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Synthesis and characterization of flexible polyoxadiazole films through cyclodehydration of polyhydrazides

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Abstract

Aiming to produce flexible films of poly(4,4′-diphenylether-1,3,4-oxadiazole), POD-DPE, the synthesis of POD-DPE through thermal cyclodehydration of polyhydrazide in solutions of poly(phosphoric acid), PPA, and in film form is studied here. It was observed that POD-DPE polymer samples obtained when the cyclodehydration of polyhydrazide is performed in solutions of PPA are insoluble in the solvents normally used for film preparation. On the other hand, the cyclodehydration of polyhydrazide in film form can lead to brittle POD-DPE films due to the high temperatures required for reaction to occur. In order to obtain flexible POD-DPE films with high conversion through cyclodehydration of polyhydrazide films, it is shown here that it is very important to adjust the cyclodehydration temperature (T_c) as a function of the glass transition temperature (T_g) and the weight average molecular weight (M_w) of the polyhydrazide. In all cases analyzed, polyhydrazides were synthesized by low temperature solution polycondensation reactions and were characterized by intrinsic viscosity measurements, size exclusion chromatograpy, nuclear magnetic resonance, infrared spectroscopy and thermal analysis. Polyhydrazides with weight average molecular weights up to 74,100 g/mol were obtained. The POD-DPE films obtained were characterized by infrared spectroscopy and nuclear magnetic resonance, showing that the production of POD-DPE films is indeed possible from cyclodehydration of polyhydrazide films.

Keywords: Polyhydrazide; Polyoxadiazole; Thermal cyclodehydration

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1. Introduction

Aromatic poly(1,3,4-oxadiazole), POD, is known by its high chemical and thermal resistance being stable up to 450 °C [1]. For this reason, the use of POD to prepare membranes for gas separation [2–4] and fuel cells [5] has been investigated. Different methods for POD synthesis have been described in the literature [2,3,6–12]. However, two of these methods present more advantages to synthesize POD (such as higher molecular weight and lower residual hydrazide content), the polymerization of a dicarboxylic acid and a salt of hydrazine in solution [2,3,10–12], and the solid state cyclodehydration of polyhydrazides [6–10]. Both methods are presented schematically in Fig. 1.

Recently, Gomes et al. [12] studied the direct POD synthesis through polymerization of a dicarboxylic acid and hydrazine sulphate in solutions of poly(phosphoric acid), PPA. The authors reported a large variation in the final average molecular weight, and of the final macromolecular structure, even when the reactions were carried out under similar conditions. This variation was attributed to the high viscosity of the reaction medium, to the degradation reactions caused by the acid solvent, and to occurrence of secondary reactions. The complexity of this synthesis method motivates further investigation of alternative routes.

The POD can also be obtained through thermal treatment of polyhydrazide. The thermal treatment leads the cyclodehydration of the hydrazide groups and, consequently, the formation of oxadiazole ring [8]. Long reaction times and high temperatures may be required and, depending on the reaction conditions, polymers are obtained with low molecular weight, high residual hydrazide content and very low solubility in common organic solvents. According to Gebben [2], it is difficult to produce flexible POD films

