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Study of the synthesis of poly(4,4′-diphenylether-1,3,4-oxadiazole) in solutions of poly(phosphoric acid)

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Abstract

Using statistical design of experiments, samples of poly(4,4′-diphenylether-1,3,4-oxadiazole)s, POD–DPE, were synthesized through solution polycondensation of 4,4′-diphenylether dicarboxylic acid, DPE, and hydrazine sulphate, HS, in poly(phosphoric acid), PPA, under different reaction conditions. Final polymer molecular structure (average molecular weights, polymer composition, amount of hydrazide groups) is shown to depend strongly upon the polymerization conditions and that adequate properties for membrane synthesis (high average molecular weight, low amounts of hydrazide groups and low gel contents) can only be obtained if high synthesis temperatures (160°C) are used. Empirical and semi-theoretical models are developed to describe the kinetics of POD–DPE production in PPA solutions, showing that the likely existence of cross-linking reactions may explain both the relatively high values and the large fluctuations of the average molecular weight obtained experimentally. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Oxadiazole; Polymerization kinetic; Experimental design

1. Introduction

In spite of the industrial interest, gas separation processes based on polymer membranes will only become competitive commercial processes after the development of polymers which combine both selective permeation and adequate membrane preparation properties. Besides gas permeability, many other properties are important for the membrane gas separation technology, such as the thermal, chemical and mechanical resistance of the final polymer films, which can usually be associated with the chemical structure and the molecular weight distribution of the polymer species. A considerable amount of research has been concentrated on the synthesis of new polymers for gas separations and on the understanding of the structure–properties relationship of polymers used for membrane production. Among these new polymers, polyoxadiazoles [1–4], polytriazoles [5,6] and polyimides [7,8] apparently lead to the most promising combination of properties for the development of membranes for gas separations.

Aromatic poly-1,3,4-oxadiazoles are considered to be interesting alternatives for the development of gas separation applications at high temperatures because of their excellent combination of chemical, physical, mechanical and outstanding gas separation properties. However, most of these polymers are insoluble in common organic solvents, which is a serious drawback for the membrane production. It has been found [1,2], though, that the introduction of ether groups into the polymer chains of poly-1,3,4-oxadiazoles can raise the solubility of the polymer resin in organic solvents considerably, without loss of the thermal stability. Among the family of poly(ether-oxadiazoles), the poly(4,4′-diphenylether-1,3,4-oxadiazole)s, POD–DPE, have been found to present extremely high gas selectivities [9] and excellent thermal and chemical stabilities [10]. Besides, they are soluble in common solvents, such as *N*-methyl-pyrrolidone, NMP [6].

The synthesis of POD–DPE is usually carried out in solution, where a polycondensation reaction takes place, leading to an intermediate polymer species, the poly(hydrazide), PH. The cyclization of the hydrazide groups, which can be performed simultaneously with the polycondensation [9] or can be performed during a second temperature treatment step, produces the final poly(oxadiazole) [11]. The use of a second temperature treatment step to promote the cyclization of the PH groups seems not to be adequate, because significant thermal degradation of the polymer chains may occur [11]. If the cyclization of the PH groups is expected to take place simultaneously with the polycondensation, then

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the POD–DPE synthesis usually requires that a strong acid be used as a solvent, which also promotes some parallel degradation reactions [9,12]. Therefore, competitive reactions occur simultaneously during the poly(oxadiazole) synthesis in strong acid medium, so that, depending on the reaction conditions, the final polymer may present different structures and molecular weight.

Despite the potential interest of using POD–DPE for membrane separations, very little is known about the kinetics of the POD–DPE synthesis and how the polymer properties respond to changes of the reaction conditions. Previous works focus mainly upon the formulation of chemical routes for production of different POD–DPE and characterization of the polymer samples obtained. Important engineering aspects for polymer production, such as sensitivity to process operation conditions and reproducibility of final polymer properties at actual lab-scale polymerization conditions, have been neglected.

The main objective of this work is to study the POD–DPE synthesis in strong acid medium in order to produce polymers with the minimum amounts of residual hydrazide groups and the maximum molecular weight possible, for future preparation of gas separation polymer membranes. The required characteristics are important to achieve high thermal, mechanical and chemical stabilities and high gas selectivities. Statistical design of experiments is used as a tool to optimize the experimental plan and enhance the data analysis capability. Empirical and semi-theoretical models are built to allow the interpretation of the experimental data obtained and the optimization of the synthesis conditions. It is shown here that soluble POD rich polymer samples of high molecular weight can be produced at temperatures around 160°C, although final polymer properties are subject to large fluctuations and may be very sensitive to small changes of the operation conditions. These characteristics must be taken into consideration during the production of the large amounts of polymer material needed for membrane synthesis.

2. Experimental

The POD–DPE synthesis was carried out using poly(phosphoric acid), PPA (Aldrich), as solvent, and 4,4′-diphenylether dicarboxylic acid, DPE (Amoco), and hydrazine sulphate, HS (Janssen Chimica), as monomers. The selected reaction variables were temperature, T, batch time, t, monomer ratio, HS/DPE, and dilution ratio, PPA/HS. Experiments were carried out in accordance to a statistical experimental plan and the polymer samples obtained were characterized by thermal gravimetric analysis (TGA), nuclear magnetic resonance (NMR), elemental analysis, size exclusion chromatography (SEC) and viscometry. The HS/DPE and PPA/HS molar ratios were varied through manipulation of the initial amounts of HS and PPA added to the reactor vessel. The DPE content was kept constant and equal to 19.35 mmol (5 g) in all batches. This was intended to avoid the manipulation of very small amounts of reactants and therefore reduce possible fluctuations induced by weighing and transferring of chemicals between flasks.

2.1. Preparation of polymer samples

Polymerizations were carried out in a 250 ml three-necked flask equipped with a mechanical stirrer, with a dean stark connected to a condenser and with a dry nitrogen inlet tube, to keep the reaction atmosphere free of oxygen and water. Specified amounts of PPA (depending on the specific reaction condition) and 5.0 g (19.35 mmol) of DPE were initially added to the flask and vigorously stirred. The temperature was then increased slowly, in order to reach the desired reaction temperature. After reaching the specified reaction temperature, a specified amount of HS was added to the flask, in accordance with the experimental plan. The reacting medium was then kept at constant reaction temperature under constant stirring for the specified batch time. Reaction temperature was controlled with a thermal oil bath with precision of 1°C. After finishing the batch, the reaction medium was cooled down to approximately 80°C, poured into tepid water (containing 5% of sodium hydroxide) and kept overnight under continuous stirring at room temperature. The final polymer powder was then obtained through filtration. In order to remove residuals, the filtered polymer material was then kept in water at 80°C for an additional period of 3 h under continuous stirring conditions. The polymer was finally dried through sequential liquid exchange, suspending the polymer powder in ethanol for a period of 2 h, filtering the polymer material, and afterwards suspending the filtered polymer sample in *n*-hexane for an additional period of 2 h. Then, the polymer material was filtered once more and dried in a vacuum oven at 80°C for 18 h. The final polymer yield was always close to 100% in respect to the limiting reactant (HS or DPE, depending on the experimental condition). Fig. 1 shows a scheme of the reaction synthesis.

