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# Polyimides Based on 4-4'-Diaminotriphenylmethane (DA-TPM)

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Additional information is available at the end of the chapter

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## 1. Introduction

Rigid-rod aromatic polyimides (PIs) constantly attract wider interest because of their unique combination of properties, such as the excellent thermo-oxidative stability and mechanical properties, good dielectric strength and dimensional stability.<sup>[1-4]</sup> Additionally in recent years, PIs have been considered as one of the best materials for gas separation membranes due to their reasonable permeability to CO<sub>2</sub> and high selectivity against CH<sub>4</sub>.<sup>[5]</sup> However, synthesis and processing of these polymers are generally very difficult because of their limited solubility and infusibility.<sup>[6]</sup> Considerable efforts have been made to improve the solubility through the synthesis of new diamine or dianhydride monomers. The common strategy consists in the incorporation of bulky lateral substituents,<sup>[4,7-15]</sup> flexible alkyl side chains,<sup>[16,17]</sup> non-coplanar biphenylene moieties,<sup>[18]</sup> and kinked units,<sup>[19-22]</sup> into rigid polymer backbones.

4-4'-Diaminotriphenylmethane (DA-TPM) and its derivatives, have attracted the attention of our research group as monomers for the synthesis of various rigid-rod polyamides (PAs) and PIs.<sup>[23,24]</sup> The pendant phenyl ring and practically free internal rotation of the triphenylmethane bridging group predicted from the theoretical calculations make DA-TPM an excellent candidate for synthesis of processable PAs and PIs without sacrificing the high thermal stability.<sup>[23]</sup> Earlier research carried out for the structurally similar N,N-diamine triphenylamine (DA-TPA) showed that the incorporation of a pendant phenyl group into the polymer backbone is a successful approach to increase solubility and processability of PIs.<sup>[15,20,25-26]</sup> The synthesis of DA-TPM developed in our group is simple and highly efficient using commercially available and cheap starting materials such as aniline and benzaldehyde. This is a big advantage in comparison to N,N-diamine triphenylamine, whose synthesis is much more complicated and required expensive reagents. Besides, the use of microwave irradiation instead of traditional heating allows reducing the reaction times as well as the amount of aniline employed, that facilitates the purification process. A

wide variety of diamines derived from DA-TPM using different substituted anilines and benzaldehydes has been successfully synthesized.<sup>[27]</sup>

In spite of all these advantages, there was only one report on application of DA-TPM as a monomer for the PIs from the Koton group dated 1980,<sup>[28]</sup> where PIs based on DA-TPM and two anhydrides, pyromellitic and 4,4'-oxydiphtalic, had been obtained by traditional two-stage method using thermo-imidization. However the PIs synthesized yielded relatively low molecular weights and, as a result, their thermo-mechanical properties were not as good as those reported for other PIs based on traditional 4,4'-Diaminodiphenylmethane.

The two-stage process involving low temperature condensation with formation of prepolymer, poly(amic acid), followed by the thermal cyclodehydration or imidization at 250-300 °C is the most frequently employed method for formation of PIs. This process has some inherent limitations for example, the generation of water, which would create voids and stresses in the final materials.<sup>[29]</sup> Additionally, high temperature leads to several undesirable side reactions, such as crosslinking or scissoring polymer chains that can result in brittle films.<sup>[1,2]</sup> The thermal imidization step may be substituted by the catalytic cyclodehydration at room temperature. Normally, a mixture of acetic anhydride with tertiary amines is applied for the chemical cyclization. Much milder reaction conditions in this process permitted to produce less damaged PIs and therefore the films of higher elasticity. Another method employed for producing soluble PIs is a one-step synthesis. It had been shown by various authors that this method may be the most effective for preparation of processable PIs of large molecular weights and linear structure.<sup>[30-33]</sup>

In this article we would like to report a comparative study of PIs based on DA-TPM and various dianhydrides, obtained by different methods: the two-step and one-step syntheses. The solubility, thermal, mechanical and preliminary gas transport properties of these materials have been studied.

