Polymer Bulletin 33, 439–444 (1994)

Polymer Bulletin

Effect of the reaction conditions on the properties of poly(4,4′-diphenylether-1,3,4-oxadiazole)s

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Summary

Poly(4,4'-diphenylether-1,3,4-oxadiazole)s have been prepared by polycondensation of 4,4'-diphenylether dicarboxylic acid and hydrazine sulphate, HS, in poly(phosphoric acid), PPA, under different reaction conditions. The products were characterized by viscometry, gel permeation chromatography, ^{1}H-NMR spectrometry and thermogravimetric analysis. Dense membranes have been prepared and submitted to gas transport and wide angle X-ray diffraction, WAXD, experiments. The differences found in permeability and selectivity parameters, as well as in density and WAXD results, are discussed in terms of their solution viscosities and hydrazide repeat unit contents.

Introduction

The preparation of heteroaromatic polymers has deserved much attention, due to their industrial application as thermally stable and chemically resistant materials. Poly(1,3,4-oxadiazole)s are heteroaromatic polymers, which have been obtained by several synthetic routes. Low molecular weight products have been prepared from tetrazoles and acid chlorides at high temperatures in pyridine (1). The cyclodehydration of aromatic polyhydrazides, carried out by dehydrating agents such as chlorides and sulfuric acids, or by thermal treatment has also been reported (2-4).

The introduction of ether groups in the polymer chain of polyhydrazides and poly(1,3,4-oxadiazole)s, obtained by low temperature solution polycondensation of 4,4'-diphenylether dicarboxylic acid dichlorides and dihydrazides of dicarboxylic acids in hexamethyl phosphoramide, has raised their solubility in organic solvents, without considerably decreasing their thermostability (5).

Poly(p- and m-phenylene-1,3,4-oxadiazole)s of high molecular weights have been prepared by solution polycondensation in fuming sulphuric acid or poly(phosphoric acid), PPA, of phenylenedicarboxylic acids and hydrazine sulphate. The polymers were soluble in concentrated sulphuric acid and PPA, but insoluble in common organic solvents (6). A mixture of chlorosulphonic, fuming and concentrated sulphuric acids has been also used as solvent in polycondensation reactions leading to high molecular weight poly(p- and m-phenylene-1,3,4-oxadiazole)s (7).

In this work, the reaction conditions and the products resulting from the polycondensation of 4,4'-diphenylether dicarboxylic acid, DPE, and hydrazine sulphate, HS, in PPA have been investigated. The products, POD-DPE, were characterized by viscosity measurements, nuclear magnetic resonance, NMR,

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differential scanning calorimeter, DSC, and thermal gravimetric analysis, TGA. The concentration of residual hydrazide groups were determined from NMR spectra and TGA weight loss curves. The gas transport properties of the POD-DPE membranes have been investigated for the CO_2/CH_4 pair, and are discussed in relation to their hydrazide contents.

Experimental

In a 250ml three-necked, round-bottom flask, equipped with a mechanical stirrer and a nitrogen inlet tube, 237g poly(phosphoric acid) (PPA, Fluka A.G., FRG) were added. 5.04g (38.7mmol) Hydrazine sulphate (HS, Janssen Chimica, Holland) were mixed to PPA and the temperature was raised to 150°C. Then, 10.00g (38.7mmol) 4,4'-diphenylether dicarboxylic acid (DPE, Amoco Chemical Co., USA) were added and the resulting mixture was kept at 150°C under constant stirring for 4h. After cooling to ≈ 80°C, the reaction mixture was poured into tepid water, treated with 0.5M NaOH, and kept overnight under stirring in water at 50°C. The product was recovered by filtration under stirring and dried under vacuum at 80°C. Purification was carried out by dissolving the product in a good solvent, most frequently formic acid, and reprecipitating in water. Reactions have also been carried out with PPA/HS ratio equal to 27, and for different reaction periods.

Inherent viscosities were determined in a Ubbelohde type viscometer (size 1 n° 85583), at a concentration of 0.5% (w/w) in sulphuric acid at 30°C.

^{1}H-NMR spectra were obtained in DMSO-d_6 at 80°C, in a Bruker CPX-200 spectrometer.

