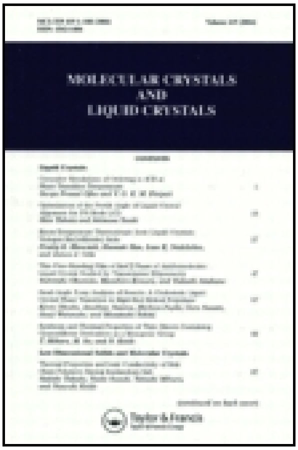

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Polyetherimides for Gas Separation Membranes

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POLYETHERIMIDES FOR GAS SEPARATION MEMBRANES

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A series of polyetherimides were synthesized by polycondensation reaction at high temperature of 2,2-bis[4,4-(3,4-dicarboxyphenoxy) phenyl]propane dianhydride with various aromatic diamines. These polymers are easy soluble in polar aprotic solvents such as N-methylpyrrolidinone, dimethylformamide or dimethylacetamide or even in less polar liquids such as chloroform. They show high thermal stability, with decomposition temperature being above 400°C and glass transition temperature in the range 200–275°C. Polymer solutions in chloroform were processed into thin films which were tested as gas separation membranes. Transport parameters for light gases were measured. The dependence of glass transition and decomposition temperature on conformational rigidity parameters was calculated.

1. INTRODUCTION

Among high performance polymers, the greatest interest was payed to aromatic polyimides due to their outstanding thermal stability, good chemical and electroinsulating properties, low dielectric constant and good adhesion to common substrates [1–3]. But, the application of fully aromatic polyimides is limited in many fields because they are normally insoluble and intractable after conversion from the polyamidic acid to the polyimide

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form. One approach to increase the solubility and processability of polyimides is the introduction of flexible linkages or bulky units into the polymer chain. It has been generally recognized that aromatic ether linkages provide the respective polymers with a significantly lower energy of internal rotation, which leads to the decrease of the melting points or glass transition temperature without significant effect on thermal stability [4,5]. On the other hand, polyethers are well known for their good mechanical properties. Thus, the combination of good solubility and robust mechanical properties makes poly(ether-imide)s especially interesting for membrane application and ultimately can allow easy fabrication.

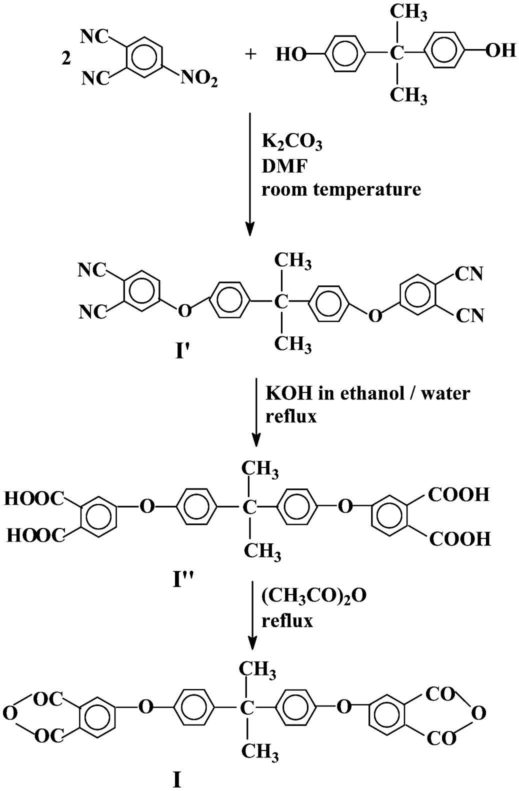
Poly(ether-imide)s are a particularly attractive class of polymers for structure-property investigation. Our aim was to study structural features which influence combination of permeabilities and selectivities for various gas separations and to examine the well known trade-off between gas permeability which is normally associated with reduced selectivity. Thus, a series of three polyetherimides have been synthesized by polycondensation reaction of certain aromatic diamines with a dianhydride containing two ether linkages, namely 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (**I**).