## 2. Experimental

### 2.1. Materials

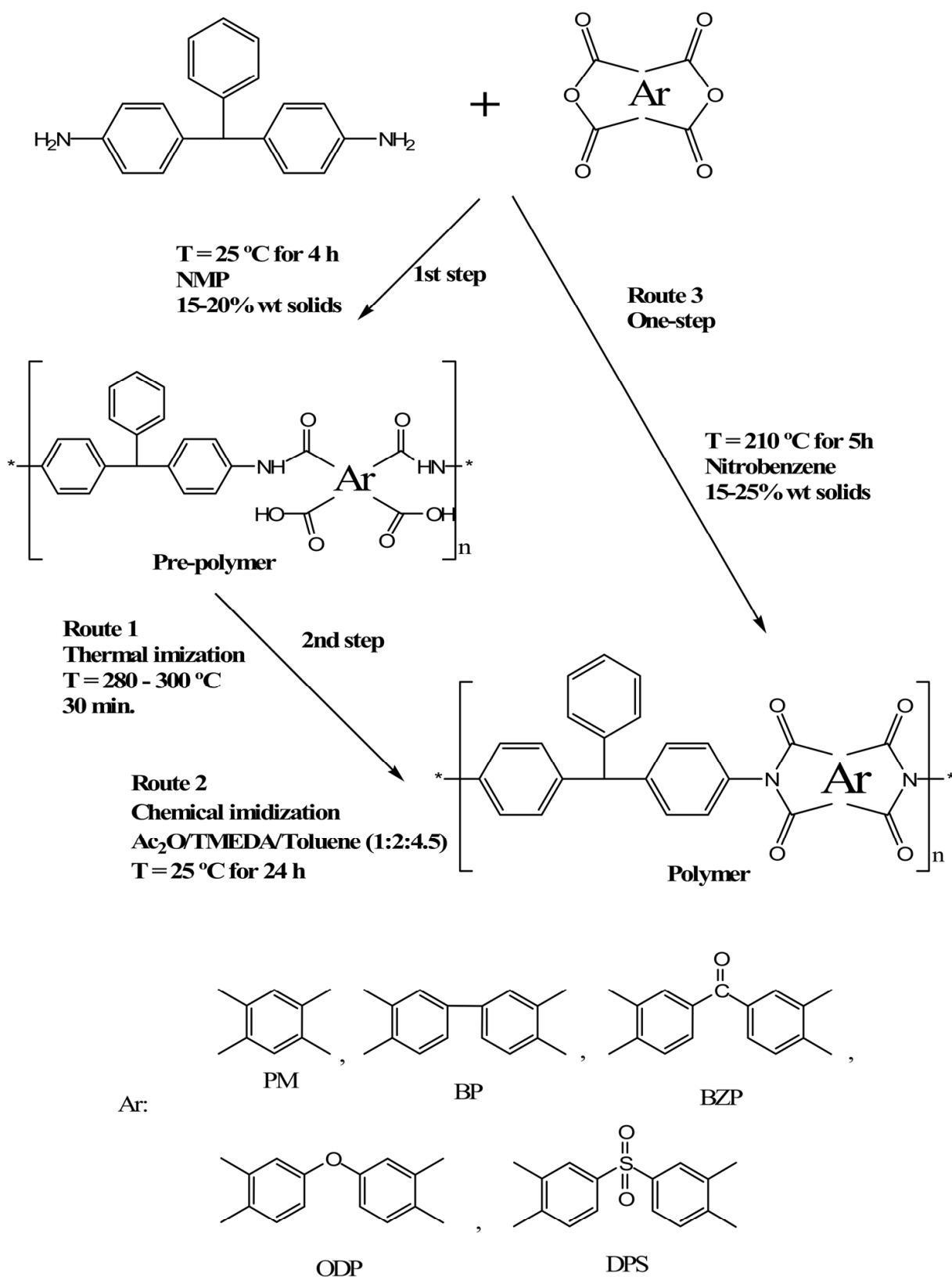
The reagents were purchased from Aldrich Co. and Chriskev. Dianhydrides were recrystallized from acetic anhydride (Ac<sub>2</sub>O). Solvents: N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF) were dried and stored over molecular sieves. The nitrobenzene was distilled under vacuum prior to use. All other reagents and solvents were used as received.

### 2.2. Synthesis of DA-TPM

DA-TPM was prepared according to the literature.<sup>[23]</sup>

### 2.3. Polymerization procedures

The polymerizations were performed by two different routes; two-step and one-step polycondensations. The imidization in two-step synthesis was carried out thermally and chemically (Figure 1)



**Figure 1.** Synthesis of DA-TPM based PIs.

## 2.4. Synthesis of poly(amic acid)s

Poly(amic acid)s (PAA) were prepared by low-temperature solution polycondensation of DA-TPM and the corresponding dianhydride (25 wt % of solids). A stoichiometric amount of the solid dianhydride was added to the diamine solution in NMP at 0°C. The continuously stirred mixture was gradually heated to room temperature and allowed to stir for another 4-5 h.

## 2.5. Thermal imidization of PAA

The solutions of PAA were cast onto glass plates and dried at 60°C under vacuum for 5 h to produce solid transparent PAA films. The dry films were stripped off the glass plates, placed into metal frames, and heated at 270 °C or at 300 °C for ~ 0.5 h to produce the desirable PIs.