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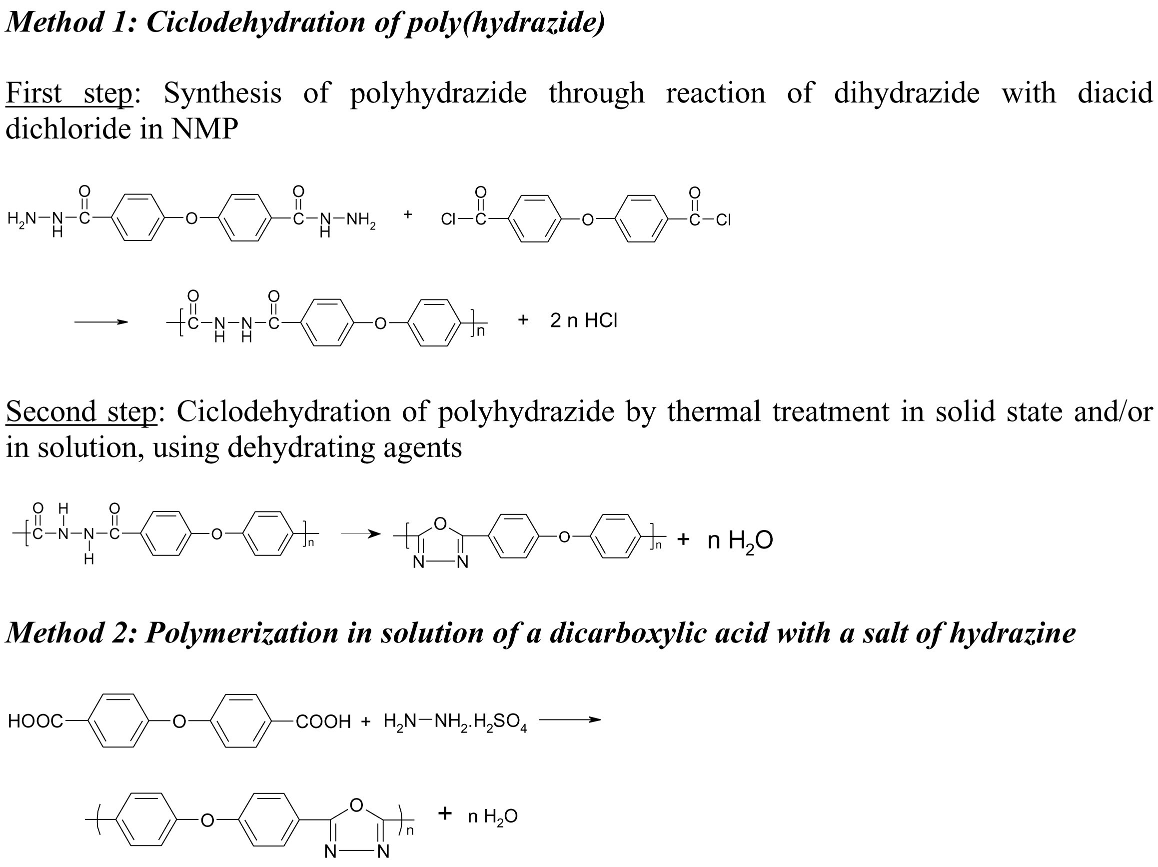


Method 1: Ciclodehydration of poly(hydrazide)

First step: Synthesis of polyhydrazide through reaction of dihydrazide with diacid dichloride in NMP

Second step: Ciclodehydration of polyhydrazide by thermal treatment in solid state and/or in solution, using dehydrating agents

Method 2: Polymerization in solution of a dicarboxylic acid with a salt of hydrazine

Fig. 1. Common methods used for the POD synthesis.

through thermal cyclodehydration, mainly because of the simultaneous degradation of hydrazide groups. Hensema et al. [10] also raised some questions related to the difficulty to prepare flexible POD films through thermal cyclodehydration. One of them is the shrinkage of the macromolecule caused by the ring closure of hydrazide groups into 1,3,4-oxadiazole groups. However, Cassidy and Fawcett [13] reported that the degradation reaction can be minimized if the reaction is accomplished 25–50 °C below the cyclohydration transition temperature, as observed by thermal analysis (T_c). Besides, according to Hamciuc et al. [14], the probability to obtain brittle polyhydrazide films increases when the rigidity of the chains increases (which contain only *p*-phenylene rings). The brittle polyhydrazide films obtained by Hamciuc et al. [14] can show T_g up to 226 °C [15].

In this work, polyhydrazide was synthesized by solution polycondensation at low temperature and further cyclodehydrated to POD. In order to obtain flexible POD films and low contents of hydrazide groups, the reaction conditions were investigated and optimized. The final POD properties were correlated to the influence of cyclodehydration conditions and to the original polyhydrazide properties, such as the glass transition temperature (T_g), the cyclodehydration temperature (T_c) and the weight average molecular weight (M_w).

2. Experimental

2.1. Materials

Chemicals used were: dicarboxylic acid of 4,4′-diphenylether, DPE (99%, Aldrich), dichloromethane (99%, Merck), ethanol (99.8%, Merck), dimethyl ester of 4,4′-diphenylether dicarboxylic acid, DE (99%, Aldrich), hydrazine hydrate (98%, Aldrich), lithium chloride and bromide (99%, Merck), *N*-methyl-2-pirrolidone, NMP (99%, Merck), *N*,*N*-dimethylformamide, DMF (99%, Merck), thionyl chloride (+99%, Merck), poly(phosphoric acid), PPA (Aldrich). All chemicals were used as received.