2. EXPERIMENTAL

2.1. Synthesis of the Monomers

The bis(ether-anhydride) **I** was prepared by a multistep reaction, starting with the nitro displacement reaction of 4-nitro-phthalodinitrile with isopropylidene-bisphenol which is named bisphenol A, as shown in scheme 1 [6,7]. Such a reaction is possible because the cyano group is one of the strongest activating groups in the nucleophilic displacement process. The reaction is performed in the presence of K_2CO_3 which produces the potassium bisphenolate. Nitro displacement by phenoxide on nitrobenzonitrile proceeds under mild conditions, at room temperature, by using dimethylformamide (DMF) as solvent. The bis(ether dinitrile) **I′** resulting at room temperature condition was subsequently hydrolyzed in an alkaline solution and acidified to yield the tetracarboxylic acid **I″**. Dehydration with acetic anhydride afforded the bis(ether anhydride) **I**. The yield in each step was satisfactory and the structures of the intermediate bis(ether dinitrile) **I′**, tetracarboxylic acid **I″** and the final bis(ether anhydride) **I** were confirmed by IR spectra and melting point (m.p.) measurements. M.p. of **I′**: 195–196°C; m.p. of **I″**: 208–216°C; m.p. of **I**: 189–190°C.

Aromatic diamines (**II**) which were used in the synthesis of polymers are: hexafluoro-isopropylidene-4,4′-dianiline, 2,3,5,6-tetramethyl-*p*-phenyl-



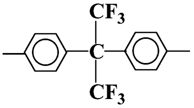
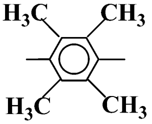
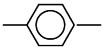
SCHEME 1 Synthesis of bis(ether-anhydride) **I**.

ene-diamine and *p*-phenylene diamine. These three diamines were provided by commercial sources and used as received.

2.2. Synthesis of Polyetherimides

The polyetherimides **III** were prepared by polycondensation reaction of equimolar amounts of 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (**I**) and an aromatic diamine, in NMP as solvent. The reaction was performed in two steps, without isolating the polyamidic acid resulting in the first step (Scheme 2). Thus, the solid diamine was added to the solution of dianhydride in NMP at room temperature and the reaction was run for 2 h, resulting the polyamidic acid **III′**. The second step was performed by heating the polyamidic acid solution at 185–190°C for 3–4 h. The polyetherimides **III** were isolated by precipitation in water. The details on polymers' preparation are given in Table 1.

TABLE 1 Preparation of Polyetherimides **III**

Polymer	Ar	Amount of dianhydride (g)	Amount of diamine (g)	NMP (mL)	Conc. (%)	Reaction time at room temp. (h)	Reaction time at high temp. (h)	η_{inh} (dL/g)
IIIa		2.6	1.67	25	14.5	2	4	0.5
IIIb		3.12	0.984	25	14.0	2	3	0.6
IIIc		3.9	0.81	35	12.0	2	3	0.7

2.3. Measurements

Melting points of the monomers were measured on a Melt-Temp II (Laboratory Devices) apparatus without correction. Infrared spectra were recorded with a Specord M 80 spectrometer in transmission mode by using KBr pellets. The inherent viscosities (η_{inh}) of the polymers were determined with an Ubbelohde viscometer, by using polymer solutions in NMP, at 20°C, at a concentration of 0.5 g/dL. The molecular weight was determined by gel permeation chromatography (GPC) using a Waters GPC apparatus provided with refraction and UV detectors and PL Mixed C Column. Measurements were carried out with polymer solutions of 2% concentration in DMF containing 0.1 M $NaNO_3$ and by using DMF with 0.1 M $NaNO_3$ as eluent. Standard polystyrene of known molecular weight was used for calibration. Thermogravimetric analyses (TGA) were performed on a MOM derivatograph made in Budapest, Hungary, at a heating rate of 12°C/min in air. The initial decomposition temperature (IDT) is characterized as the temperature at which the sample achieves a 5% weight loss. The temperature of 10% weight loss (T_{10}) was also recorded. The glass transition temperatures (T_g) of the precipitated polymers were determined with a Mettler differential scanning calorimeter DSC 12E, at a heating rate of 10°C/min under nitrogen. The mid-point of the inflection curve resulting from the typical second heating was assigned as the glass transition temperature of the respective polymers. The Kuhn segments were calculated by using the Monte Carlo method [8]. The Kuhn segment (A_{fr}), the characteristic ratio (C_∞) and the number of aromatic rings in the Kuhn segment (p) were chosen as the conformational parameters and were discussed in correlation with some physical properties of the present polymers. As is known, the Kuhn statistical segment can be written as