## 2.6. Chemical imidization of PAA

PPAs films were immersed in the imidization mixture of Ac<sub>2</sub>O/TMEDA/Toluene (TMEDA=N,N,N',N'-tetramethylethylenediamine) (1:2:4.5) for 24 h at room temperature. Then the films were washed with distilled water and dried at 80 °C in vacuum till a constant weight (for ca. 6 h).

## 2.7. One-step high-temperature polycondensation

A solution of DA-TPM in nitrobenzene was placed into a three-neck round-bottom flask, equipped with a reflux condenser, under nitrogen atmosphere. A stoichiometric amount of the corresponding dianhydride was added to the DA-TPM solution (total 15-25 wt % solids). The reaction mixture was heated under intensive stirring and nitrogen flow at 210 °C for 5 h.. Films were cast from the reaction solutions at 50-60 °C onto glass plates and dried at 200 °C in vacuum till a constant weight (for ca. 12 h).

## 2.8. Measurements

Infrared (FT-IR) and UV-vis spectra were recorded with a Nicolet 510P FT-IR and a Shimadzu 3101PC UV spectrophotometer, respectively. Inherent viscosity ( $\eta_{inh}$ ) was determined in 0.5 g/dL DMF solutions with an Ubbelohde viscometer at 25 °C. For BP-TPM,  $\eta_{inh}$  was determined in 0.5 g/dL nitrobenzene solution at 50 °C, because this polymer was insoluble in DMF at room temperature. A Du Pont, high resolution Thermogravimetric Analyzer, TGA 2950, was used for the thermal analysis at a heating rate of 5 °C/min. The glass transition temperature,  $T_g$ , was determined by a film-elongation technique using a Du Pont Thermo-mechanical Analyzer, Model TA 2940 (nitrogen atmosphere and 5 °C/min). Mechanical tests of polymer films (about 25  $\mu$ m thickness) were performed by using an INSTRON Tester, Model 111, at a drawing rate 50 mm/min, on samples of 20 X 5 X 0.0025 mm size. Wide-angle x-ray diffractometry (WAXD) was performed on a Siemen's D-500 diffractometer, with CuK $\alpha$ 1 radiation of 1.5406 Å.

### 3. Results and discussion

The one-step polycondensation in nitrobenzene was less sensitive to the stoichiometry of reagents than the two-step synthesis.<sup>[1,34,35]</sup> FT-IR spectra of the obtained PIs showed intensive characteristic imide bands at 1773 cm<sup>-1</sup> (imide C=O asymmetrical stretching), 1714 cm<sup>-1</sup> (imide C=O symmetrical stretching), and 1380 cm<sup>-1</sup> (imide CNC axial), confirming the complete imidization.

The solubility behavior of DA-TPM based PIs in common organic solvents is summarized in Table 1. The solubility was strongly correlated to the imidization technique. Remarkable differences in solubility were observed between the samples prepared by one step or two step syntheses with chemical imidization and those resulted from thermal imidization. Chemical imidization and one-stage methods yielded polymers readily soluble in NMP, DMF and pyridine (maximum concentration up to 10-20% by weight) at room temperature. In contrast, PIs obtained by thermal imidization exhibited poor or null solubility even at high temperature. The insoluble fraction increased with the temperature of imidization (270 or 300 °C), this behavior might be attributed to crosslinking occurred during the thermal process.<sup>[1-2,36-37]</sup> Thus, DA-TPM polymers displayed excellent solubility owing to the presence of the bulky pendent phenyl group in comparison to the analogue structures but obtained with conventional 4,4'-diaminodiphenylmethane.<sup>[38]</sup> Due to the bulkiness and free internal rotation in DA-TPM moieties, the chain packing of the polymer was disturbed, and consequently, the solvent molecules could easily penetrate between chains and dissolve the polymer. It should be noted that even PM-TPM showed good solubility in polar solvents although it was derived from dianhydride without any bridging groups and therefore had the most rigid structure. Only partial solubility at elevated temperature for the similar poly(triphenylaminepyromellitimide) has been reported.<sup>[15,25]</sup> Thus, PM-TPM is one of a few soluble poly(pyromellitimide)s. Besides, other soluble poly(pyromellitimide)s reported were synthesized using expensive 4,4'-hexafluoroisopropylidene dianiline.<sup>[39]</sup>