A Waters 510 apparatus, equipped with a Waters 410 detector, a Rheodyne 7125 injector valve and an integrator, was employed to analyze the POD-DPE polymers. Measurements were made by using T20351C-01 and T20271B-02 Ultrastyragel columns from Waters, connected in series. N-Methyl-pyrrolidone (NMP, Aldrich Chemical Co., USA), with 0.01 M lithium bromide was used as the eluent at a flow rate of 1.5 ml/min, at 40°C and 500 psi. Polystyrene standards from Waters, of weight-average molecular weights in the range 1800 to 450000 were employed. The 0.2% (w/w) POD-DPE solutions were filtered through 0.45μm membranes and a 100μl fraction of each solution was injected.

POD-DPE dense membranes were prepared from 10% (m/v) formic acid solutions. The solutions were filtered through 5μm filter-paper (Millipore, USA), 25-45μm layers were cast on glass plates with a cylindrical stainless steel knife. The solvent was evaporated under nitrogen at 23°C. The films were recovered by dipping the plates into a water-bath, and were dried under vacuum at 80°C.

Thermogravimetric Analysis (TGA) experiments were carried out in a Perkin-Elmer TGA-7 associated with a System-4 Microprocessor Controller and a Thermal Analysis Data Station (TADS) model 3700. About 5 mg of dry polymer sample were treated under nitrogen stream from 100 to 150°C at 10°/min, cooled and then heated from 100 to 700°C, at the same conditions.

Density measurements of POD-DPE dry membranes were performed according to ASTM-D792-66.

Gas transport properties of POD-DPE membranes were evaluated in a permeability cell, constructed at the Department of Chemical Technology, Twente University, according to ASTM-D1434-80, and using a mixture of 75% CH_4 and 25% CO_2 at 23°C and $4x10^3$ mmHg. Permeability was determined by Equation 1,

$$P = L\,Q\,/\,A\,\Delta P \qquad \text{Equation 1}$$

where P is the permeability of the CO_2/CH_4 mixture; l is the thickness of the membrane, in cm; Q is the flux of the gas mixture, in cm^3/s; A is the area of the membrane, in cm^2; ΔP is the increase in pressure, in cmHg. Selectivity was determined by Equation 2,

$$\alpha_{CO_2/CH_4} = (X_{CO_2}/X_{CH_4})\,/\,(Y_{CO_2}/Y_{CH_4}) \qquad \text{Equation 2}$$

where X_{CO_2} and X_{CH_4} are the CO_2 and CH_4 contents in the permeate (% vol) and Y_{CO_2} and Y_{CH_4} are the CO_2 and CH_4 contents in the feed (% vol).

Wide angle X-ray diffraction (WAXD) experiments were carried out on a Philips diffractometer, model PW1710, with copper irradiation (CuKα=1.5418Å).

Results and Discussion

The one-step polycondensation reaction of dicarboxylic acids and hydrazine sulphate in PPA had been carried out at temperatures varying from 110 to 180°C (5). In this work, the reaction temperature was maintained at 150°C.

The effect of the reaction time on the polymer inherent viscosity has been investigated for reaction batches carried out with two different PPA/HS ratios. Table 1 shows that the viscosity reaches a maximum value in both cases and, similarly to the products obtained from terephthalic and isophthalic acids (6), long reaction times seem to cause polymer degradation. Products with excellent film formation properties were prepared after 4h reaction. A hydrosoluble product of very low viscosity in sulphuric acid, ME-63, has been obtained after 30h. for PPA/HS=27. Sulphonation at the aromatic groups and degradation of the polymeric chain might have contributed to these characteristics.

Table 1: Effect of reaction time on the POD-DPE viscosity.

Sample	PPA/HS ratio	Reaction time (h)	$\eta_{inh}{}^a$ (dl/g)
ME-79	18	1	0.42
ME-76	18	2	0.20
ME-74	18	4	1.60
ME-78	18	8	1.15
ME-77	18	16	1.00
ME-60	27	4	0.67
ME-61	27	7	1.13
ME-62	27	23	0.92
ME-63	27	30	0.04

[a] Measured in sulphuric acid at 30°C.