2.2. Polymer characterization

Intrinsic viscosities $[\eta]$ of polymer samples were determined in an Ostwald type viscometer ($D_\mathrm{I} = 1.27$ mm), using solutions of sulphuric acid at 30°C. Polymer concentrations ranged between 0.12–0.50 (g/dl). Intrinsic viscosities were computed as [13]:

$$\eta_\mathrm{sp} = [\eta]\cdot c \tag{1}$$

where c is the polymer concentration and η_sp is the specific viscosity,

$$\eta_\mathrm{sp} = \frac{t - t_0}{t_0} \tag{2}$$

where t is the flow time of the polymer solution and t_0 is the flow time of the solvent. As shown afterwards, the intrinsic

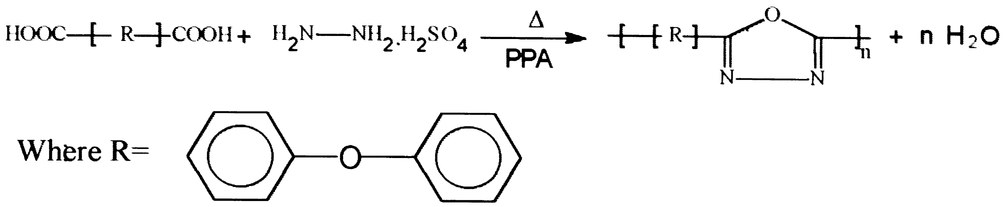

Fig. 1. Scheme of the POD–DPE synthesis.

viscosity may be regarded as a direct evaluation of the weight average molecular weight of the polymer sample.

The ^{1}H NMR spectra were collected for monomers and polymer samples for qualitative analysis and were obtained in DMSO-d_6, in a Bruker DPX 200 spectrometer.

A Waters 510 SEC apparatus equipped with a Waters 410 detector was employed to evaluate molecular weight distributions of polymer samples. *N*-methyl-2-pyrrolidone (NMP, Aldrich), with 0.05 M lithium bromide, was used as the carrier at a flow rate of 0.3 ml/min, at 75°C and 500 psi. Solutions with 0.2% (w/w) of polymer were prepared, filtered through 0.5 μm membrane and injected into the chromatograph.

Thermogravimetric analysis (TGA) experiments were carried out in a Perkin Elmer TGA-7 to characterize the PH content and thermal stability of the final polymer samples. About 5–10 mg of polymer samples were first treated under nitrogen stream from 100 to 150°C at 10°C/min (to remove volatiles), cooled down to 100°C and then heated again from 100 to 700°C, at similar heating conditions. The second heating period was used for polymer characterization.

Elemental analysis of C, H and N of monomers and final polymer samples were carried out in a standard Perkin Elmer 2400 apparatus.

Polymer solubility tests were carried out in NMP. The solubility test consisted of adding 0.1 g of the polymer to NMP (5 ml) at 60°C, under continuous stirring conditions for approximately 2 h, and cooling down the solution to room temperature. After cooling, soluble polymer samples (given the label 0) lead to clean solutions, while non-soluble polymer samples (given the label 2) lead to powder suspensions where almost the whole polymer sample could be recovered through filtration. Certain samples (given the label 1) lead to powder suspensions, where only part of the original sample could be recovered through filtration, and others samples (given the label 1.5) lead to the formation of a gel.

2.3. The experimental design

The experimental design used here was a combination of the full two-level factorial design and the full three-level cross-design for four variables (T, t, PPA/HS, HS/DPE), with replicates at the central point. The ranges of variation of the synthesis variables were selected in order to maximize the amount of POD–DPE and the weight average molecular weight of the final polymer samples, in accordance with the results reported previously by Sena [9] and Krongauz [12]. The experimental design contains a large number of experiments, including 16 experimental conditions of the full factorial design, 9 experiments of the cross-design and additional replicates of the central point, to allow the characterization of experimental fluctuations. (As shown later, the central point replicates were fundamental for proper interpretation of final results.) The complete sets of experimental conditions and results are presented in Tables 1 and 2, respectively. The experimental design was proposed to allow the independent evaluation of the main variable effects (linear variable contributions), of all variable interactions (non-linear first-order variable monomials) and of second-order variable effects (cubic variable contributions). Variable interactions are very common in kinetic problems, where reaction rates are usually described by the multiplication of reactant concentrations and temperature effects. Besides, batch time is usually multiplied by reaction rates (or reaction rate averages) to allow the computation of product yields. Second-order terms may be important to

Table 1
Experimental conditions

Polymer	Design	*t* (h)	*T* (°C)	PPA/HS	HS/DPE
d1	2-Level factorial	7	160	20	1.2
d2		7	160	10	0.8
d3		7	100	20	0.8
d4		7	100	10	1.2
d5		3	160	20	0.8
d6		3	160	10	1.2
d7		3	100	20	1.2
d8		3	100	10	0.8
d10		7	160	20	0.8
d11		7	160	10	1.2
d12		7	100	20	1.2
d13		7	100	10	0.8
d14		3	160	20	1.2
d15		3	160	10	0.8
d16		3	100	20	0.8
d17		3	100	10	1.2
d18	Three-level cross	7	130	15	1.0
d19		3	130	15	1.0
d20		5	160	15	1.0
d21		5	100	15	1.0
d22		5	130	20	1.0
d23		5	130	10	1.0
d24		5	130	15	1.2
d25		5	130	15	0.8
Central		5	130	15	1.0

Table 2
Experimental results

Polymer	[η] (dl/g)	M_w (kDa)	$M_{w,calc}$ (kDa)	Soluble in NMP	HZ (%)
d1	0.30	54.0	49.5	Yes	100
d2	0.59	94.0	88.2	Yes	10
d3	0.35	–	56.3	No	100
d4	0.42	–	65.4	No	23
d5	0.30	54.0	50.0	Yes	83
d6	1.07	138.0	152.6	Yes	10
d7	0.20	–	35.9	No	95
d8	0.64	–	94.6	No	100
d10	0.77	128.0	113.3	Yes	15
d11	0.43	81.0	67.1	Yes	34
d12	0.66	–	97.8	No	5
d13	0.75	–	110.2	No	100
d14	0.10	17.0	21.9	Yes	100
d15	0.13	26.0	26.2	Yes	78
d16	0.81	–	118.1	No	100
d17	0.10	–	22.0	No	86
d18	0.42	–	65.5	Partial	26
d19	0.51	–	78.0	No	20
d20	0.24	30.0	41.8	Yes	100
d21	0.36	–	57.3	No	46
d22	0.22	–	39.2	Partial	24
d23	0.25	–	43.0	No	20
d24	0.39	50.0	61.5	Yes	15
d25	0.52	–	79.6	Partial	84
Central	0.4–1.3	–	57–180	Gel	0–87

model non-linear surfaces, when a maximum or a minimum is sought. A more detailed description of the experimental plan may be found elsewhere [14].

3. Results

3.1. Structural characterization

Elemental analysis of C, H and N were carried out for monomers and polymer samples. For DPE, the ratio H/C found experimentally was equal to 0.060 (weight), which is equal to the expected theoretical value and confirms the purity of the DPE. For HS, the ratio H/N found was equal to 0.240 (weight), while the expected theoretical value is 0.214. Additional melting point and TGA measurements, described below, confirmed that the HS used does not contain any appreciable amount of water and can be regarded as pure. As the C/N ratio expected for PH–DPE and POD–DPE polymers is equal to 6.0 (weight) and the values obtained experimentally were in the range (5.94–7.56), it was concluded that polymerization took place. The results obtained for the H/C and H/N ratios led to similar conclusions. Experimental results were in the range (0.054–0.069) and (0.331–0.438) for the ratios H/C and H/N respectively, while theoretical values were expected to be in the range (0.048–0.060) and (0.286–0.357), where the inferior limits are computed for POD–DPE and the superior limits are computed for PH–DPE. However, the experimental values for the ratios H/C and H/N found were somewhat higher than the theoretical ones. We believe that this fact can probably be due to the small difference between hydrogen atoms of PH–DPE and POD–DPE and the hygroscopic nature of these polymers. Then, these values could not be used for quantitative analysis of hydrazide groups.