Inherent viscosities, as molecular weight characteristics, and mechanical properties of the DA-TPM PIs are given in Table 2. Generally, the Young's modulus ( $E_0$ ) and tensile strength ( $\sigma_b$ ) decrease, and the elasticity increases with increasing chain flexibility. The rigidity of dianhydride moiety decreases in the following order PM>BP>DPS>BZP>ODP and their mechanical properties changed as should be expected. As seen from the table, the molecular weights of PM-TPM and BZP-TPM, prepared by one-step, were practically the same or even slightly higher than those of their analogues obtained by chemical imidization of the corresponding PAAs. No big difference in mechanical properties between PI films prepared by one-step synthesis or by chemical imidization was noted, but it was not so for the PIs obtained through the thermal imidization. These PIs were not soluble and resulted in very brittle films in comparison to the same PIs synthesized by two other methods. The only suitable for analysis films formed by thermo-cyclization were casted from PAAs with flexible dianhydride moieties, having -CO- or -O- groups between the phenyl rings; namely, BZP-TPM and ODP-TPM. Their mechanical properties were very poor; for example, the elongation at break ( $\epsilon_b$ ) was only 6 - 7 % whereas the elongations for the

Polymer	Route	DMF	NMP	THF	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	Py	NB*	<i>p</i> -chlorophenol*	<i>m</i> -cresol*
PM-TPM	Thermal	PS*	PS*	i	i	i	i	i	i
	Chemical	S	S	S	S	S	S	S	S
	One-step	S	S	-	-	S	S	S	S
BP-TPM	Thermal	PS*	PS*	i	i	i	i	i	i
	Chemical	S	S	S	S	S	S	S	S
	One-step	PS	PS	-	-	PS	S	S	S
BZP-TPM	Thermal	PS*	PS*	i	i	i	i	i	i
	Chemical	S	S	PS	PS	S	S	S	S
	One-step	S	S	-	-	S	S	S	S
ODP-TPM	Thermal	PS*	PS*	i	i	i	i	i	i
	Chemical	S	S	PS	PS	S	S	S	S
	One-step	S	S	-	-	S	S	S	S
DPS-TPM	Thermal	PS*	PS*	i	i	i	i	i	i
	Chemical	S	S	PS	PS	S	S	S	S
	One-step	S	S	-	-	S	S	S	S

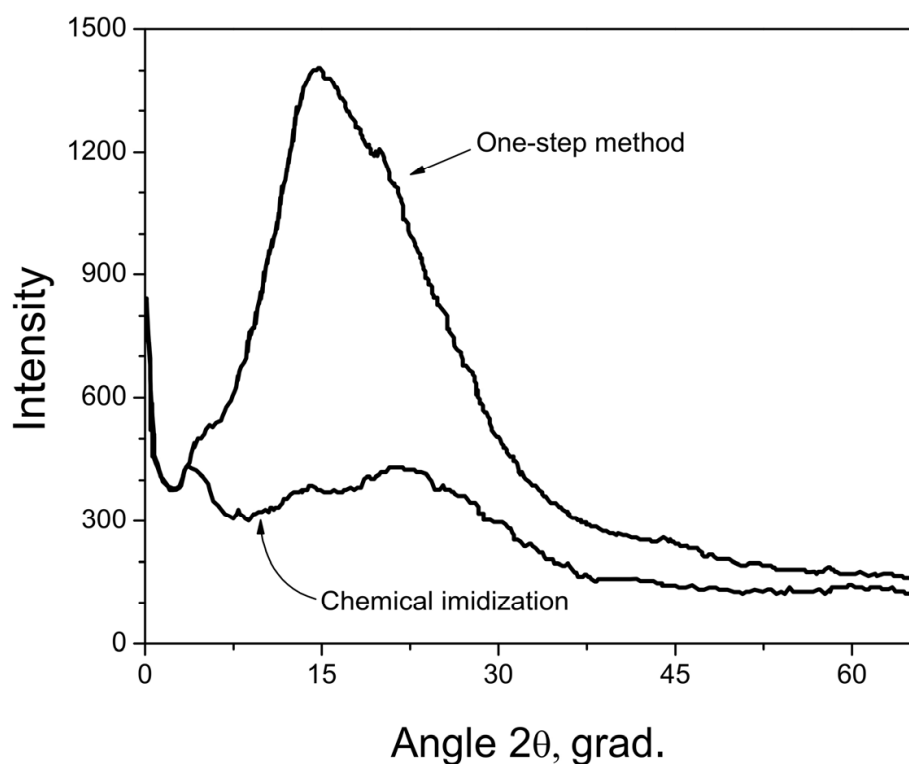
Solubility at room temperature, S=totally soluble, PS=partially soluble, i=insoluble. DMF=N,N-dimethylformamide; NMP= N-methyl-2-pyrrolidone; Py=Pyridine; THF=Tetrahydrofuran; NB=Nitrobenzene.