$$A = \lim_{n\to\infty}\left(\frac{\langle R\rangle^2}{nl_0}\right)$$

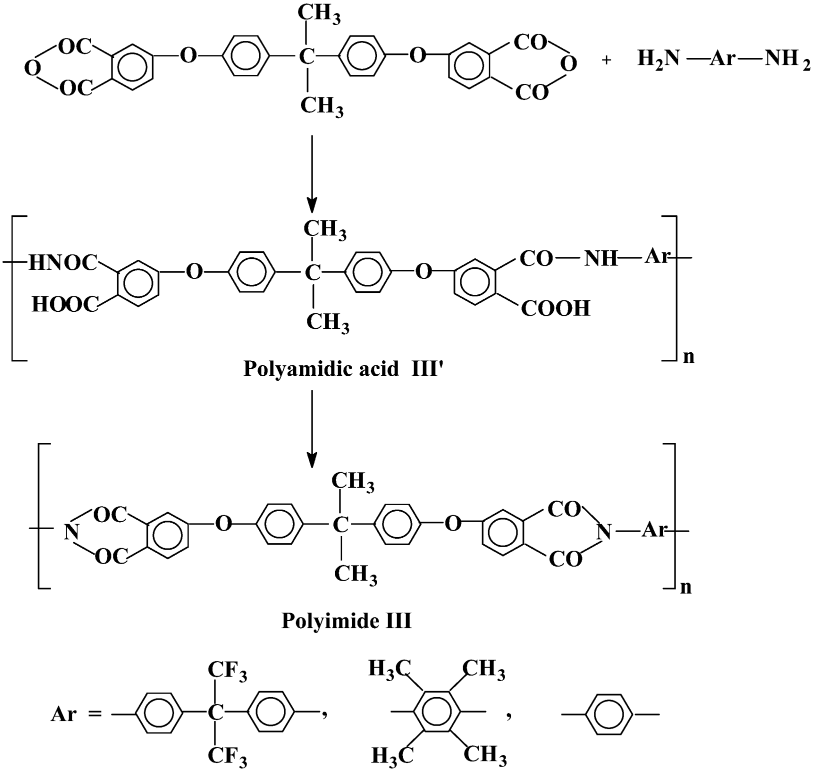
where $\langle R^2\rangle/nl_0$ is the ratio of the average square end-to-end distance of a chain to its contour length; n is the number of repeating units; l_0 is the contour length of a repeating unit. In the case of polyheteroarylenes, when the structure of the repeating units consists of virtual bonds of different bond length and angles, the contour length of polymer is the length of broken line connecting the centers of virtual bonds. The term "virtual bond" is taken to mean a rigid section of a chain, approximated by a straight line about which a rotation is possible. In a particular case it may be an ordinary valence bond; more generally, it may contain rings as well. A comparison between the experimental values of the Kuhn segment (A_{exp}) for polyheteroarylenes and those calculated under assumption of a free rotation (A_{fr}) showed them to be nearly equal [9–11].

3. RESULTS AND DISCUSSION

Polycondensation of equimolar amounts of dianhydride **I** and diamine **II** in NMP, at high temperature, yielded polyetherimides **III** (Scheme 2).