The PH content was evaluated by thermogravimetric measurements, TGA. All copolymers POD–PH lose weight during heating experiments in the range of temperatures between 200 and 400°C. The weight loss may be associated with the loss of water (%H_2O) caused by the formation of oxadiazole groups from residual hydrazide groups [15]. The PH content (%HZ) can be computed as [9]

$$\%\mathrm{HZ} = \frac{236,23\cdot(\%\mathrm{H_2O})}{[1801,5 - 18,015\cdot(\%\mathrm{H_2O})]}\cdot 100 \tag{3}$$

Fig. 2 shows typical TGA curves for PH–DPE and POD–DPE samples. As it can be observed in this figure, the TGA spectrum of PH–DPE is more complex than that of POD–DPE. Typically, TGA spectra of PH–DPE show four distinct regions of weight loss. The first region, around 100°C, corresponds to the loss of adsorbed water. The second region, in the range of 200–400°C, is related mainly to the loss of water produced during the conversion of PH to POD. The third region, in the range of 350–450°C, corresponds to a loss of water involved in secondary

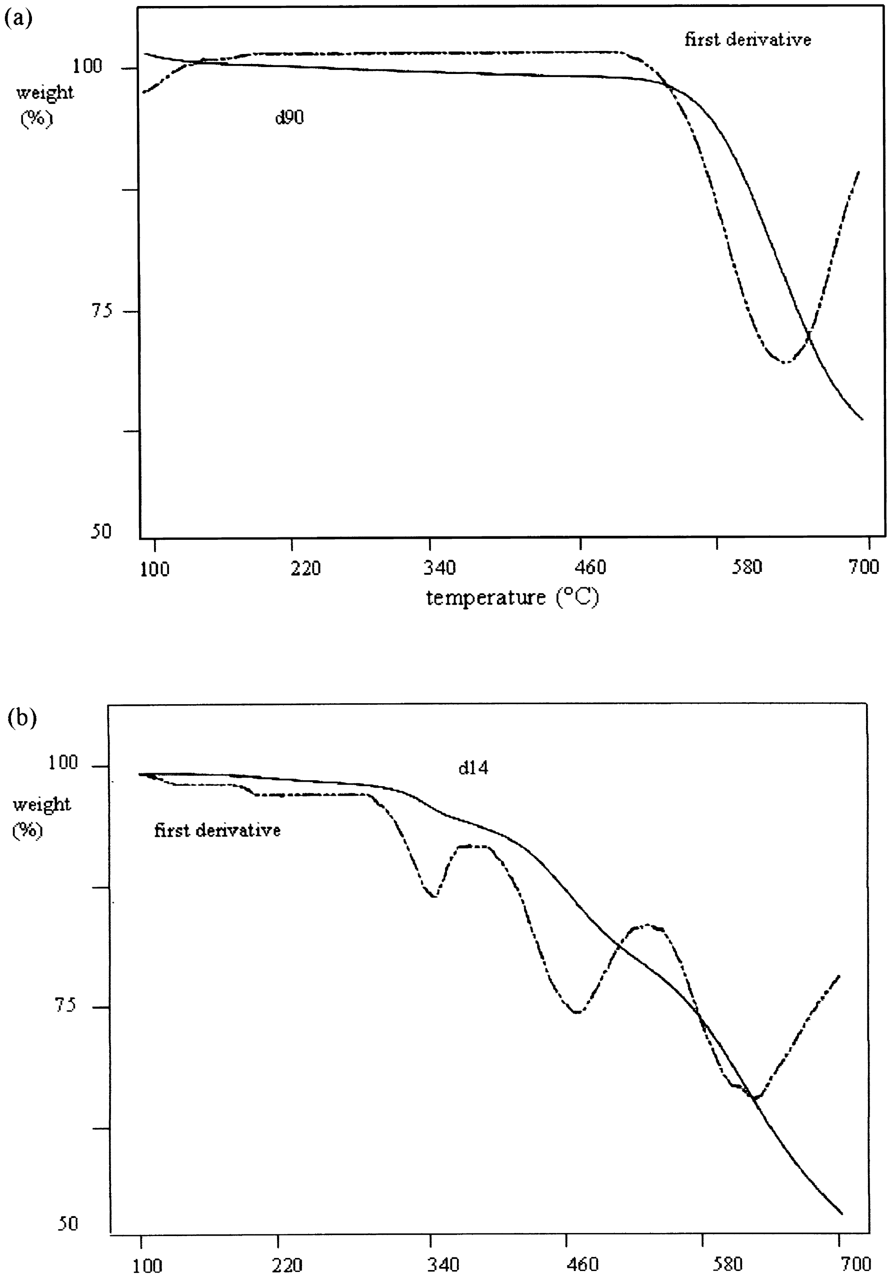

Fig. 2. Thermogravimetric analysis (TGA) of polymer samples under nitrogen (a) POD–DPE, polymer sample d90; (b) PH–DPE, polymer sample d14.

reactions, such as crosslinking, degradation and non-linear cyclization of PH groups. A final region, above 450°C, represents the decomposition of the POD–DPE structure. For POD–PH copolymers, however, the four regions could not be detected so easily, as significant overlaps of the regions may be present. Therefore, the PH content computed from Eq. (3) is subject to fluctuations, as some sort of deconvolution technique has to be carried out in some cases. Final results obtained are presented in Table 2.

The TGA spectra of pure monomers did not indicate any weight loss up to 150°C, which indicates that monomers were free of water. The purity of monomers were confirmed through melting point (T_m) evaluation for HS (253°C for an expected T_m of 254°C) and ^{1}H NMR spectrometry for DPE. Fig. 3 shows the structure of DPE monomer and Table 3 presents the absorption peaks from spectra taken in DMSO-d_6.

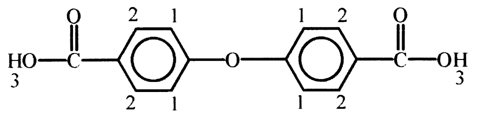

Fig. 3. Structure of the DPE monomer.

Table 3
Absorptions of protons 1, 2 and 3 of DPE monomer in DMSO-d_6

Proton	δ (ppm)[a]
1	7.18 (4H,d)
2	8.01 (4H,d)
3	12.93 (2H,s)

[a] d-duplet, s-singlet.

3.2. Statistical analysis

Standard statistical analysis of experimental data presented in Tables 1 and 2, including the computation of main effects, variable interactions and second-order effects for molecular weight and PH content, did not show any statistically significant variable effects upon the final polymerization results. This means that either uncontrolled variables may play an important role during the course of polymerization or that final results are too sensitive to small unavoidable variations of the polymerization conditions. Fig. 4 gives us a clue to explain these unexpected results. Fig. 4 shows that polymer solubility depends very strongly on the reaction temperature. It may be seen that all polymers prepared at 160°C were soluble in NMP, as expected for POD–DPE or PH–DPE [6,11], while all polymers synthesized at 100°C were not soluble in NMP. When the reaction temperature was 130°C, all sorts of solubility behavior could be observed. According to these results, one may assume that significant changes occur in the polymer structure as the reaction temperature grows from 100 to 160°C, which are confirmed qualitatively by ^{1}H NMR spectra and quantitatively by TGA analysis (see Table 2). Therefore, polymer structure changes very significantly along the experimental grid analyzed and this may be a possible source of variability in the system.

Fig. 5 shows ^{1}H NMR spectra of polymer samples with 100% HZ (a) and 10% HZ (b), as determined by TGA. Peaks related to hydrazide protons (10.7), to aromatic protons in the neighborhood of the ether (7.3), to hydrazide (8.2) and to oxadiazole (8.2) groups can be seen in Fig. 5. Additional peaks usually connected to aromatic protons of degradation products (8.5) and more complex structures can also be observed in the ^{1}H NMR spectra of the polymer samples. When the HZ content is higher, peaks related to complex structures also tend to be stronger. Therefore, it is assumed here that some polymer samples are not soluble in NMP because of the existence of complex chemical structures (branching), which tend to increase as the HZ content increases. This analysis indicates that side reactions may be minimized and that soluble polymer containing high amounts of polyoxadiazole may be obtained if polymerization is performed at 160°C, which is of fundamental importance for membrane preparation. This does not guarantee, however, that polymer containing 100% of polyoxadiazole may always be obtained at such high temperatures.