\* Solubility at high temperature (100-150°C)

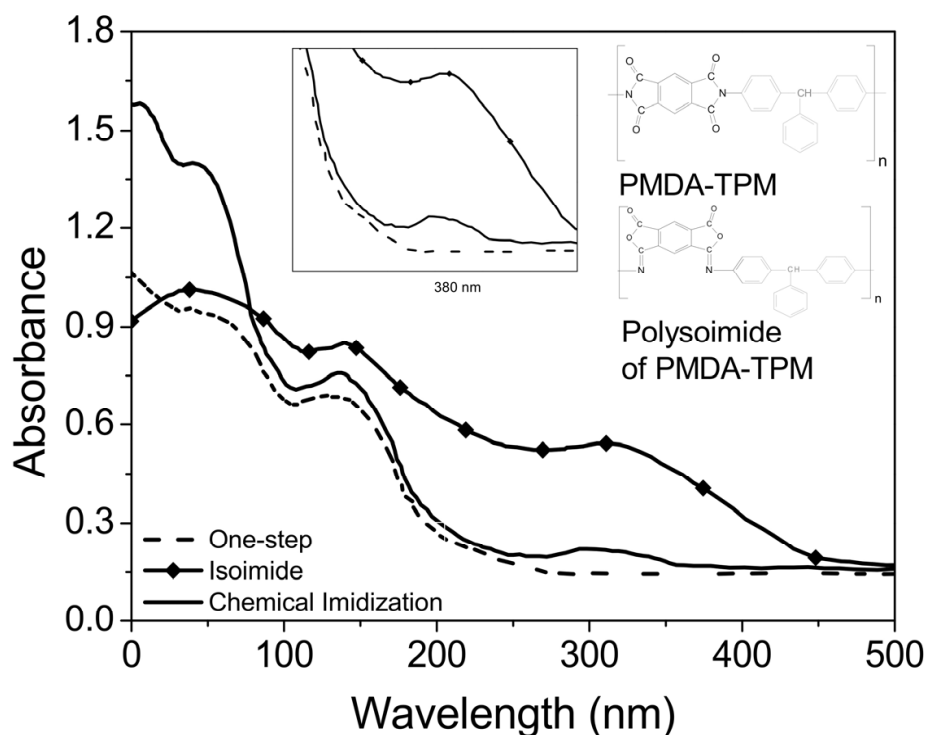
**Table 1.** Solubility of DA-TPM Based PIs Obtained by Different Methods.

chemically cyclized or resulted from one-step method PIs were ten times higher (60 – 70 %). The same tendency was noted for other mechanical properties, Young's modulus and tensile strength. Such results can be explained considering the reduction of the molecular weights and possible crosslinking occurred under the severe conditions of the thermal process. In spite of similar mechanical properties an important difference between one-step and chemically cyclized PIs was observed on the supramolecular structure level. It has been shown that one-step and chemical imidization processes led to remarkably different packing of polyimide molecules.<sup>[40]</sup> The WAXD diffraction patterns of PM-TPM films obtained by the chemical imidization of PAA and one-step high temperature polycondensation are presented in Figure 2. The significant difference in the positions, intensities and half-widths of the X-ray reflections suggested much better chain packing in the polymer prepared by one-step route. It is important to note that the PI films prepared by the one-step synthesis showed no changes of their initial properties after 6 months of storage at room temperature, even under long exposure to air and humidity, while PIs produced by chemical imidization rapidly lost their elasticity after several weeks under the same conditions. The higher stability of PIs from the one-step polycondensation may be attributed to their more regular structure. It is common even to find slight traces of imide isomeric unit, isoimide, or residual amic acid in PIs obtained by two-step synthesis with thermo- or chemo- cyclization.<sup>[1,2]</sup> These units should be considered as defective sites, because of their susceptibility to hydrolysis. This kind of defects is inevitable in the imidization process; it is particularly difficult to avoid formation of isoimide units because of their equilibrium with the imide structures. Isoimides are reactive and susceptible to nucleophilic attack, so the polymer chain may break and, as a consequence, the polymer molecular weights decrease. This





**Figure 2.** WAXD patterns of PM-TPM films obtained by the chemical imidization or by the one-step method.



**Figure 3.** UV-vis spectra of PM-TPM obtained by chemical imidization (—) or by one-step high temperature polycondensation (---), and the spectrum of the polyisoimide based on DA-TPM and PMDA (—◆—)



process is accelerated in wet media. Figure 3 shows the UV-vis spectra of two PM-TPMs obtained by one-step (dash line) and two-step (solid line) methods. Spectrum of polyisoimide is also given in Figure 3 for comparison. As can be seen, isoimide exhibits strong absorption at 380 nm. The absorption in this area is stronger for chemically cyclized PM-TPM (two-step method) than that for one-step PM-TPM which practically does not absorb at these wavelength. Therefore, the long wave tail in the UV-vis spectrum of PIs indicates the presence of isoimide units in the backbone.

