not only the homogeneous films prepared by evaporation appear to be amorphous, also the asymmetric porous membranes and powders prepared from formic acid solutions by immersion precipitation in water show an amorphous behaviour. In figure 6.9 the DSC curves are presented of these differently prepared samples. The temperature position of the cold crystallization peaks seems to be dependent upon the sample preparation method. For the powder sample the crystallization immediately follows the glass-rubber transition. Also the temperature position of the melting peaks are different, perhaps indicating different crystal structures. Obviously the preparation history of the sample influences the cold crystallization process.

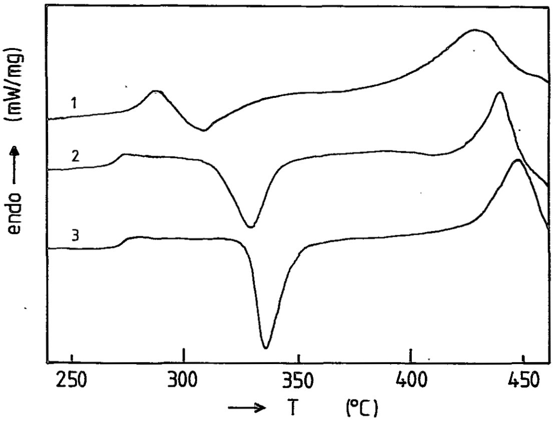


Figure 6.9: *DSC curves for TIPT3 samples prepared from the same formic acid solution: a powder, by pouring in water (curve 1), a porous film by immersing in water (curve 2) and a homogeneous film prepared by evaporation of solvent (curve 3).*

The fact that amorphous TIPT films have the ability to cold crystallize makes it possible to give the initially amorphous films of this polymer a certain crystallinity through a thermal treatment at a temperature above the glass transition temperature. Holsten and Lilyquist[7] gave their polytriazole fibers a treatment of one hour at 295°C and analogously the polytriazole membranes (TIPT1), used in the previous chapter, were given the same thermal treatment. Figure 6.10 shows the effect of such a thermal pretreatment on TIPT1 and TIPT2 homogeneous films.

In both pretreated films the exothermic peak enthalpy has decreased while the endothermic peak enthalpy has remained unchanged, indicating that the thermal pretreatment has indeed introduced some crystallinity. Because of the higher T_c of polymer TIPT2 the same treatment has introduced relatively less crystallinity. In both cases however the one hour treatment has been insufficient to render the polymers their maximal crystallinity. Longer times or higher temperatures, depending on their T_c values, will be necessary to render the membranes their maximal crystallinity.

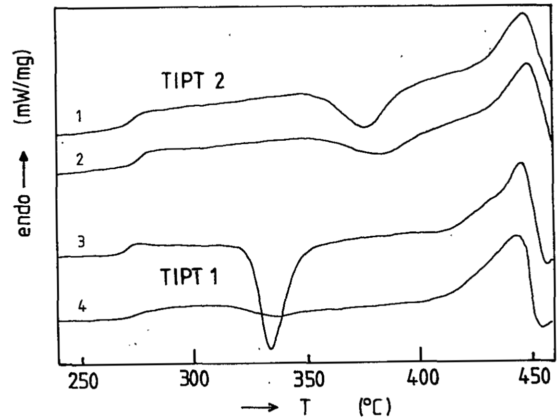


Figure 6.10: DSC curves for homogeneous films of TIPT1 and TIPT2 without a thermal pretreatment (curves 3 and 1) and after a pretreatment of one hour at 295 °C (curves 4 and 2).

The influence of annealing TIPT films at a temperature below T_g is shown in figure 6.11, where DSC curves are shown for a TIPT2 film after different annealing times at 265°C. It can be observed from this figure that a so-called specific heat hysteresis peak or a relaxation endotherm appears at the glass-rubber transition, which is also observed for other amorphous polymers, such as poly(ethylene terephtalate) and polycarbonate, upon physical aging[13,14].