The inherent viscosities and the values of $\bar{M}_w$, $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ from GPC experiments of the POD-DPE samples prepared at 150°C, during 4h, were correlated to the PPA/HS ratio in Table 2. All samples were soluble in sulphuric acid. Samples

ME-70, 72 and 74 were also soluble in formic acid and NMP. The highest PPA/HS ratio has led to a POD-DPE sample of high polydispersity and low viscosity. Sufficiently high molecular weight polymers, which have formed transparent and resistant films, have been obtained when the PPA/HS ratio felt in the interval 15-18.

Table 2: Effect of the PPA/HS ratio on the inherent viscosity and average molecular weights of POD-DPE samples, obtained at 150°C during 4h.

Sample	PPA/HS	η_{inh}[a] (dl/g)	$\bar{M}_w$ x10^{-5}	$\bar{M}_n$ x10^{-5}	$\bar{M}_w/\bar{M}_n$
ME-70	27	0.67	4.04	0.65	6.21
ME-73[b]	20	0.66	-	-	-
ME-74	18	1.60	3.36	1.31	2.56
ME-72	15	1.56	2.86	1.08	2.65
ME-22[b]	10	0.85	-	-	-
ME-71[b]	7	0.75	-	-	-
ME-19[c]	7	0.29	0.27	0.15	1.79

[a] Measured in sulphuric acid at 30°C; [b] Insoluble in NMP; [c] Reaction time t = 18h.

The thermal behaviour of POD-DPE polymers was evaluated by thermogravimetric measurements, TGA. All polymer samples have produced similar patterns of thermal decomposition, reproduced in Figure 1. The first step, 100-150°C may be related to the elimination of humidity from the hygroscopic polymers. From 290 to 360°C, a second process takes place, which may be associated with loss of

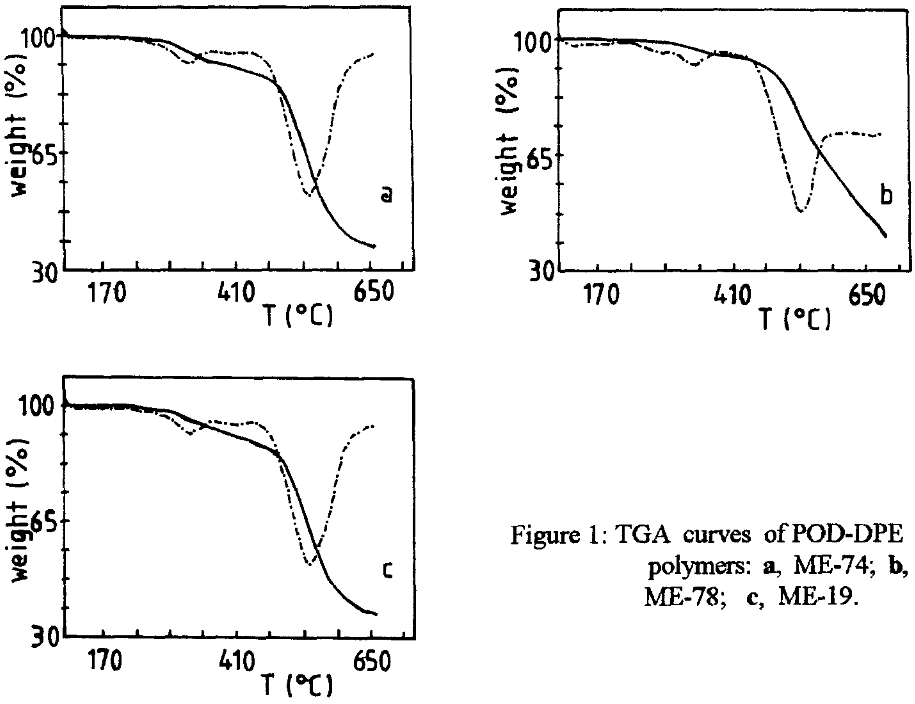


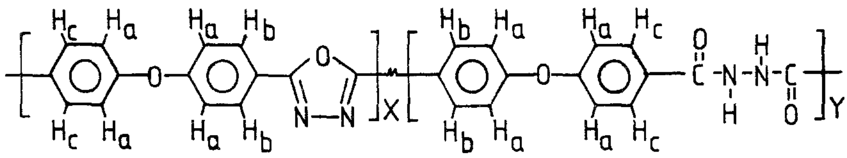
Figure 1: TGA curves of POD-DPE polymers: **a**, ME-74; **b**, ME-78; **c**, ME-19.