Polymer	Route	$\eta_{inh}$ dL/g	Young's Modulus ( $E_0$ ) GPa	Tensile Strength ( $\sigma_b$ ) MPa	Elongation at Break ( $\epsilon_b$ ) %
PM-TPM	Thermal	-	*	*	*
	Chemical	1.1	1.8	158	28
	One-step	1.5	2.0	164	38
BP-TPM	Thermal	-	-	-	-
	Chemical	-	-	-	-
	One-step	0.6	1.8	150	42
BZP-TPM	Thermal	-	0.85	27.8	7
	Chemical	1.4	1.5	135	70
	One-step	1.2	1.5	138	75
ODP-TPM	Thermal	-	0.63	21.5	6
	Chemical	-	-	-	-
	One-step	1.1	1.4	134	58
DPS-TPM	Thermal	-	-	-	-
	Chemical	-	-	-	-
	One-step	0.5	1.6	107	20

\* Brittle

**Table 2.** Mechanical Properties of DA-TPM Based PIs.

Glass transition temperatures,  $T_g$ , and temperatures for 5 and 10% weight loss of PIs obtained by all methods are listed in Table 3. The TMA analysis showed that PIs obtained by chemical imidization and one-step polycondensation exhibit well-distinguished  $T_g$ s in the range of 260 - 320 °C, depending on the chain rigidity.  $T_g$ s for the films formed by thermal imidization were not so well defined and difficult to detect. Flexible linkages, such as -O- in ODP-TPM, tend to lower  $T_g$ . The  $T_g$  values are close to those reported for the flexible chain polyimides based in 4,4'-diaminodiphenylmethane.<sup>[38]</sup> All synthesized polymers demonstrated excellent thermal stability. According to TGA data (Table 3), thermal decomposition of DA-TPM based PIs started above 400 °C, no important difference was observed for PIs obtained by chemical imidization and one-step method. The difference in the weight loss values for the different PIs depended on the dianhydride moiety. The highest thermal and thermo-oxidative resistance, among the synthesized polymers, was observed for PM-TPM, which shows a 5 and 10% weight loss in an inert atmosphere at 540 °C and 560 °C respectively.

Polymer	Route	Glass Transition Temperature [°C]	Weight Loss Temperature by TGA [°C]			
			Air		Nitrogen	
			5%	10%	5%	10%
PM-TPM	Thermal	-	470	500	-	-
	Chemical	365	505	529	538	564
	One-step	321	502	524	530	556
BP-TPM	Thermal	-	-	-	-	-
	Chemical	-	-	-	-	-
	One-step	315	498	516	525	541
BZP-TPM	Thermal	-	-	-	-	-
	Chemical	288	457	482	506	531
	One-step	282	463	488	509	536
ODP-TPM	Thermal	-	460	510	-	-
	Chemical	-	-	-	-	-
	One-step	269	459	476	502	538
DPS-TPM	Thermal	-	-	-	-	-
	Chemical	-	-	-	-	-
	One-step	305	431	457	492	519

**Table 3.** Thermal Properties of DA-TPM Based PIs.

Preliminary gas transport properties for some of the PIs and ideal separation factors for selected gas pairs are summarized in Table 4. The polymer permeability coefficients decreased in the following order  $P(\text{H}_2) \approx P(\text{He}) > P(\text{CO}_2) > P(\text{O}_2) > P(\text{N}_2) > P(\text{CH}_4)$ . This tendency is very similar to the behavior reported for the most glassy polymer membranes indicating a relationship between the permeability and the kinetic diameter of the tested gases.<sup>[5]</sup> Gas permeability typically increases with increasing free volume of the polymer which is determined in a great extent by the chemical structure. The presence of bulky pendant groups enhances interchain spacing and reduces the packing efficiency of the polymer chains and, thus, free volume and gas permeability increase.<sup>[41,42]</sup> Results of structure/property optimization studies for polymers suitable for such separation suggest that polymers with high selectivity exhibit low permeability and vice versa.<sup>[5]</sup> Aromatic PIs are one of the best candidates for gas separation membranes, particularly for the natural gas purification, due to their high  $\text{CO}_2/\text{CH}_4$  selectivity. However, the low permeability is the principal obstacle for their wide industrial applications.<sup>[43]</sup> The goal is to improve permeability of PIs with the minimum loss in the selectivity. PIs containing DA-TPM exhibit much better gas separation characteristics combined with higher permeability coefficients than the similar polymers but synthesized with other non-fluorinated diamines.<sup>[5]</sup> Such good membrane characteristic of our PIs may be related to the pendant phenyl group, which creates a larger free volume and the possibility of molecular rotations. The anhydride bridging groups with low rotational barriers, such as  $-\text{O}-$ , facilitate chain motions and results in higher  $\text{CO}_2$  permeability while the incorporation of the bulky linkage groups, like  $-\text{SO}_2-$ , lowers the gas permeability. This tendency could be seen for DA-TPM PIs, the order of  $P(\text{CO}_2)$  is the following  $\text{ODP-TPM} > \text{DPS-TPM} > \text{BZP-TPM}$ . The polarity may also affect

chain-to-chain interactions and subsequently modify the chain rigidity and packing efficiency. The greater polarity of C=O group in BZP-TPM explains the lower permeability and higher selectivity of this polymer in comparison to ODP-TPM and DPS-TPM.