Based on the results presented above, the experimental data set was divided into three groups, based on the

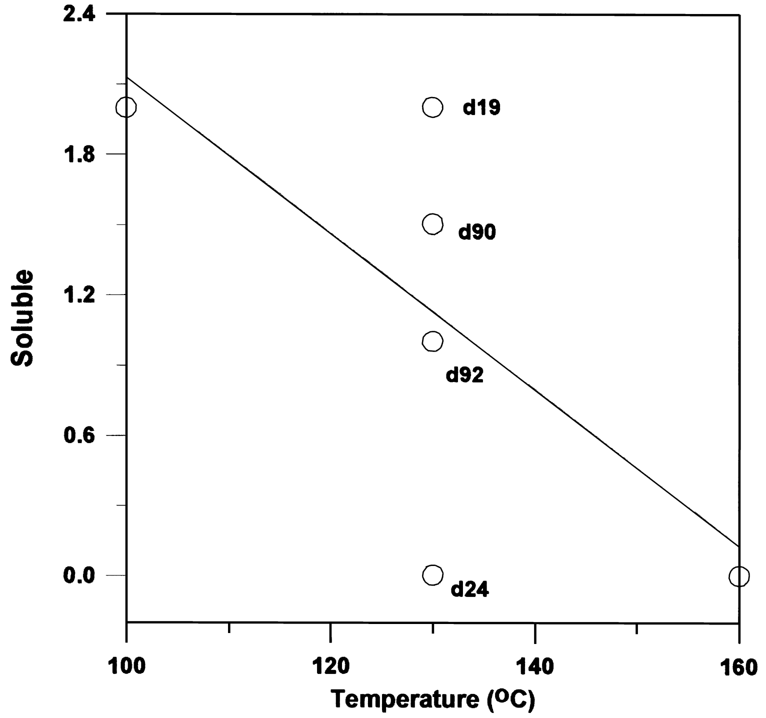

Fig. 4. Solubility of polymer samples as a function of reaction temperature.

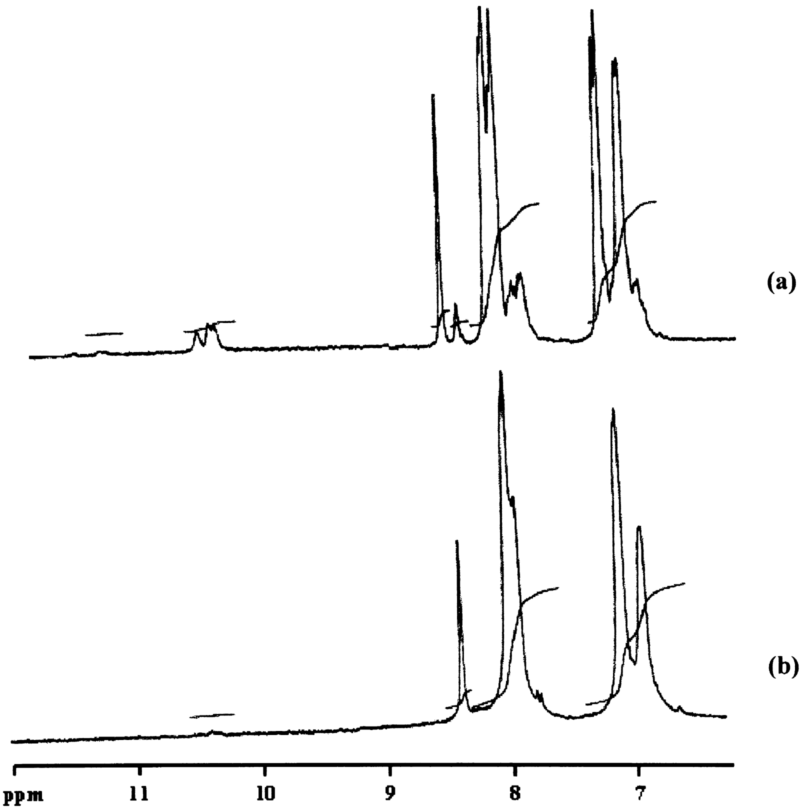

Fig. 5. ^{1}H NMR spectra of polymer samples: (a) d1 (with 100 %HZ); (b) d6 (with 10 %HZ).

temperature used to prepare the polymer material. Independent analysis was carried out for each class of experimental results, but once more the computation of main effects, variable interactions and second-order effects for molecular weight, did not reveal the existence of statistically significant effects upon the final results obtained. This probably indicates that additional sources of process variability and sensitivity to polymerization conditions are present in the system. (It is important to say that average molecular weight of polymer samples insoluble in NMP were computed with a correlation developed for intrinsic viscosity as a function of the weight average molecular weight, built with data collected for soluble samples in sulphuric acid. Fig. 6 shows the excellent correlation obtained between these two variables.)

As correlations between experimental data and simulation results obtained through empirical modeling were always smaller than 0.70 for all cases analyzed [13], it was assumed that exogenous effects might be playing an important role during the POD–DPE synthesis. It seems that two extremely important effects are the amount of water present in the reaction medium and the quality of agitation. Although the water concentration is a controllable variable if drying of PPA and control of reaction atmosphere are performed, the fact is that PPA is extremely hygroscopic and absorbs water from the atmosphere extremely fast. Table 4 presents results of intrinsic viscosities obtained when known initial amounts of water are added to the reaction environment. It is clear that the water concentration exerts a major influence upon the final properties of the polymer obtained, reducing the average molecular weight of the polymer produced and apparently reducing the variability of the final properties of polymer samples obtained in different batches. Besides, Fig. 7 shows that as the water concentration increases, the viscosity of the reaction medium is reduced very significantly, which may also change the mixing characteristics of the reaction mixture and affect the polymer synthesis.

By the time this work was done, we were unable to control rigorously and measure in-line the amount of water in PPA during the polymer synthesis. Gomes [13] showed that even when reaction is carried out under vacuum, no water can be removed from the reaction medium, given the extremely high dehydration properties of PPA. Besides, carrying out the polymerization in the presence of strong dehydration species, such as P_2O_5, as mentioned by Krongauz et al. [12], does not lead to any significant improvement of the reproducibility of the results obtained [13]. It must be pointed out that as much as 0.70 g of water may be produced during the polymerization, which means that the water concentration may reach a few percents after the polymerization is over. Given the results presented in Fig. 7, dramatic changes of system viscosity may occur along the experimental grid analyzed and during