2.2. Synthesis of monomers

2.2.1. Synthesis of acid dichloride (DC)

The acid dichloride was prepared by refluxing 15.5 g of DPE with 60 ml of thionyl chloride, in presence of small amount of DMF (ca. 0.05 ml). Following procedure described in the literature [16], the mixture was kept under stirring conditions at 60 °C for 10 h. Dichloromethane and excess thionyl chloride were removed by distillation. The solid was filtrated and dried at 100 °C under vacuum and recrystallized from dichloromethane. The resulting yellow solid had a melting point of 91 °C.

2.2.2. Synthesis of dihydrazide (DH)

A mixture of 1 mol (22.9 g) of DE and 3 mol (11.6 ml) of hydrazine hydrate was kept under stirring and refluxed in ethanol for 24 h. Afterwards, DH was precipitated by cooling down the solution to room temperature, filtrating and recrystallizing from dichloromethane [6]. The resulting white solid gave a melting point of 236 °C. Table 1 presents ^{1}H NMR spectra for both monomers in DMSO-d$_6$ at 25 °C.

2.3. Synthesis of polyhydrazide (PH)

Polycondensation reactions were carried out in solution at low temperature, under argon atmosphere, and using equimolar amounts of DH and acid dichloride [6,7,17]. NMP was used as solvent and lithium chloride was used as co-solvent. The syntheses of polyhydrazide were performed following a statistical design [18]. A minimum two-level factorial design for four variables with four replicates at the central point was applied, to allow the characterization of experimental fluctuations, as well as the main variable effects. The selected reaction variables were temperature (*T*), batch time (*t*), dilution ratio (DH/NMP) and LiCl concentration in solution (AA/NMP).

After complete dissolution of lithium chloride and DH in NMP, the polymerization was initiated by addition of the acid dichloride. The reaction was finished by precipitation of the polymer in water. The polymer was filtered, washed with excess water and dried at 50 °C under vacuum for 24 h.

2.4. Synthesis of polyoxadiazole (POD)

Two methods were used to convert polyhydrazide into POD: cyclodehydration either in solution of PPA or in film form. In the first case, the reactions were performed under argon atmosphere. In the second case, reactions were carried out in a vacuum oven.

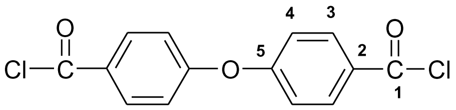
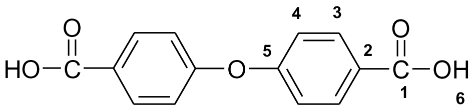
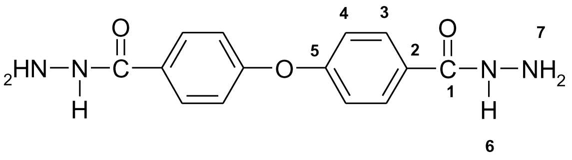
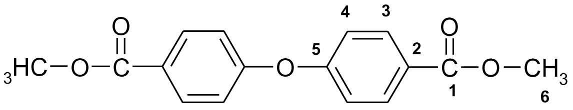
2.4.1. Cyclodehydration of polyhydrazide in solution of PPA

The synthesis of POD by cyclodehydration of polyhydrazide in PPA solution was carried out in a 100 ml three-necked flask, equipped with a mechanical stirrer and kept under argon atmosphere. Polyhydrazide and PPA were added to the flask in a molar ratio PPA/PH of 20, thus vigorously stirred until dissolution was complete. The solution was continuously stirred and kept at constant temperature for a specified time. The temperature and time of reaction ranged from 160 to 200 °C and from 4 to 6 h, respectively.

2.4.2. Cyclodehydration of polyhydrazide films

Flexible and transparent polyhydrazide films were prepared by casting a 10 wt% polyhydrazide solution in NMP onto a glass plate, followed by evaporation of the