Polymer	Permeability (Barrers*)						Ideal separation factors	
	H <sub>2</sub>	He	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	$\alpha_{O_2/N_2}$	$\alpha_{CO_2/CH_4}$
BZP-TPM	8.69	7.86	0.46	0.17	0.086	2.94	2.7	34.2
DPS-TPM	10.95	10.75	0.90	0.16	0.14	4.53	5.6	32.4
ODP-TPM	9.42	9.36	0.73	0.14	0.13	3.66	5.2	28.2

\* Barrer =  $1 \times 10^{-10}$  cm<sup>3</sup>(STP)cm/(cm<sup>2</sup> s cmHg)

**Table 4.** Permeability Coefficients and Ideal Separation Factors Measured for Pure Gases at 35 °C and 10atm Upstream Pressure.

## 4. Conclusions

DA-TPM was found to be a suitable monomer for synthesis of processable PIs with good mechanical and thermal properties. Influence of synthetic method on the polymer properties has been studied. The PIs obtained by one-step high-temperature polycondensation and by two-step method with chemical imidization demonstrated better solubility and mechanical properties than PI films synthesized by thermo-imidization. However, PI films prepared by one-step method conserved their properties for much longer time upon exposure to air and humidity than the chemically imidized films. This is probably because of the formation of the isoimide defect units during the chemical imidization and differences in the supramolecular structures. The high solubility can be attributed to the effect of pendant phenyl ring and the free internal rotation in DA-TPM. Preliminary studies demonstrated that PIs based on DA-TPM exhibit also very promising gas transport properties.

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## 5. References

- [1] Sroog, C.E. *Prog. Polym. Sci.* 1991, 16, 561.
- [2] Bessonov, M.I.; Koton, M. M.; Kudryavtsev, V.V.; Laius, L. A. (Eds.) *Polyimides, Thermally Stable Polymers*, Consultants Bureau: New York, 1987.
- [3] Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. *Polyimides*, Blackie: New York, 1990.