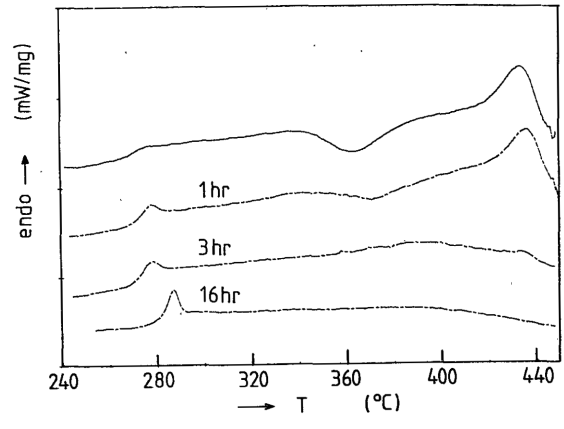


Figure 6.11: DSC curves for TIPT2 films before and after annealing at 265 °C for several annealing times

In general during annealing and physical aging an amorphous polymer undergoes relaxation towards thermodynamic equilibrium of the glassy state. With increased annealing time of the TIPT2 films, the endothermic peak area at T_g and the T_g itself increase but surprisingly the crystallization and melting endotherm resolve. After 3 hours annealing time no crystallization and melting are observed anymore. The jump in specific heat at T_g is in the order of what is usually found for the amorphous state, so the polymer is still expected to be amorphous after annealing.

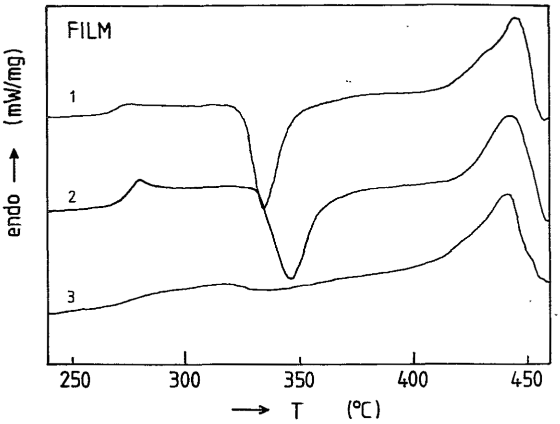


Figure 6.12: DSC curves for TIPT1 films before (curve 1) and after annealing at 265 °C for 16 hours (curve 2) compared to the one hour pretreatment at 295 °C (curve 3)

The DSC curves of TIPT1 upon annealing are presented in figure 6.12. TIPT1 upon annealing also shows an increase in the T_g and an endothermic peak at T_g but instead of resolving crystallization peaks only an increase in T_c is observed (curve 2). Obviously upon annealing the films do not become noticeably more crystalline but do crystallize more difficultly upon subsequent heating. This phenomenon can not be explained satisfactorily yet by the authors.

In addition to the DSC experiments described above the same polymer treatments were also followed with thermogravimetry. Figure 6.13 shows the TG curves for the 4 consecutive heating runs of TIPT2 powder (see DSC curves in figures 6.5 and 6.8). During run 1 a steady weight loss of about 0.5% is observed between 210°C and 390°C followed by another additional weight loss of 0.5% till the scan is stopped at 445°C and the sample is cooled. This weight loss process can not be observed in any heat effect during DSC runs possibly because it is too slow and steadily. After the first run no weight loss is observed in subsequent runs in the range till 400°C and after 400°C only a very small weight loss of about 0.1% is observed with every run. This last small weight loss is only the beginning of a much bigger weight loss after 445°C and represents possibly the beginning of the polymer decomposition. The weight losses in the temperature range between 200 and 400°C are presented in table 6.1.

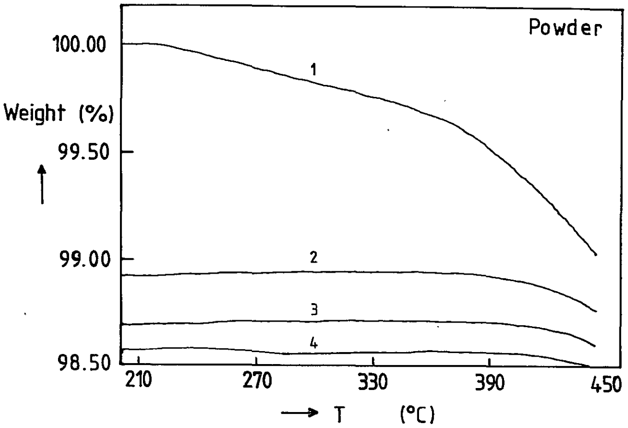


Figure 6.13: TG curves of 4 consecutive heating runs for TIPT2 powder from 200 till 445 °C.