Table 1
^{1}H NMR peaks for monomer spectra taken in DMSO-d$_6$ at 25 °C

Monomer	Structure	δ (ppm)	
		H	C
DC		**3** 8.00 (d) **4** 7.17 (d)	**1** 166.43 **2** 126.33 **3** 131.76 **4** 118.79 **5** 159.29
DPE		**3** 7.99 (d) **4** 7.18 (d) **6** 12.95 (s)	**1** 166.54 **2** 126.29 **2** 126.29 **3** 131.72 **4** 118.61 **5** 159.41
DH		**3** 7.90 (d) **4** 7.10 (d) **6** 9.73 (s) **7** 4.47 (s)	**1** 165.08 **2** 128.67 **3** 129.64 **4** 118.29 **5** 158.19
DE		**3** 8.00 (d) **4** 7.19 (d) **6** 3.85 (s)	**1** 165.49 **2** 125.41 **3** 131.55 **4** 118.77 **5** 159.64 **6** 51.89

solvent at 80 °C for 18 h. In order to remove the residual solvent, the polyhydrazide films were suspended in water for 6 h. The polyhydrazide films were dried and kept at constant temperature for 24 h. The temperature investigated for cyclodehydration ranged from 100 to 260 °C.

2.5. Measurements

Intrinsic viscosities $[\eta]$ of polymer samples were determined in an Ubbelohde viscometer ($D_\mathrm{I} = 0.58$ mm) using NMP solutions at 30 °C, with polymer concentrations ranging from 0.12 to 0.50 g/dl. Intrinsic viscosities $[\eta]$ were computed using Eq. (1), as described in a previous work [19]

$$[\eta] = \frac{\eta_\mathrm{esp}}{C} \tag{1}$$

A Viscotek SEC apparatus equipped with Eurogel columns SEC 10.000 and PSS SDV 10^5 (Knauer), with serial numbers HC286 and 1515161 and size 8×300 mm was employed to evaluate the weight average molecular weights of polymer samples. The equipment was calibrated using polystyrene standards (Merck) with weight average molecular weights ranging from 5.1 to 750 kDa. A solution with 0.05 M lithium bromide in NMP was used as the carrier at a flow rate of 0.8 ml/min at 50 °C. Solutions with 0.5% (w/w) of polymer were prepared, filtered through 0.5 μ m filter and injected into the chromatograph.

The ^{1}H NMR spectra were collected for monomers and polymer samples and were obtained in DMSO-d$_6$ at 25 °C using a Bruker DCX 300 spectrometer. Differential scanning calorimetry (DSC) measurements were performed with a Netzsch 204 DSC, equipped with a TASC 414/2 thermal analysis controller. Polymer samples were placed in aluminum sample pans, and the temperature was increased with a heating rate of 20 °C/min from 100 to 450 °C, under a nitrogen atmosphere. For determination of polyhydrazide glass transition temperature, only one DSC heating run was used. Thermogravimetric analysis (TGA) experiments were carried out in a Netzsch 209 TG, equipped with a TASC 414/3 thermal analysis controller. The polymer samples, under nitrogen atmosphere, were first heated from 100 to 450 °C at 10 °C/min, to remove volatiles. Then, the sample was cooled down to 100 °C and heated again from 100 to 700 °C, using similar heating conditions. The second heating was used for polymer characterization. Infrared spectra were recorded in a Bruker Equinox IFS 55 spectrophotometer, using polymer films.

3. Results and discussion

3.1. Synthesis of polyhydrazides

The experimental conditions using the experimental design and the results obtained for intrinsic viscosity are presented in Table 2. The results indicate a large fluctuation of$[\eta]$ values at the central point, which is characteristic of polycondensation reactions, as discussed by Gomes et al. [12]. Nevertheless, considering that high molecular weight is a necessary condition to obtain flexible polymer films with good mechanical properties, the central point, which leads to the highest values of $[\eta]$, may be considered as the best investigated reaction condition for the polyhydrazide synthesis.

Table 3 presents the glass transition temperature (T_g), intrinsic viscosity and weight average molecular weight (M_w) for some polyhydrazide polymer samples. The results indicate that both the T_g and $[\eta]$ increase with the weight average molecular weight, as expected. This is a solid indication that both T_g and $[\eta]$ provide indirect evaluation of M_w of the polymer samples in the samples analyzed.

According to the literature [2,10,13–15], the T_c and T_g of polyhydrazide are also important parameters that influence the final properties of POD. It seems to be necessary that the cyclodehydration reaction occur below the T_c, although the polyhydrazide should not present a high T_g. As a high M_w (T_g) is also a condition to obtain flexible POD films, these parameters have to be analyzed simultaneously and somehow optimized.