- [4] Spiliopoulos, I. K.; Mikroyannidis, J. A.; Tsiygoulis, G.M. *Macromolecules* 1998, 31, 522.
- [5] Ayala, D.; Lozano, A. E.; de Abajo, J.; Garcia-Perez, C.; de la Campa, J. G.; Peinemann, K.V.; Freeman, B. D.; Prabhakar, R. *J. Membr. Sci.* 2003, 215, 61.
- [6] Ballauff, M. *Angew. Chem., Int. Ed.* 1989, 28, 253.
- [7] Liaw, D.J.; Liaw, B.Y. *Macromol. Symp.* 1997, 122, 343.
- [8] Jeong, H.J.; Oishi, Y.; Kakimoto, M.A.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem* 1990, 28, 3193.
- [9] Liaw, D.J.; Liaw, B.Y.; Li, L.J.; Sillion, B.; Mercier, R.; Thiria, R.; Sekiguchi, H. *Chem. Mater.* 1998, 10, 734.
- [10] Sun, X.; Yang, Y.K.; Lu, F. *Macromolecules* 1998, 31, 4291.
- [11] Akutsu, F.; Inoki, M.; Araki, K.; Kasashima, Y.; Naruchi, K.; Miura, M. *Polym. J.* 1997, 29, 529.
- [12] Lozano, A.E.; de Abajo, J.; de la Campa, J. G.; Preston, J. *J. Polym. Sci., Part A: Polym. Chem.* 1995, 33, 1987.
- [13] Park, K.H.; Tani, T.; Kakimoto, M.A.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem.* 1998, 36, 1767.
- [14] Kasashima, Y.; Kumada, H.; Yamamoto, K.; Akutsu, F.; Naruchi, K.; Miura, M. *Polymer* 1995, 36, 645.
- [15] Liaw, D.J.; Hsu, P.N.; Chen, W.H.; Lin, S.L. *Macromolecules* 2002, 35, 4669.
- [16] Ballauff, M.; Schmidt, G.F. *Macromol. Chem. Rapid Commun.* 1987, 8, 93.
- [17] Steuer, M.; Horth, M.; Ballauff, M. *J. Polym. Sci., Part A: Polym. Chem.* 1993, 31, 1609.
- [18] Kaneda, T.; Katsura, T.; Nakagawa, K.; Makino, H.; Horio, M. *J. Appl. Polym. Sci.* 1986, 32, 3151.
- [19] Liaw, D.J.; Liaw, B.Y.; Hsu, P.N.; Hwang, C.Y. *Chem. Mater.* 2001, 13, 1811.
- [20] Liaw, D.J.; Liaw, B.Y.; Yang, C.M. *Macromolecules* 1999, 32, 7248.
- [21] Liaw, D.J.; Liaw, B.Y. *Macromol. Chem. Phys.* 1998, 199, 1473.
- [22] Glatz, F.P.; Mulhaupt, R. *Polym. Bull.* 1993, 31, 137.
- [23] Likhatchev, D.; Alexandrova, L.; Tlenkopatchev, M.; Vilar, R.; Vera-Graziano, R. *J. Appl. Polym. Sci.* 1995, 57, 37.
- [24] Likhatchev, D.; Alexandrova, L.; Tlenkopatchev, M.; Martinez-Richa, A.; Vera-Graziano, R. *J. Appl. Polym. Sci.* 1996, 61, 815.
- [25] Vasilenko, N.A.; Akhmet'eva, Ye.D.; Sviridov, Ye.B.; Berendyayav, V.I.; Rogozhkina, Ye.D.; Alkayeva, O.F.; Koshelev, K.K.; Izyumnikov, A.L.; Kotov, B.V. *Polym. Sci. USSR* 1991, 33, 1439.
- [26] Oishi, Y.; Ishida, M.; Kakimoto, M.; Imai, Y.; Kurosaki, T. *J. Polym. Sci., Part A: Polym. Chem.* 1992, 30, 1027.
- [27] Guzmán-Lucero, D.; Guzmán, J.; Likhatchev, D.; Martínez-Palou, R. *Tetrahedron Lett.* 2005, 46, 1119.
- [28] Koton, M.M.; Romanova, M.S.; Laius, L.A.; Sazanov, Yu.N.; Fjodorova, G.N. *Z. Prikl. Khim.* 1980, 53, 1591.
- [29] Hergenrother, P.M. *High Perform. Polym.* 2003, 15, 3.
- [30] Kuznetsov, A.A.; Yablokova, M.; Buzin, P.V.; Tsegelskaya, A.Y. *High Perform. Polym.* 2004, 16, 89.

- [31] Imai, Y.; Maldar, N.N.; Kakimoto, M.A. *J. Polym. Sci., Part A: Polym. Chem.* 1984, 22, 2189.
- [32] Giesa, R.; Keller, U.; Eiselt, P.; Schmidt, H.W. *J. Polym. Sci., Part A: Polym. Chem.* 1993, 31, 141.
- [33] Kaneda, T.; Katsura, T.; Nakagawa, K.; Makino, H. *J. Polym. Sci., Part A: Polym. Chem.* 1986, 32, 3133.
- [34] Dine-Hart, R.A.; Wright, W.W. *J. Appl. Polym. Sci.* 1967, 11, 609.
- [35] S. V. Vinogradova, S.V.; Slonimskii, G.L.; Vygodskii, Ya.S.; Askadskii, A.A.; Mzhel'skii, A.I.; Churochkina, N.A.; Korshak, V.V. *Polym. Sci. USSR* 1969, 11, 3098.
- [36] Saini, A.K.; Carlin, C.M.; Patterson, H.H. *J. Polym. Sci., Part A: Polym. Chem.* 1993, 31, 2751.
- [37] Snyder, R.W.; Thomson, B.; Bartges, B.; Czerniawski, D.; Painter, P.C. *Macromolecules* 1989, 22, 4166.
- [38] St. Clair, T.L. *Polyimides* Wilson, D.; Stenzenberger, H.D.; Hergenrother, P.M. (Eds.) Blackie, London, 1990.
- [39] Likhatchev, D.; Gutierrez-Wing, C.; Kardash, I.; Vera-Graziano; R. *J. Appl. Polym. Sci.* 1996, 59, 725.
- [40] Likhatchev, D.; Chvalum, S. *Advances in Polyimides and Low Dielectric Polymers* Sachdev, H.S.; Khojasteh, M.M; Feger, C. (Eds.) SPE, Inc., New York, 1999, 167.
- [41] Xiao, Y.; Low, B.T.; Hosseini, S.S.; Chung, T.S.; Paul, D.R. *Prog. Polym. Sci.* 2009, 34, 561.
- [42] Coleman, M.R.; Koros, W.J. *J. Membr. Sci.* 1990, 50, 285.
- [43] Scholes, C.A.; Stevens, G.W.; Kentish, S.E. *Fuel* 2012, 96, 15.