water due to oxadiazole group formation from the residual hydrazide groups (8). At last, the thermal decomposition occurs by loss of other gases (9). In this study, the onset of thermal decomposition was observed at 470-500^{o}C. Both cyclization and degradation temperatures vary with the sample.

^{1}H-NMR spectrometry has been used to characterize the POD-DPE polymers. Figure 2 shows spectra taken in DMSO-d_6 at 80^{o}C, in the range 7.0-9.0 ppm, in which the absorptions **a**, **b** and **c** have been attributed to aromatic protons in the neighbourhood of the ether, oxadiazole and hydrazide groups, respectively. The content of repeat units with a hydrazide group, %Y, of POD-DPE samples (Table 3) has been calculated according to Equation 3,

$$\%Y = [I_c / I_a] \times 100 \qquad \text{Equation 3}$$

where I_a and I_c are the areas of the corresponding peaks.



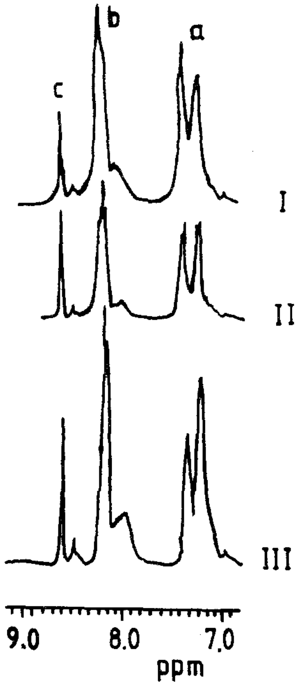


Figure 2: 1H-NMR spectra of POD-DPE polymers in DMSO-d6, at 80oC; trace I, ME-74; trace II, ME-78; trace III, ME-19.

The Y content has also been determined by TGA, taking into consideration the percent water lost during the cyclization process. The values tabulated below, together with permeability (P), selectivity (α), density (ρ) and WAXD ($d_{spacing}$) results (Table 3) are the average from 2-3 experimental determinations.

Table 3: Effect of %Y on the gas transport properties.

Sample	%Y		PCO_2 (Barrer)	$\alpha CO_2/CH_4$	ρ (g/cm^3)	$d_{spacing}$ (Å)
	NMR	TGA				
ME-72	-	10	1.4	110	1.422	3.91
ME-74	23	25	1.4	98	1.432	3.99
ME-78	30	23	0.98	160	1.470	3.72
ME-77	65	22	0.50	180	1.492	3.90
ME-19	22	30	0.30	> 200	-	3.80

The POD-DPE samples studied are amorphous polymers of high glass transition temperatures (Tg ≈ 300-360°C). According to Table 3, both the permeability and the selectivity to the CO2/CH4 gas mixture vary significantly for the POD-DPE samples. As expected, density results suggest that the more aggregated samples present lower permeability (higher selectivity) to the gas mixture than the others. Slight reduction in the interchain distance, or d-spacing, accounts for the high selectivity obtained for the samples ME-78, ME-77 and ME-19. These samples have shown the lowest solution viscosities. The reduction in their interchain distances and the consequential gas properties, should be attributed to the higher average content of residual hydrazide groups, which are subjected to stronger intermolecular forces than the oxadiazol rings existing in higher proportion in the sample ME-72.

Acknowledgments

The authors acknowledge E.R. Hensema, M.H.V. Mulder and C.A. Smolders (Twente University, Holland), and the Laboratory of Membrane Processes (COPPE-UFRJ, Brazil) for laboratory facilities. MES is grateful to CNPq for a fellowship.

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Received: 2 June 1994/Accepted: 20 June 1994