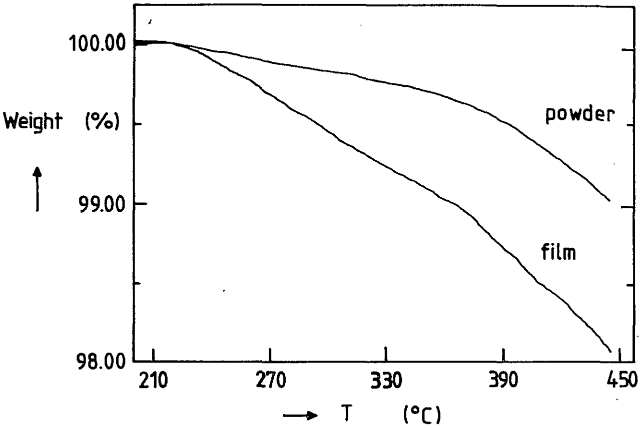


Figure 6.14: TG curves for the first heating runs of TIPT2 powder and film of which the DSC curves are shown in figure 6.9

The film samples show exactly the same trend in the TG curves of the consecutive heating runs, although the weight loss during the first run is in all cases a little higher than is the case for the powder as can be seen in figure 6.14.

There are several possibilities to account for the processes which cause weight loss during the first heating run. It can be the loss of strictly bound solvent, water or impurities, like reaction residues, from the polymer matrix. It could also represent a final cyclization reaction either to triazole or to oxadiazole rings (see figure 6.15) which can be expected in case the polymer preparation reaction was incomplete.

The oxadiazole ring closure reaction in the solid state is known to occur at temperatures higher than 250°C like is shown in chapter 2 to 4. Especially the last groups, which are difficult to bring to a closure because of the strongly reduced mobility of the chains, are expected to do so above 300°C. The same may be expected for the triazole cyclization. The decomposition of endgroups or other groups which might be unstable in this temperature range is another possibility. However the loss of solvent or water seems to be the most probable explanation for the weight loss starting already from 210°C. In case of the films the higher weight loss might be caused by an additional loss of traces of formic acid from which the films have been cast.

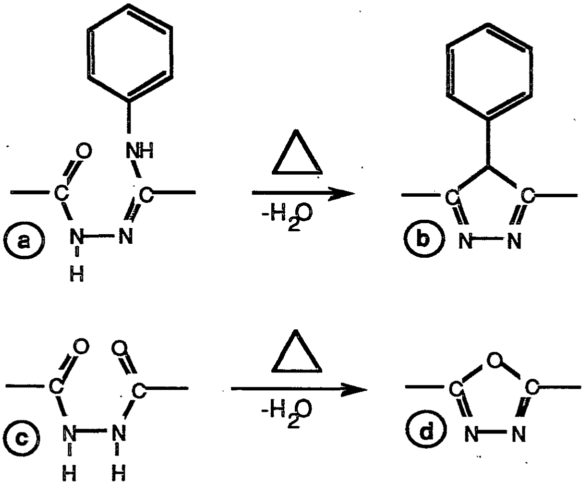


Figure 6.15: Schematic representation for possible final ringclosure reactions inside an incomplete polytriazole chain, respectively a triazole cyclization (a to b) and an oxadiazole cyclization (c to d).

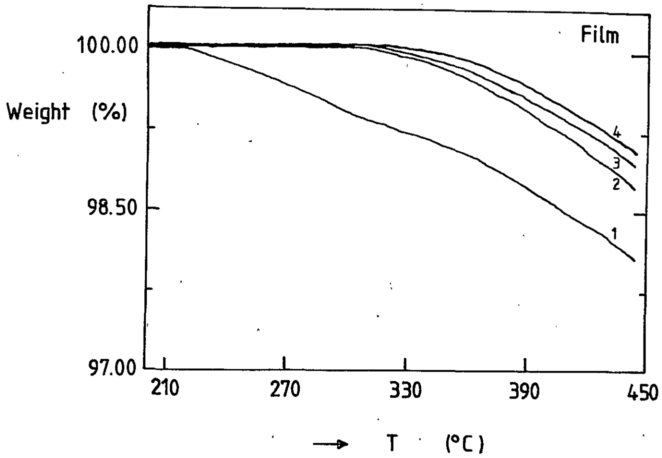


Figure 6.16: *TG curves for of TIPT2 film before (curve 1) and after some thermal pretreatments, respectively one hour at 265 °C(curve 2), 16 hours at 265 °C (curve 3) and one hour at 295 °C (curve 4).*

All thermal pretreatments for homogeneous films, which were discussed above, result in a reduced weight loss in the investigated temperature range, as shown in figure 6.16. During both pretreatments, either above or below T_g, the polymer film obviously undergoes a process that leads to weight loss in the temperature range between 200 and 400°C. Despite this effect we know from the DSC experiments that the treatment above T_g induces crystallinity while the treatment below T_g does not.