3.2. Synthesis of polyoxadiazoles

3.2.1. Cyclodehydration of polyhydrazide in solution of PPA

Experiments were carried out to determine the best combination of temperature and time for cyclodehydation of polyhydrazide dissolved in PPA. The polymer chosen for initial experiments was PH94 ($[\eta] = 1.01$ dl/g). The resulting polymers obtained at 140 °C for 2 h (POD941) and at 160 °C for 4 h (POD942), were analyzed by TGA. Fig. 2 shows the POD941 thermogram. No weight loss is observed until 500 °C, when the decomposition of the polymer begins. Considering that loss of water originated by the oxadiazole ring formation occurs from 200 to 400 °C [12], this result is evidence of very low residual hydrazide content.

The resulting PODs were not soluble in common organic solvents. However, Gomes et al. [12] showed that high reaction temperatures (160 °C) favor the solubility of the resulting polymers when the direct POD syntheses in PPA solutions are performed. Hence, new polyhydrazide cyclodehydration conditions were investigated, as presented in Table 4. The polymer with the highest molecular weight, PH90 ($[\eta] = 1.51$ dl/g), was selected for these experiments. Once again, only insoluble polymers were obtained with all conditions investigated. As discussed before [12], branching and crosslinking may occur during the POD formation, leading to solubility problems.

As POD is synthesized for membrane preparation, insoluble polymers are not desired. Therefore, polyhydrazide cyclodehydration in PPA solution cannot be used for membrane preparation purposes. Thus, thermal

Table 2
Reaction conditions used for PH synthesis and intrinsic viscosity of final PH polymer samples

Polymer	Condition	t (h)	T (°C)	DH/NMP (mol/l)	AA/NMP (% w/v)	$[\eta]$ (dl/g)
PH 1	2-Level factorial design	24	0	0.5	5	0.53
PH 2		24	0	0.1	1	1.14
PH 3		24	−20	0.5	1	0.78
PH 4		24	−20	0.1	5	0.54
PH 5		2	0	0.5	1	1.18
PH 6		2	0	0.1	5	1.12
PH 7		2	−20	0.5	5	0.91
PH 8		2	−20	0.1	1	1.10
PH 90	Central point	13	−10	0.3	3	1.51
PH 91		13	−10	0.3	3	1.23
PH 92		13	−10	0.3	3	1.45
PH 94		13	−10	0.3	3	1.01

cyclodehydration of dense films of polyhydrazide was investigated as an alternative for POD membrane preparation.

3.2.2. Cyclodehydration of polyhydrazide films

Dense films of PH94 ($[\eta] = 1.01$ dl/g) were prepared and used to evaluate the influence of the temperature during thermal treatment. Characterization of the resulting polymers by ^{1}H NMR indicate no conversion of hydrazide groups for the experiments performed at 150 and 200 °C. Fig. 3 shows the ^{1}H NMR spectrum of the polymer after 24 h at 200 °C. The presence of a peak at 10.5 ppm, which is related to hydrazide protons, indicates a very low conversion of hydrazide groups.

The polymer sample obtained through thermal treatment at 260 °C could not be analyzed by NMR because it was soluble neither in NMP nor in DMSO. However, a high conversion of polyhydrazide to POD was verified by FTIR characterization. Fig. 4 shows the spectra of the polymer before (a) and after the thermal treatment (b). Table 5 presents the main infrared absorption bands related to functional groups of polyhydrazide and POD.

The oxadiazole ring can be characterized through the absorption band at 1650–1550 cm^{-1}, related to C=N stretching, while hydrazide groups can be characterized by the band placed at 1680–1640 cm^{-1}, related to carbonyl stretching. The band at 3300–3250 cm^{-1} related to NH stretching of polyhydrazide is not a good indicator of the cyclodehydration reaction because of the hydrophilic nature of the polymers, i.e. the absorption band of OH groups is in same spectral region. The absorption band at 1040–980 cm^{-1}, related to =C–O–C= stretching of the oxadiazole ring, is not a good indicator of the cyclodehydration reaction either, because of the overlap absorption bands of diphenyl ether group at the same spectral region.