The structure of polyetherimides **III** was identified by IR spectra. Strong bands at 1780 $cm^{-1}$and 1730 cm^{-1} are commonly attributed to the symmetrical and asymmetrical stretching vibrations of carbonyl groups of imide. The absorption band at 1375 cm^{-1} is due to C–N stretching in imide ring and the absorption at 750 cm^{-1} is due to imide ring deformation. All the polymers exhibited IR bands at 1225 cm^{-1}due to ether linkages.

These polymers are easily soluble in polar amidic solvents such as NMP and DMF, and even in less polar liquids such as chloroform. The inherent viscosities measured in NMP solution, at a concentration of 0.5% were in the range of 0.5–0.7 dL/g (Table 1). The good solubility is due to the relatively high flexibility of macromolecular chains which was obtained by the introduction of ether and isopropylidene linkages into the structure of the polymer. Also, the hexafluoroisopropylidene and the methyl groups introduced a factor of asymmetry and steric hindrance in the macromolecules **IIIa** and **IIIb** that prevent a dense packing of the chains. The disturbed packing of macromolecular chains facilitates the diffusion of small molecules of solvents between the polymer chains which leads to better



SCHEME 2 Synthesis of polyetherimides **III**.

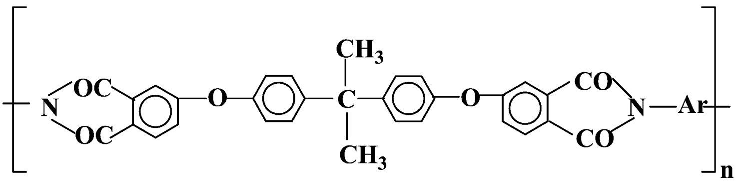
solubility. The good solubility makes the present polymers potential candidates for practical applications in spin coating and casting processes for the preparation of thin polymer films and membranes.

The molecular weight of polymers was determined by gel permeation chromatography. The values of weight-average molecular weight Mw are in the range of 83000–94800, the number-average molecular Mn are in the range of 64300–70900 and the polydispersity Mw/Mn is in the range of 1.29–1.34 (Table 2). These values show that the present polymers have fairly high molecular weights and narrow molecular weight distribution.

All these polymers possess film-forming ability. Their solutions in NMP or in chloroform having a concentration of about 10% were cast onto glass substrates and dried to yield thin transparent free-standing films having a thickness of tens of micrometers. The films obtained from polymers **IIIb** and **IIIc** were quite brittle and only the film made from polymer **IIIa** was enough flexible in order to be tested for gas separation membrane.

TABLE 2 The Properties of Polyetherimides **III**

General formula:



Polymer	T_g(°C)	IDT (°C)	T_{10} (°C)	Mw	Mn	Mw/Mn	A_{fr} (Å)	A_{hin} (Å)	p
IIIa	205	490	510	94800	70900	1.34	24.95	26.45	4.92
IIIb	275	400	420	83000	64300	1.29	29.04	29.91	5.44
IIIc	220	500	520	–[a]	–[a]	–[a]	29.04	35.18	6.40

T_g = Glass transition temperature.

IDT = Initial decomposition temperature = temperature of 5% weight loss.

T_{10} = Temperature of 10% weight loss.

[a] The polymer was not soluble in DMF.

A_{fr} = Kuhn segment value calculated under the assumption of free rotation.

A_{hin} = Kuhn segment value calculated under the assumption of hindered rotation.

p = parameter of conformational rigidity.

The permeability (P) of a membrane made from polymer **IIIa** was tested for four gases at 20°C. The following results were obtained: $P(H_2)$ = 13.40 Barrer; P(He) = 15.60 Barrer; P(O2) = 1.28 Barrer; $P(CO_2)$ = 6.62 Barrer.