The possible loss of solvent or water could account for the inhibition of the cold crystallization process observed after the heat treatment below T_g. Additional analysis techniques of the volatilization products will be necessary for a better understanding of the weight loss processes that take place during these thermal treatments. Radio active labelling of formic acid might be an interesting possibility.

6.4 Conclusions

The polymer poly(1,3-phenyl-1,4-phenyl)-4-phenyl-1,2,4-triazole can be considered to be a semi-crystalline polymer. While the polycondensation reaction product is partially crystalline, films prepared from formic acid solution, either by evaporation or immersion precipitation in water, appear to be completely amorphous. Because the polymer is able to cold crystallize, the films can be partly crystallized by a heat treatment between the glass-rubber transition temperature and the melt temperature. The cold crystallization temperature of the amorphous films was different for all batches and appeared to be influenced by the preparation history. Upon rapid cooling from above T_m and upon annealing the films at temperatures just below the glass transition temperature for periods of 16 hours no crystallization in the films was observed. The latter treatment however inhibits subsequent cold crystallization of the films. After repeated melting the polymer samples also loose their ability to cold crystallize. An exothermic reaction is observed just after the crystalline melting process at 430°C representing possibly the beginning of polymer decomposition.

Thermal pretreatments either shortly above or below T_g are accompanied by a small weight loss of about 1%, which takes place between 200 and 400°C.

6.5 References

1] P.E. Cassidy,"Thermally Stable Polymers", Marcel Dekker, NewYork,1980
2] R.J. Cotter, M.Matzner, Organic Chemistry, Vol 13-B1 "Ring-Forming polymerizations",Part B1, Academic Press, New York, 1972
3] C.H.Abshire, C.S.Marvel, Macromol.Chem.,44/46, 338(1961)
4] M.Saga, T.Shono, J. Polym. Sci.,B, 4, 869(1966)
5] P.M.Hergenrother, Macromolecules, 3(1), 10(1970)
6] J.R.Holsten, M.R.Lilyquist, J.Polym.Sci.,A3,3905(1965)
7] M.R.Lilyquist, J.R.Holsten, J.Polym.Sci., Part C,19, 77(1967)
8] M.R.Lilyquist, J.R.Holsten, Belg.Patent 645,926(Monsanto Co.)(1964)
9] M.R.Lilyquist, U.S.Patent 3,318,728 (Monsanto Co.)(1967)
10] A.H.Frazer, F.T.Wallenberger,J.Polym.Sci.,A2,1137(1964)
11] P.Cebe, S.Hong, Polymer,27, 1183(1986)
12] J.Menczel, B.Wunderlich, Polym. Prepr.,1,255(1986)
13] J.Menczel, B.Wunderlich, J.Polym.Sci.:Polym. Lett.Ed.,19,261-264(1981)
14] H.Keskkula, D.R.Paul, J.Appl.Polym.Sci.,31,941-950(1986)

Summary

This thesis concerns the preparation of membranes from thermally stable and chemically resistant polymers. Two polymer families from the category of heterocyclic and aromatic polymers have been selected for investigation, the polyoxadiazoles and the polytriazoles, respectively. A major problem concerning these types of polymers is their bad processability due to their insolubility and infusibility. For the polyoxadiazoles this problem is circumvented by using a two-step preparation process through the preparation of a processable prepolymer membrane followed by a thermal conversion of the prepolymer into the desired polyoxadiazole. For the polytriazoles solubility is acquired by using a phenylated form of a polytriazole backbone.