Table 3
Glass transition temperature (T_g), intrinsic viscosity and weight average molecular weight (M_w) of some PH samples

Polymer	T_g (°C)	$[\eta]$ (dl/g)	M_w (g/mol)
PH4	NA	0.54	18,300
PH3	240	0.78	NA
PH94	252	1.01	58,400
PH8	261	1.10	NA
PH92	263	1.45	NA
PH90	265	1.51	74,100

NA—not available

The analysis of FTIR spectra points out a high conversion of hydrazide groups into oxadiazole rings for the polymer treated at 260 °C. However, the film was too brittle for using as membrane. To improve the mechanical properties of the resulting polymer, T_c and T_g influence of initial polyhydrazide was evaluated. Two polymers were tested: PH3 ($T_g = 240$ °C, $T_c = 345$ °C, $[\eta] = 0.78$ dl/g) and PH90 ($T_g = 265$ °C, $T_c = 354$ °C, $[\eta] = 1.51$ dl/g). After thermal treatment, the PH3 films became brittle for all temperatures investigated (230, 245 and 260 °C). For this polymer, high conversion of hydrazide groups was only observed at 260 °C, above the T_g of the original

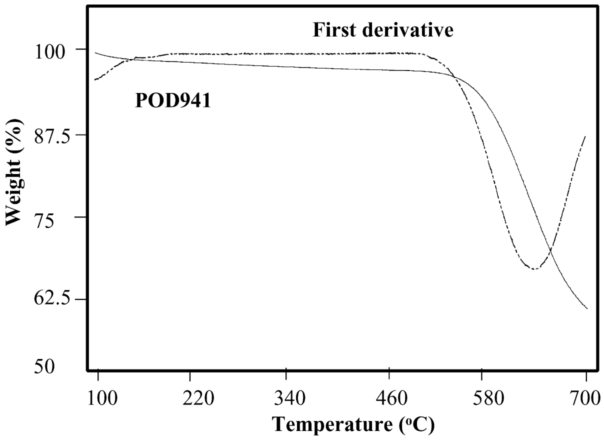


Fig. 2. TGA spectrum of POD941.

Table 4
Reaction conditions of POD synthesis in PPA solutions

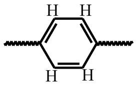
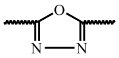
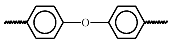
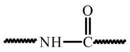
t (h)	*T* (°C)
6	200
6	160
4	200
4	160
8	180

polyhydrazide sample. On the other hand, the films obtained after thermal treatment of PH90 films were flexible, although conversion of hydrazide groups was incomplete, as indicated by the presence of an absorption band at 1650 cm^{-1} in the FTIR spectrum. For PH90, the highest hydrazide conversion was observed for thermal treatment performed at 260 °C. The results obtained clearly indicate that flexible POD films can be obtained through proper optimization of the cyclodehydration step.

4. Conclusions

Polyhydrazides with high weight average molecular weight up to 74,100 g/mol can be synthesized by low temperature solution polycondensation. The cyclodehydration by thermal treatment of polyhydrazide films can produce flexible POD films. The results of this work also show that the final mechanical properties of POD film depend on the T_g of the starting polyhydrazide. To achieve a flexible POD film, adequate to be used as membrane, the temperature during thermal cyclodehydration has to be lower than T_g of initial polyhydrazide. The T_c affects the temperature required to obtain high conversion of hydrazide groups into oxadiazole rings. The higher the T_c of the polyhydrazide, the higher the temperature required to obtain low hydrazide content in the resulting polymer. Thus, the best condition for thermal cyclodehydration of polyhydrazide film depends on prior polyhydrazide characterization. The synthesis of soluble POD through polyhydrazide

Table 5
Infrared absorption bands related to PH and POD-DPE functional groups [11]

Group	Increment	Absorption range (cm^{-1})
	CH stretching C=C stretching in-plane CH bending	3100–300 1650–1430 1275–1000
	(C–O–C) stretching C=N stretching	1040–980 1650–1550
	C–O–C stretching C–O stretching	1200–1280 1000–1050
Absorbed water	–C=O···H =NH···O= OH···H	3200–2500 3500–3100 3650–3450
	NH stretching C=O stretching	3300–3250 1680–1640