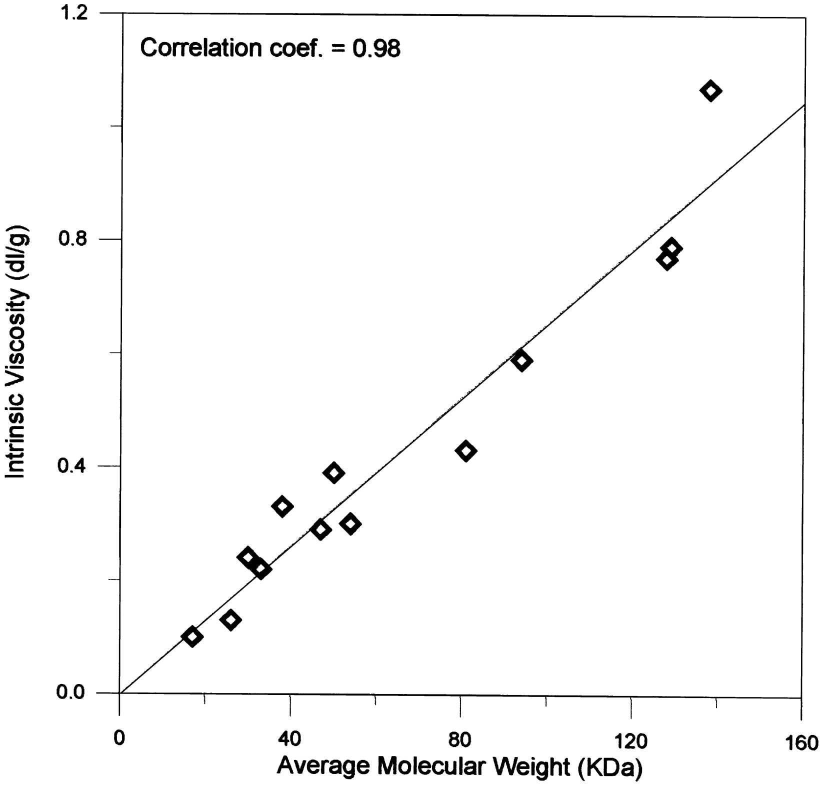

Fig. 6. Intrinsic viscosity as a function of weight average molecular weight of soluble polymer samples.

the course of polymerization. This water effect has been completely overlooked in previous publications. However, given the experimental constraints, it is not completely clear whether variations of water concentration during reaction time might be the main reason to explain the experimental fluctuations observed. In spite of that, even if it is assumed that the water content is the origin of the fluctuations observed experimentally, the in-line drying of the PPA seems to be so hard that this “water effect” will probably have to be dealt with during the formulation of a process strategy for production of large amounts of polymer material for membrane preparation.

Table 4
Intrinsic viscosity of final polymer samples as a function of the water content of PPA

Polymer	Water content added (g)	[η] (dl/g)	R^2
D6	–	1.07	1.00
D61		0.38	0.95
D62		0.44	0.97
D65	2	0.56	0.94
D652		0.69	0.98
D653		0.54	1.00
D64	7	0.34	0.98
D642		0.33	0.96
D643		0.27	0.99

Besides the possible influence of water concentration upon the reaction course, the occurrence of side reactions may also be contributing to the observed variation of the weight average molecular weight. (Perhaps, both effects may be coupled.) Table 2 shows very clearly that very large weight average molecular weights can be obtained during the polymerization, even when the monomer concentration ratios are very different from the ideal value of 1, which is expected to lead to the largest molecular weights in 1:1 bi-functional condensation polymerizations. In order to evaluate the influence of branching reactions upon the final polymer weight average molecular weight, a simple kinetic model was formulated and analyzed, as described in the following section.

4. Semi-empirical modeling of the POD–DPE synthesis

The final average molecular weight of POD–DPE synthesized through solution polycondensation of DPE and HS in PPA is apparently subject to large fluctuations, perhaps due to exogenous uncontrollable effects induced by small changes of the water concentration and mixing of the reaction medium. In order to understand the kinetics of the polymerization, a very simple model is built below to allow the computation of average molecular weight as functions of reaction conditions. Based on the synthesis variables and reaction conditions (high temperature, intermediate polymer

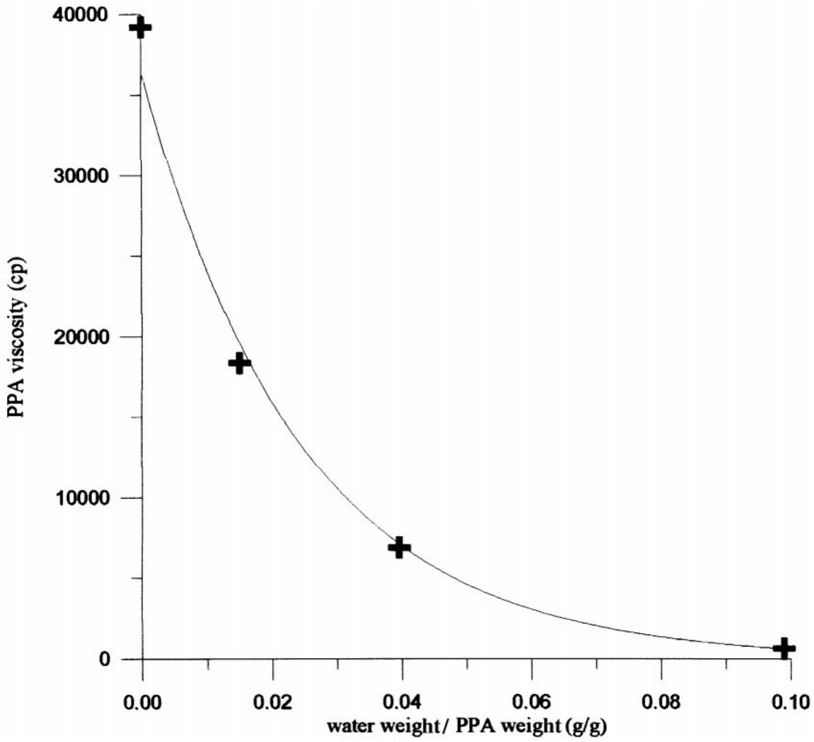

Fig. 7. Viscosity of PPA as a function of the water content.

and acid solvent), many side reaction steps may occur during the synthesis of POD–DPE, so that the kinetic mechanism must include steps other than the condensation of DPE and HS and cyclization of PH bonds. The main reaction steps already described in the literature are presented below.

4.1. The kinetic mechanism

4.1.1. Formation of PH bonds

The formation of PH bonds is due to the main condensation reaction of DPE and HS and occurs in acid medium, as presented in Fig. 8. Because of its hygroscopic properties, the acidic solvent decreases the activity of water and displaces the reaction equilibrium towards the formation of the polymer species. As shown in Table 4, however, this step is probably very sensitive to variations of the water content in the solvent.

4.1.2. Cyclodehydration of hydrazide groups

Hydrazide groups generate oxadiazole groups through cyclodehydration of the PH bonds. According to Frazer and Wallenberger [16], however, the cyclization of hydrazide groups is not complete, which leads to the formation of copolymers of polyoxadiazole and polyhydrazide. This fact is related to the different conformations presented by hydrazide groups. Hydrazide groups can present different geometric conformations, such as the extended and the folded forms, shown in Fig. 9, which are the commonest ones. It is necessary that PH present the folded conformation for the ring closure reaction to take place. However, the folded conformation is the less favorable form because of the higher electronic repulsion of the oxygen atoms. Thus, the transition of the extended form to the folded form is believed to be the rate determining step of the cyclodehydration reaction. Fig. 10 presents the expected scheme for the cyclodehydration reaction of PH.

4.1.3. Thermal degradation of residual hydrazide groups

As the oxadiazole groups are formed, the chain mobility decreases, favoring the presence of residual hydrazide groups. Contrary to the high thermal stability of oxadiazole groups, hydrazide groups are more susceptible to thermal degradation. Fig. 11 shows a possible scheme for the thermal degradation of the hydrazide groups.

4.1.4. Depolymerization

For polycondensation and cyclization reactions to occur it is necessary that water molecules be removed from the reaction medium, as shown in Fig. 8. This way, it is necessary that solvents with significant dehydration properties, such as PPA, be used. However, the presence of water in the reaction medium decreases the efficiency of the water removal. In this case, the polycondensation reaction equilibrium may be displaced towards the reactant species and to depolymerization.