In chapter 1 a general introduction is given on membranes and thermally stable polymers, including a short review on polyoxadiazoles and polytriazoles.
Chapters 2 to 4 describe the thermal conversion of the prepolymer, polyhydrazide, into a polyoxadiazole. This conversion reaction, which takes place in the solid state, includes a cyclo dehydration reaction of the hydrazide groups into oxadiazole rings. The kinetics of this cyclo dehydration process are followed using thermogravimetry (TG).
In chapter 2 dynamical thermogravimetry is applied to obtain the kinetic parameters of the conversion reaction. For the dynamical method polyhydrazide samples are heated with constant heating rates from 200 till 450°C. Poly(1,3-phenyl- 1,4-phenyl)-hydrazide in powder form and in the form of a homogeneous membrane was used for the investigations. For the evaluation of the kinetic parameters a method developed by Ozawa was used for which a set of different heating rates is needed. This method allows the calculation of the kinetic parameters at any degree of conversion so that the process(es) or changes in the process(es) can be followed throughout the whole conversion reaction. In this way two parallel processes besides the cyclo dehydration were observed, one in the very beginning probably representing simultaneous loss of solvent residues, and one at the end of the conversion process possibly representing a decomposition or degradation reaction.
In chapter 3 isothermal thermogravimetry is discussed. Following the conventional isothermal method the polymer is brought at a constant temperature and the degree of conversion is followed in time. Using a set of isotherms at several temperatures and assuming an Arrhenius behaviour the kinetic parameters for the isothermal conversion have been calculated. The second order isotherms showed straight lines with a breakpoint at a

certain degree of conversion. This is explained in terms of a rubber-glass transition which the polymer undergoes upon conversion from a flexible polyhydrazide to the more rigid polyoxadiazole. Distinctly different kinetic parameters were found for the areas before and after the breakpoints. Besides an influence of the physical state of the sample on the conversion kinetics also a remarkable difference between the two tested morphological states, powders and films, was observed. As a mechanism for the rate determining step in the conversion process a rotation of segments in the polyhydrazide chain is proposed.

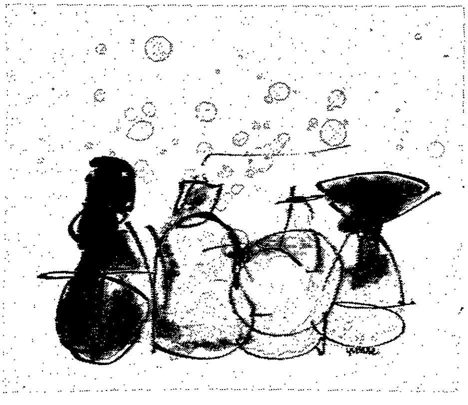
Chapter 4 is directed to investigate the influence of the sample preparation history on the conversion kinetics explaining the observed differences between powder and film form of the sample. Contact with nonsolvent water during the sample preparation seemed to have a decisive influence; it decreases the conversion rate. The pH of the water used appeared to be important, a distinct change in the conversion rate was observed for water at a pH of 7. This influence is explained in terms of the keto-enol tautomerism of the polyhydrazide. A shift in the keto-enol equilibrium changes the degree of conjugation of the polymer thus influencing the resistance against rotation.

In two appendices following these chapters the brittleness of the polyoxadiazole membranes is discussed. Polyoxadiazole membranes prepared through the thermal cyclo dehydration of polyhydrazide membranes appeared to be extremely brittle and broke upon handling. In appendix B the preparation of polyoxadiazole membranes using a one-step process is discussed. In this case the polyoxadiazole is prepared in oleum in one step and films are prepared directly from the oleum reaction solution. Tough films could be obtained in this way but the use of an aggressive solvent like sulfuric acid presented a lot of problems. In appendix C the possible factors which cause the brittle behaviour of the polyoxadiazoles prepared by the two-step process are discussed. Either the molecular weight of the final polyoxadiazoles is too low for film forming or the brittleness is caused by a build up of internal stresses during the thermal conversion process.

The second type of polymer studied in this thesis, the polytriazole, presented no problems in the manufacturing of membranes. Because of its good solubility in formic acid it could be processed into membranes of any configuration by casting from formic acid solutions followed by phase-inversion.

In chapter 5 membranes of poly(1,3-phenyl-1,4-phenyl)-4-phenyl- 1,2,4-triazole have been investigated for their gas separation properties. Homogeneous membranes have been tested with respect to their permeability for several gases. The polymer shows excellent selectivities and reasonable permeabilities for several gases, compared to other glassy polymers. The influence of temperature and time upon permeation has also been investigated, showing an Arrhenius behaviour of the permeability with temperature and a maintenance of permeation properties in time.