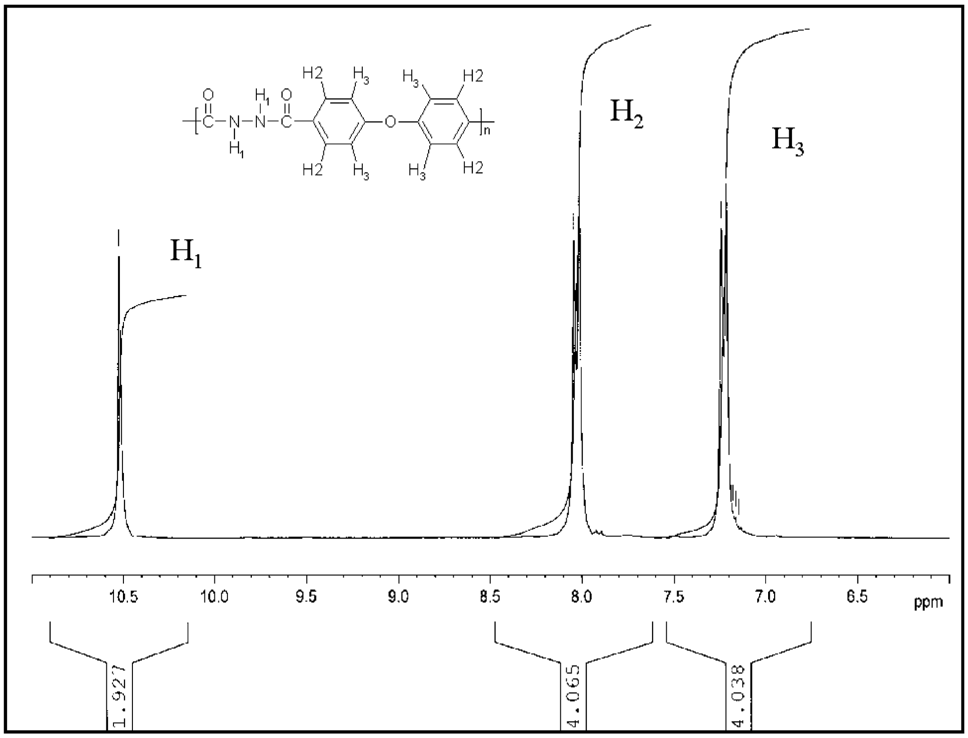


Fig. 3. ^{1}H NMR spectrum of PH94 taken in DMSO-d$_6$ at 25 °C.

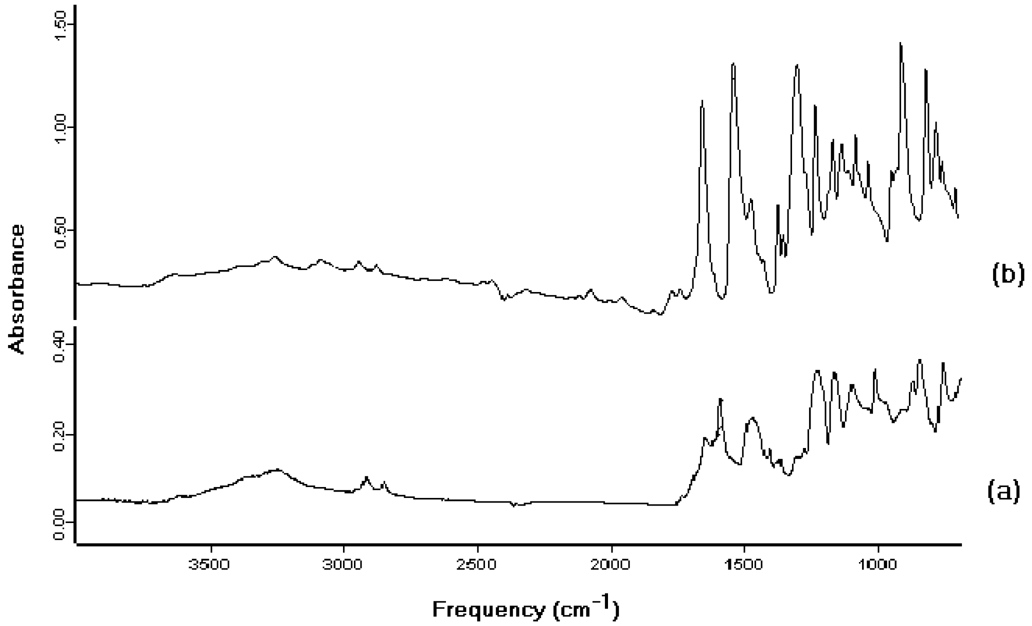


Fig. 4. Infrared spectrum of PH94 film before (a) and after (b) treated at 260 °C.

cyclodehydration in solutions of PPA and in film form is difficult. The second route is advantageous because the final POD film can be used as membrane for gas separation or in fuel cell directly.

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