4.1.5. Crosslinking reactions

The occurrence of crosslinking reactions during the formation of POD–DPE is very likely, given the availability

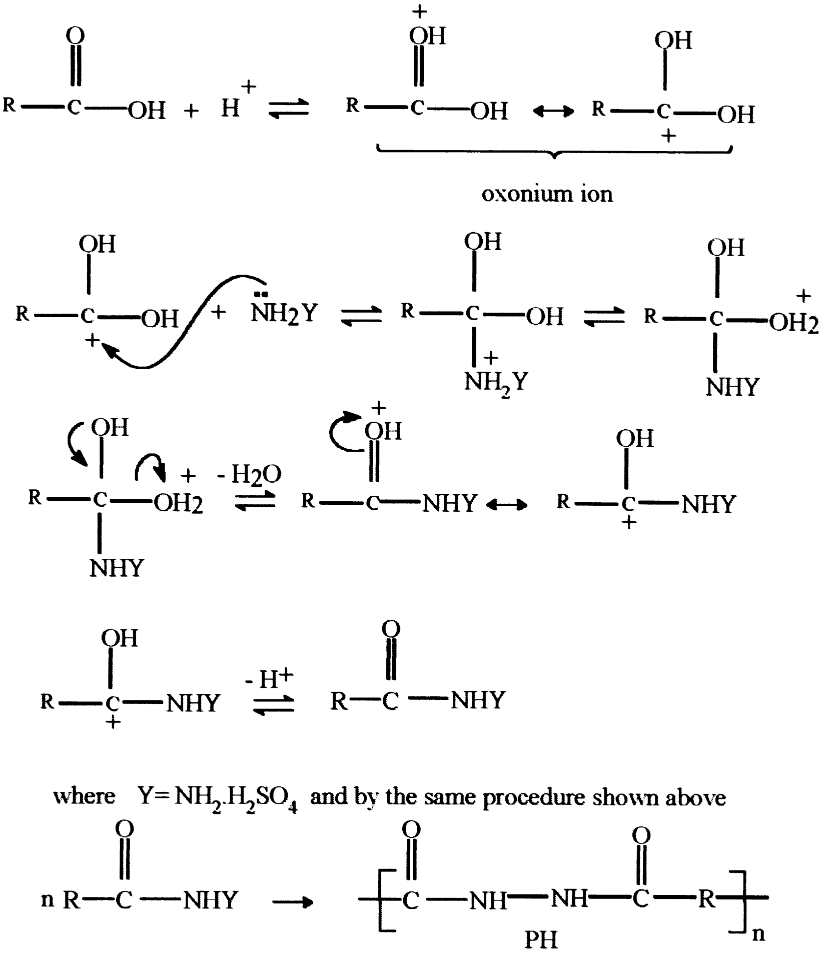

Fig. 8. Formation of PH bonds.

of an electron pair in the NH groups of PH, which confers a nucleophilic nature to PH groups [17]. The expected scheme for the crosslinking reaction is shown in Fig. 12. Frazer and Sarasohn [15] suggested that additional side reactions, such as the crosslinking reactions, may compete with the linear cyclodehydration, when high conversions are reached. Frazer and Sarasohn's remark is based on the decrease of the first-order rate constants when conversion increases above 80%. As the oxadiazole content increases, the polymer chain becomes more rigid, which may limit the cyclization due to the low segmental mobility.

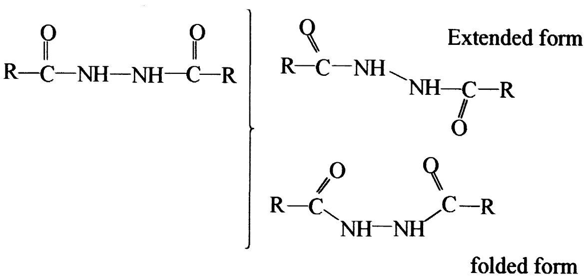

Fig. 9. Commonest conformations of the hydrazide group.

A strong argument against the occurrence of crosslinking reactions is the high solubility of copolymers of polyhydrazide and polyoxadiazole in concentrated sulphuric acid [15]. However, it is also known that these polymers can degrade in sulphuric acid [12,18,19], which may lead to unreliable solubility tests. Besides, we believe that we have

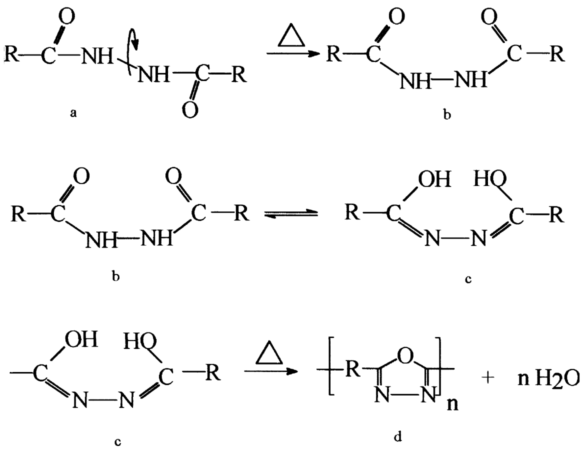

Fig. 10. Cyclodehydration of the hydrazide group.

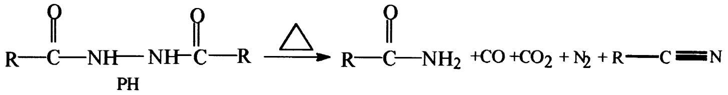

Fig. 11. Thermal degradation of the hydrazide group.

collected a significant number of experimental evidences regarding the occurrence of crosslinking reactions, such as: (1) the non-solubility and gel formation of polymer samples in NMP and DMSO, which are good solvents for both polyhydrazide and polyoxadiazole; (2) the qualitatively different degradation regions in the TGA spectra observed and the apparent inadequacy of the quantitative HZ evaluation from TGA spectra; (3) the existence of different structures in the ^{1}H NMR spectra of polymer samples (see Fig. 5); (4) the formation of polymer samples with large weight average molecular weight even when monomer feed ratios are very different from 1.

4.2. The kinetic model

Based on the previous discussion, a very simple kinetic model was developed, based on the kinetic mechanism presented in Table 5. The proposed kinetic mechanism assumes that monomers DPE and HS react to form the PH groups, which can then react with other PH group and form a branched polymer chain (cyclization is assumed to be negligible), Ret. Besides, PH groups are subject to thermal degradation and to cyclodehydration, which leads to the formation of the POD groups.

Instead of writing the complete set of mass balance equations, additional assumptions are introduced in order to simplify the equations, allowing the presentation of simple closed forms for the variable of interest (the average molecular weight) and avoiding the necessity do define unknown kinetic parameters and state variables. The first assumption is to consider that the PH formation is instantaneous. Although this may seem to be a rather gross assumption, Table 2 shows that very large weight average molecular weight were obtained for polymer samples of all groups considered, no matter whether polymer chains are PH rich or oxadiazole rich. Therefore it seems reasonable to assume that the formation of PH groups is much faster than the formation of oxadiazole groups. A second assumption is to consider that the water activity is very low in the reaction medium, which is equal to assume that the original PPA is water-free. As discussed previously, we are not able to assure that this is true. Therefore, simulation results will actually be subject to additional perturbations, that will have to be analyzed afterwards.

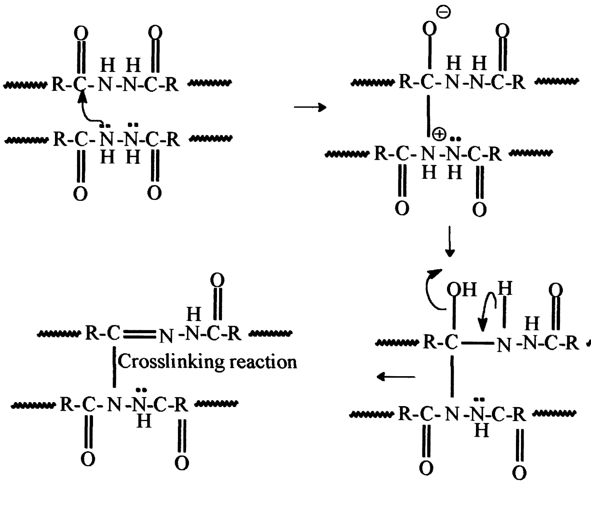

Fig. 12. Crosslinking reaction of residual hydrazide groups.