In chapter 6 the thermal behaviour of this polymer in the temperature range of 200 to 500°C has been investigated using differential scanning calorimetry (DSC). While the reaction product in powder form appeared to be partially crystalline, the membranes appeared to be completely amorphous. A thermal treatment between T_g(~270°C) and T_m(~430°C) can introduce crystallinity in the membranes because of the polymer's ability to cold crystallize. The crystallization temperature T_c seemed to be dependent on the preparation history of the sample and upon a thermal annealing step of the membranes just below T_g. At temperatures just above the crystalline melting point, T_m(~430°C), the polymer starts to decompose.



Samenvatting

Het onderzoek dat beschreven is in dit proefschrift betreft de vervaardiging van membranen van thermostabiele en chemisch resistente polymeren. Twee polymeren zijn hiervoor geselecteerd uit de groep van heterocyclische en aromatische polymeren, te weten de polyoxadiazolen en de polytriazolen. Een groot probleem met dit soort polymeren is de slechte verwerkbaarheid vanwege hun geringe oplosbaarheid en onsmeltbaarheid. Dit maakt het fabriceren van membranen byzonder moeilijk. Voor de polyoxadiazolen is dit verwerkbaarheidsprobleem omzeild door de polymeersynthese in twee gescheiden stappen uit te voeren via de bereiding van een verwerkbaar prepolymeer, een polyhydrazide. Na de vervaardiging van het prepolymere membraan volgt een thermische omzetting van het polyhydrazide in het gewenste polyoxadiazool. Voor de polytriazolen is een dergelijke tweestaps procedure niet nood- zakelijk omdat deze polymeren een zekere mate van oplosbaarheid bezitten indien een gefenyleerde vorm van de polytriazoolketen (poly-fenyl-triazool) gebruikt wordt, waardoor een directe verwerking tot membraan mogelijk is.

Het eerste hoofdstuk geeft een algemene inleiding waarin zowel membranen als thermostabiele polymeren worden belicht en waarin de gekozen polyoxadiazolen en polytriazolen worden geintroduceerd.
De hoofdstukken 2 tot en met 4 behandelen de tweede stap in de tweestaps procedure voor de polyoxadiazool bereiding, de thermische omzetting van het prepolymeer polyhydrazide in het polyoxadiazool. Deze omzettingsreactie van het polymeer in vaste toestand bestaat uit en cyclodehydratatie reactie van de afzonderlijke hydrazide groepen in het polymeer waardoor oxadiazool vijfringen gevormd worden. De kinetiek van dit cyclisatieproces wordt gevolgd met thermogravimetrische analyse (TGA). In hoofdstuk 2 wordt een dynamische methode toegepast om de kinetische parameters van het omzettingsproces te verkrijgen. Voor deze dynamische methode worden polyhydrazide monsters opgewarmd met constante opwarmsnelheden van een temperatuur van 200°C tot 450°C. Voor de metingen is het poly(1,3-fenyl- 1,4-fenyl)-hydrazide gebruikt zowel in poedervorm als in de vorm van een membraan. Voor het berekenen van de kinetische parameters zoals de activeringsenergie is gebruik gemaakt van de methode van Ozawa, waarvoor een set verschillende opwarmsnelheden vereist is. Met deze methode kunnen de kinetische parameters op elk moment tijdens de omzetting bepaald worden zodat het proces of veranderingen in het proces gevolgd kunnen worden gedurende de gehele omzetting. Op

deze manier zijn twee paralelle processen naast het cyclisatieproces waargenomen. Eén direct aan het begin, mogelijk het verlies van oplosmiddel en één aan het eind van het omzettingsproces mogelijk een decompositie reactie.

In hoofdstuk 3 wordt een isotherme thermogravimetrische methode besproken. Voor deze isotherme methode worden polyhydrazide monsters op een constante temperatuur gebracht en wordt het omzettingsproces in de tijd gevolgd. Gebruikmakend van een set isothermen bij verschillende temperaturen en gebruikmakend van het Arrhenius verband zijn de kinetische parameters berekend. De tweede orde isothermen blijken een lineair verband te vertonen met een duidelijke knik in de rechten bij een bepaalde omzettingsgraad. Dit wordt verklaard met de aanname dat het polymeer tijdens de isotherme omzetting een rubber-glas overgang ondergaat dat veroorzaakt wordt doordat de flexibele hydrazide groepen door het cyclisatieproces omgezet worden in stijve oxadiazool groepen. Voor en na deze overgang worden significant verschillende waarden voor de kinetische parameters gevonden. Naast deze invloed van de fysische toestand van het polymeer op de omzettingskinetiek wordt er ook een beduidende invloed waargenomen van de morfologie van het polyhydrazide monster, mogelijk veroorzaakt door verschillen in bereidingsgeschiedenis. Als snelheidsbepalende stap in het omzettingsproces wordt een rotatie van polyhydrazide ketensegmenten voorgesteld.