These polymers exhibit high thermal stability, as evidenced by thermogravimetric analyses. The polymer **IIIb** begins to decompose above 400°C, while the polymers **IIIa** and **IIIc** are stable up to 470°C. The temperature at which the weight loss is 10% is 420°C for polymer **IIIb** and 510–520°C for the polymers **IIIa** and **IIIc** (Table 2). By comparing the present

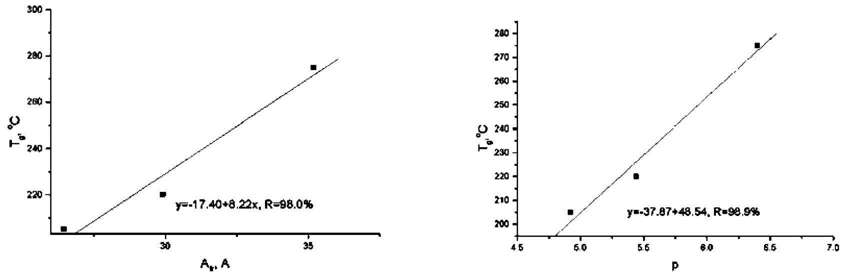


FIGURE 1 Dependence of glass transition temperature (T_g) on Kuhn segment (A_{fr}) -left and on conformational rigidity parameter p-right.

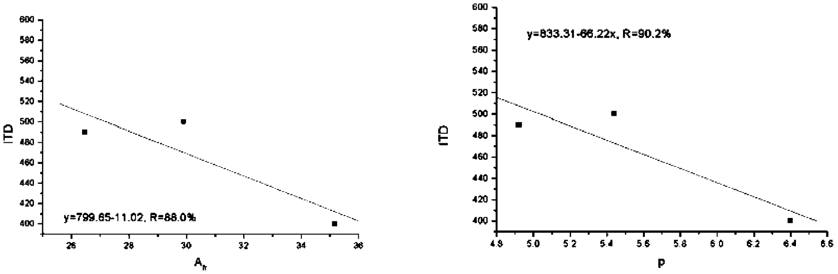


FIGURE 2 Dependence of decomposition temperature (IDT) on Kuhn segment (A_{fr})-left and on conformational rigidity parameter p-right.

polyetherimides with related wholly aromatic polyimides it can be seen that their decomposition temperatures are similar. This shows that the presence of ether linkages preserves the high thermal stability while improving the solubility.

The glass transition temperatures (Tg) of these polyetherimides **IIII** were in the range of 205–275°C (Table 2). It can be noticed that the polymer **IIIIa** containing the flexible hexafluoroisopropylidene linkage coming from the diamine segment has the lowest Tg value (205°C), while the polymer **IIIIb** having four voluminous methyl substituents on the phenylene ring shows the higher Tg value (275°C). It can also be noticed that there is a large interval between Tg and the decomposition temperature, which could be advantageous in the processing of these polymers by a thermoforming technique. The glass transition temperature and the initial decomposition temperature values are known to be significantly dependent on the presence of the aromatic rings in the polymeric chain. Therefore, one can try to find a correlation between these parameters and the number of aromatic rings in the fragment of the polymeric chain equivalent to the Kuhn segment. This correlation is described by the equation:

$$p = (A_{fr}/l_o)n$$

where p is the parameter of conformational rigidity, n is the number of aromatic rings and A_{fr}/l_O is the number of repeating units per Kuhn segment. Such dependencies for the present polymers are shown in Table 2 and Figures 1 and 2.

4. CONCLUSIONS

The incorporation of ether linkages together with isopropylidene groups into the main chain of aromatic polyimides gave products with substantially improved solubility in polar aprotic solvents, and even in less polar liquids such as chloroform. These polymers maintain high thermal stability, with the decomposition temperature being above 400°C and glass transition in the range 205–275°C. The large interval between glass transition and decomposition temperature may be advantageous for their processing by a thermoforming technique. The polymers can also be processed from NMP- or chloroform-solutions into thin and ultrathin, pinhole-free films. All these properties, associated with easy processability, make the present polymers potential candidates for practical applications as gas separation membranes.

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