Based on the additional assumptions presented, it is possible to write that:

$$\begin{cases} f > 1 \begin{cases} [\mathrm{HS}]_1 = 0 \\ [\mathrm{DPE}]_1 = [\mathrm{HS}]_0(f-1) \\ [\mathrm{PH}]_1 = [\mathrm{HS}]_0 \end{cases} \\ f < 1 \begin{cases} [\mathrm{HS}]_1 = [\mathrm{HS}]_0(1-f) \\ [\mathrm{DPE}]_1 = 0 \\ [\mathrm{PH}]_1 = [\mathrm{HS}]_0 f \end{cases} \end{cases} \tag{4}$$

where f is the monomer feed ratio

$$f = \frac{[\mathrm{DPE}]_0}{[\mathrm{HS}]_0} \tag{5}$$

and the index 1 represents the end of the first reaction step.

The number of molecules in the beginning of the reaction is

$$N_0 = \frac{[\mathrm{HS}]_0}{2} + \frac{[\mathrm{DPE}]_0}{2} \tag{6}$$

Table 5
Kinetic mechanism for the kinetic model (Res represents thermal degradation residues and Ret represents branched polymer chains)

(1) Formation of PH

$\mathrm{DPE} + \mathrm{HS} \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \mathrm{PH} + 2\mathrm{H_2O}$

(2) Cyclodehydration of PH

$\mathrm{PH} \underset{K_4}{\overset{K_3}{\rightleftharpoons}} \mathrm{POD} + \mathrm{H_2O}$

(3) Thermal degradation of PH

$\mathrm{PH} \xrightarrow{K_5} \mathrm{RES} + \mathrm{H_2O}$

(4) Crosslinking

$\mathrm{PH} + \mathrm{PH} \underset{K_7}{\overset{K_6}{\rightleftharpoons}} \mathrm{Ret} + \mathrm{H_2O}$

while the number of molecules at the end of the first reaction step is

$$N_1 = \frac{[\mathrm{HS}]_0 \cdot |f-1|}{2} \tag{7}$$

so that the number average molecular chain size after the completion of the first reaction step is:

$$\bar{i} = \frac{N_0}{N_1} = \frac{(1+f)}{|1-f|} \tag{8}$$

which is significant smaller than values presented in Table 1 for all conditions and shows that other growing mechanism must be present. It must be noticed that the presence of water leads to even lower molecular weight, as monomer conversion is not complete.

During the second reaction step, it is possible to write:

$$\frac{\mathrm{d}[\mathrm{PH}]}{\mathrm{d}t} = -K_6[\mathrm{PH}]^2 - K_5[\mathrm{PH}] - K_3[\mathrm{PH}] \tag{9}$$

$$\frac{\mathrm{d}[\mathrm{POD}]}{\mathrm{d}t} = K_3 \cdot [\mathrm{PH}] \tag{10}$$

$$\frac{\mathrm{d}[\mathrm{Res}]}{\mathrm{d}t} = K_5[\mathrm{PH}] \tag{11}$$

$$\frac{\mathrm{d}[\mathrm{Ret}]}{\mathrm{d}t} = K_6[\mathrm{PH}]^2 \tag{12}$$

$$\frac{\mathrm{dN}}{\mathrm{d}t} = -\frac{K_6 \cdot [\mathrm{PH}]^2}{2} + K_5[\mathrm{PH}] \tag{13}$$

where reaction orders are assumed to be equal to the stoichiometric coefficients.

The integration of Eqs. (9)–(13) leads to

$$[\mathrm{PH}]_2 = \frac{[\mathrm{PH}]_1 \exp(-(K_3+K_5)t)}{r[PH]_1[1-\exp(-(K_3+K_5)t)]+1} \tag{14}$$

where,

$$r = \frac{K_6}{K_3 + K_5} \tag{15}$$

and

$$[\mathrm{POD}]_2 = \frac{K_3}{K_6}\ln\{X(t)\} \tag{16}$$

$$[\mathrm{Res}]_2 = \frac{K_5}{K_6}\ln\{X(t)\} \tag{17}$$

$$[\mathrm{Ret}]_2 = \frac{1+r[\mathrm{PH}]_1}{r}\left(\frac{X(t)-1}{X(t)}\right) - \frac{1}{r}\ln\{X(t)\} \tag{18}$$

$$N_2 - N_1 = \frac{1+r[\mathrm{PH}]_1}{2r}\left(\frac{1-X(t)}{X(t)}\right) + \left(\frac{1}{2r} + \frac{K_5}{K_6}\right)\ln\{X(t)\} \tag{19}$$

where

$$X(t) = 1 + r[\mathrm{PH}]_1[1-\exp(-(K_3+K_5)t)] \tag{20}$$

Therefore, it is possible to follow the dynamic evolution of the number average chain size as a function of the reaction conditions, provided that the kinetic constants are known. As kinetic constants are not known, it may be interesting to analyze the limit conditions, when one of the parameters is much larger than the other ones. When either K_3 or K_5 are much larger than the other parameters, the number average chain size is not allowed to grow very significantly, which is not supported by results presented in Table 1. When K_6 is larger than the other parameters, then Eqs. (14)–(20) become

$$[\mathrm{PH}]_2 = \frac{1}{r}\left\{\frac{\exp(-(K_3+K_5)t)}{1-\exp(-(K_3+K_5)t)}\right\} \tag{21}$$

$$[\mathrm{POD}]_2 = \frac{K_3}{K_6}\ln\{r[\mathrm{PH}]_1\} + \frac{K_3}{K_6}\ln\{1-\exp(-(K_3+K_5)t)\} \tag{22}$$

$$[\mathrm{Res}]_2 = \frac{K_5}{K_6}\ln\{r[\mathrm{PH}]_1\} + \frac{K_5}{K_6}\ln\{1-\exp(-(K_3+K_5)t)\} \tag{23}$$

$$[\mathrm{Ret}]_2 = [\mathrm{PH}]_1 - \frac{1}{r}\ln\{r[\mathrm{PH}]_1\} - \frac{1}{r}\ln\{1-\exp(-(K_3+K_5)t)\} \tag{24}$$

$$N_2 - N_1 = -\frac{[\mathrm{PH}]_1}{2} + \left(\frac{1}{2r} + \frac{K_5}{K_6}\right)\ln\{r[\mathrm{PH}]_1\} + \left(\frac{1}{2r} + \frac{K_5}{K_6}\right)\ln\{1-\exp(-(K_3+K_5)t)\} \tag{25}$$

As the number average chain size is proportional to the inverse of N_2, Eqs. (21)–(25) show that the final results may depend heavily upon the completion of the first step (which depends on the water content and possible inhibition effects) and on the variation of the individual kinetic constants with the reaction conditions. Just to illustrate this point, Eqs. (21)–(25) are simplified even further, assuming that spontaneous chain decomposition and POD formation does not occur; which is equal to saying that the final polymer chain is PH rich. Then,

$$[\mathrm{PH}]_2 = \frac{[\mathrm{PH}]_1}{1 + K_6 \cdot t \cdot [\mathrm{PH}]_1} \tag{26}$$

and

$$\begin{cases} i = \dfrac{(1+f)(1+\tau)}{-\tau + (f-1)(1+\tau)}, & f > 1 \\ i = \dfrac{(1+f)(1+\tau)}{-(\tau f) + (1-f)(1+\tau)}, & f < 1 \end{cases} \tag{27}$$