Hoofdstuk 4 is erop gericht om de invloed van de monster- bereidingsgeschiedenis op de kinetiek te onderzoeken waarmee getracht wordt de waargenomen verschillen tussen poeder en film te verklaren. De homogene films/membranen blijken beduidend hogere omzettingssnelheden te vertonen dan de poedervorm van hetzelfde polyhydrazide. Contact met het niet-oplosmiddel water tijdens de monsterbereiding blijkt een bepalende factor te zijn. Monsters die worden verkregen via precipitatie in water, zoals poeders en poreuze membranen, blijken een geringere omzettingssnelheid te vertonen dan monsters die niet met water in contact geweest zijn, zoals homogene nietporeuze membranen die middels verdamping van het oplosmiddel gevormd zijn. De pH van het water blijkt een belangrijke factor, rond een pH van 7 vindt er een aanzienlijke verandering in omzettingssnelheid plaats. Deze pH-invloed wordt verklaard met behulp van de keto-enol tautomerisatie van het polyhydrazide. Een verschuiving van het keto-enol evenwicht beïnvloedt de mate van conjugatie van het polymeer waardoor tevens de draaibaarheid van de keten wordt beïnvloed.

In twee appendices die op deze hoofdstukken volgen wordt de brosheid van de polyoxadiazool membranen besproken. Alle polyoxadiazool membranen die door de thermische cycodehydratatie van polyhydrazide membranen zijn verkregen, zijn dermate bros dat ze breken onder de geringste belasting. Als alternatief op bovenstaande twee-staps bereidingswijze wordt in appendix B het in één stap synthetiseren van polyoxadiazolen in oleum en het direct vanuit dit reactiemengsel verwerken tot membraan besproken. Op deze manier bleek het mogelijk stevige films te verkrijgen hoewel het gebruik van oleum als oplosmiddel vele problemen met zich meebrengt. In appendix C worden de mogelijke factoren op een rij gezet die de oorzaak kunnen zijn van de extreme brosheid van de polyoxadiazolen vervaardigd met de twee-staps procedure. De mogelijke oorzaken zijn samen te vatten tot een te laag moleculair gewicht van het uiteindelijke polyoxadiazool en de aanwezigheid van interne spanningen die ontstaan tijdens het cyclisatieproces.

Het tweede polymeer dat bestudeerd is, het polytriazool, leverde geen problemen op in de membraanbereiding. Dankzij de goede oplosbaarheid in mierezuur van poly-fenyl-triazool bestaat de mogelijkheid dit polymeer tot praktisch elke gewenste membraan- structuur te verwerken met behulp van de fase-inversie methode.

Hoofdstuk 5 beschrijft de gaspermeatie- en gasscheidings- experimenten die uitgevoerd zijn met homogene membranen van poly(1,3-fenyl-1,4-fenyl)-4-fenyl-1,2,4-triazool. Er is met name gekeken naar de scheiding van koolzuurgas en methaan en naar de scheiding van zuurstof en stikstof. Het polymeer vertoont hoge selectiviteiten en redelijke permeabiliteiten voor de onderzochte systemen in vergelijking tot andere glasachtige polymeren. Uit onderzoek naar de invloed van temperatuur en tijd op het permeatiegedrag bleek dat de permeatie een Arrhenius verband met de temperatuur vertoont en dat de permeatie-eigenschappen gedurende een periode van tenminste 3 maanden behouden blijven.

In hoofdstuk 6 wordt het hoge temperatuur gedrag van dit polymeer, in het gebied van 200 tot 500°C, nader onderzocht met behulp van differential scanning calorimetry (DSC). Hieruit is gebleken dat het opgewerkte polytriazool na de reactie gedeeltelijk kristallijn is maar dat de membranen die vanuit een mierezuur oplossing zijn vervaardigd amorf zijn. Dit heeft een gunstig effect op de doorlaatbaarheid van gassen. Een warmtebehandeling bij een temperatuur die ligt tussen de glasovergangstemperatuur (~275°C) en de kristallijne smelttemperatuur (~430°C) kan kristalliniteit in het membraan introduceren door het vermogen tot koude kristallisatie van het polymeer. De kristallisatietemperatuur blijkt afhankelijk te zijn van de thermische geschiedenis van het membraan. Annealen van het membraan op een temperatuur net iets onder de glasovergangstemperatuur verhoogt de kristallisatietemperatuur. Bij temperaturen net boven de kristallijne smelt- temperatuur begint het polymeer waarschijnlijk te ontleden.