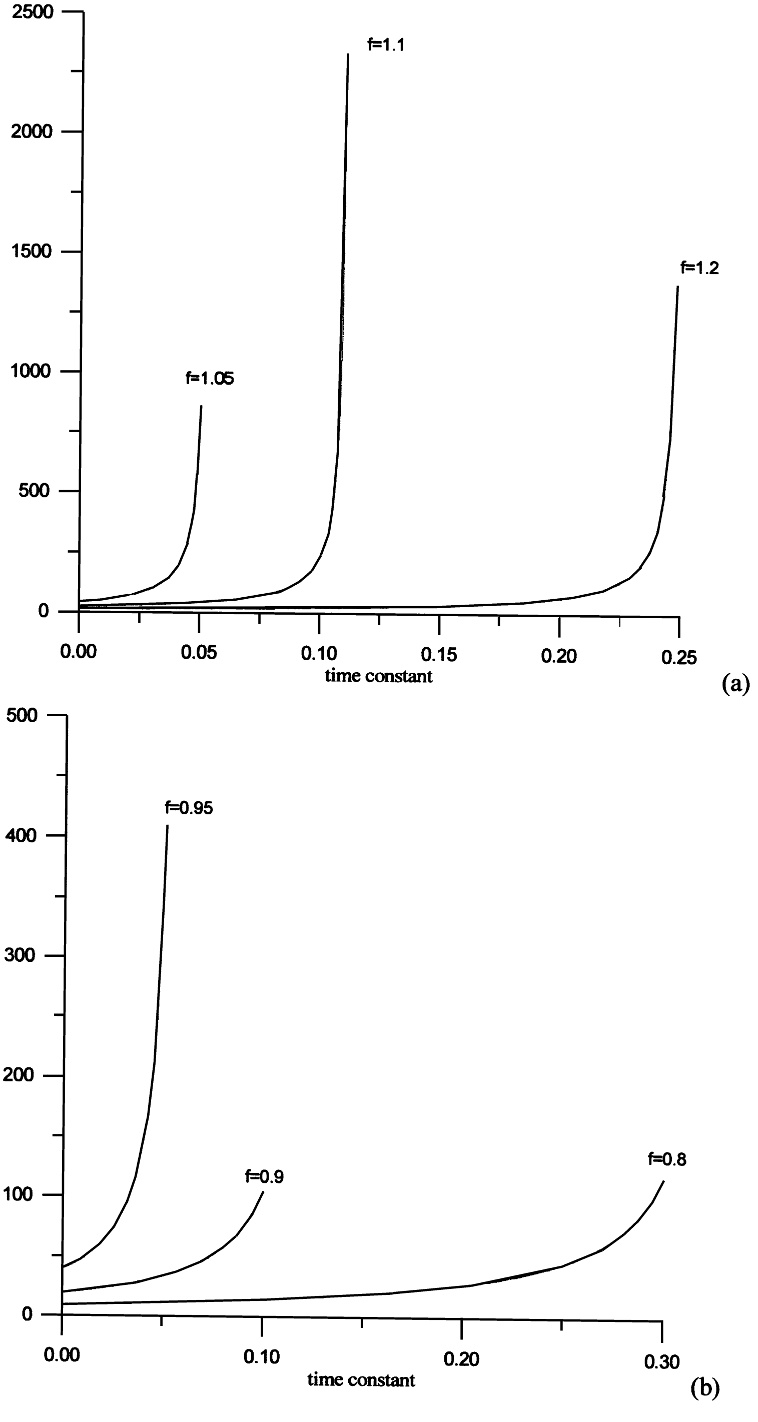

Fig. 13. Variation of average chain size as a function of dimensionless time for different feed compositions.

where,

$$\tau = K_6 t[\mathrm{HS}]_0 \tag{28}$$

which clearly predicts the gel formation for

$$\begin{cases} \tau_\infty = \dfrac{f-1}{2-f}, f > 1 \\ \tau_\infty = \dfrac{1-f}{f(2f-1)}, f < 1 \end{cases} \tag{29}$$

Eq. (29) shows that high molecular weight may be expected in the range $0.5 < f < 2$, which is in accordance with the experimental results obtained, as f was allowed to vary between 0.8 and 1.2. Fig. 13 shows the variation of the number average chain length as a function of the time constant (τ) for different values of f, as predicted by Eq. (27). It may be seen that small variations of f, within a few %, may lead to large variations of the average chain length even when all remaining experimental conditions are

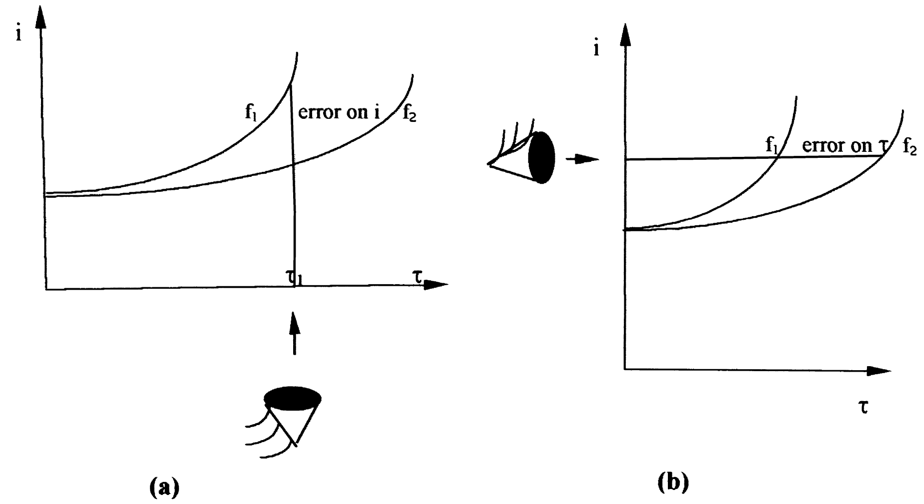

Fig. 14. Different approaches to monitor the reaction evolution (a) reaction time (b) average molecular weight.

kept constant. Model and experimental results suggest that, unless initial feed composition can be controlled very tightly, some sort of in-line evaluation of average molecular weight must be carried out to guarantee the production of polymers of large molecular weight and high contents of POD groups simultaneously, as illustrated in Fig. 14.

5. Conclusions

It was shown experimentally that polymers containing high amounts of oxadiazole groups and large molecular weights can be prepared through reaction of HS and DPE in PPA. Among the synthesis variables analyzed, reaction temperature seems to be the most important one, as soluble oxadiazole-rich polymer samples can only be prepared at higher temperatures (160°C). The influence of the remaining variables analyzed (batch time, and feed composition) upon the final polymer obtained is unclear, possibly due to the occurrence of complex side chain-growth reactions and/or uncontrolled variations of the water composition, which is very difficult to control and exerts an enormous influence upon the reaction kinetics and the medium homogeneity.

As experimental results obtained suggest that cross-linking reactions play an important role during the growth of the polymer chain, a very simple kinetic scheme based on the existence of cross-linking of HZ groups was proposed and used to build a mathematical model of the polymerization. Simulation results obtained with the model support both the finding of large molecular weights in a very broad range of feed conditions and the high sensitivity of the final average molecular weight on the initial feed composition.

It seems clear that POD–DPE for membrane preparation must be synthesized at high temperatures and that cross-linking reactions are responsible for the large molecular weights of the polymer samples obtained. It also seems clear that the development of large scale processes for POD–DPE synthesis will have to rely on the implementation of in-line procedures for continuous monitoring of polymer average molecular weight and composition.

Acknowledgements

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