Veur de Twentse leek*

Membraann, dat bint feeltrs. Gin gewone feeltrs, zoas koffiefeeltrs, mer völ fienere. De geatkes in membraann bint zo klaen daj der molecuuln met oet mekaar könt haaln. Molecuuln bint de klaenste deelkes dee der bestoat. Wie proat dan oawer deelkes van de grùtte van 'n meljoenste mm of nog klaener. Aj bieveurbeeld zeewaatr deur 'n membraan párst, dan keumt't der an de aandere kaant as zeutwaatr oet, umdat het zóolt wot teëgnhóoln deur het membraan. Dooj tzölfde met roojen wien, dan kriej witten wien, mer dat is zeun van 'n wien.

De meeste membraann deej könt koopn wot maakt van keunststoffn, ok wa neumt "plastics". Noe bint plastics deurgoans nig zo bestaand téegn hette of bietnde schoonmaakmiddel, waj alle wal ees met hebt maakt. Plastic membraann köj doarum alleene mer oonder meelde umstaandigheedn gebroekn. Wat ik noe doan heb is het zeukn noar neëe plastics dee wal téegn hette könt, um doar dan membraann van te maakn.

Noe köj natuurlijk zégn: woarum nem ie dan gin iezer of scheurweark?. Wel, van disse materiaaln köj sleg membraann maakn en ok ist zo dat iezer roest en scheurweark maklek brek.

Het vaalt nig met um van disse hettebestéendige plastics mooie dunne membraann te maakn. Ze bint dan wal bestaand téegn hette (±500 °C) mer ze lúst ok neargns in op en ze smealt nig zo daj der doarum ok nig wat van maakn könt. T'is dreugn keurnign poejer, net zaand, woar ie téegn an zit te kiekn. Mer met 'n paar scheikundige keunstgreepn is het spul toch nog wa te verwearkn.

Doar heb ik noe veer joar an wearkt en dat steet beskréem in dit beukske. Het is lukt um 'n membraan te maakn van "polytriazool", dat is de naam van't spul, dat zeulfs zo good is, dat wie 't hebt pateanteerd. Dit membraan kan heel good de gasn oet de loch oet mekaar haaln. Het löt de zoerstof oet de loch deur, mer hóolt 'n stikstof téegn. Dit zoj zak mer zegn könn gebroekn um verbraandingsmotoorn van extra zoerstof te veurzeen. Aandere meuglike toopassingn bint het verwiedern van skalike stoffn oet rookgasn of heetn ölie. Wieders bint disse membraann ok heel good chemisch skoon te maakn of te steriliseern.

---

* *vertaling E.H.Gebben*

Levensloop

Bert Gebben werd geboren op 7 januari 1960 te Hengelo (Ov.).
In 1978 werd het Atheneum B diploma behaald aan de scholengemeenschap Het Bataafse Kamp te Hengelo. In datzelfde jaar begon hij met de studie Chemische Technologie aan de toenmalige T.H. Twente, nu Universiteit Twente, te Enschede. In april 1984 behaalde hij het ingenieursdiploma. Het afstudeeronderzoek werd verricht in de vakgroep makromolekulaire chemie en materiaalkunde onder leiding van prof. dr. C.A. Smolders en handelde over de bereiding van modelcolloiden door middel van intramoleculaire crosslinking van water-oplosbare polymeren.
Met ingang van 1 mei 1984 trad hij in dienst van de T.H. Twente als wetenschappelijk assistent in de onderzoeksgroep "Membraanfiltratie" onder leiding van prof. dr. C.A. Smolders. In de periode tot 1 mei 1988 is onderzoek verricht naar de ontwikkeling van thermostabiele en chemisch resistente polymere membranen dat in dit proefschrift beschreven is.
Vanaf 1 juli 1988 zal hij in dienst zijn als research medewerker van AKZO BV Corporate Research te Arnhem.