

Use of New Diimide–Dinaphthols in Preparation of Novel Thermally Stable Poly(ester–imide)s

Shahram Mehdipour-Ataei,¹ Shahriar Keshavarz²

¹*Polyurethane Group, Iran Polymer Institute, P. O. Box 14965/115, Tehran, Iran*

²*Department of Chemistry, Lorestan University, Khoram Abad, Iran*

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ABSTRACT: Reaction of 5-amino-1-naphthol with pyromellitic dianhydride, benzophenonetetracarboxylic dianhydride, and hexafluoroisopropylidene diphthalic anhydride afforded aromatic diols with preformed imides structure. High temperature solution polycondensation reactions of the obtained diimide–dinaphthols with aromatic and aliphatic diacid chlorides resulted in preparation of nine dif-

ferent poly(ester–imide)s. They were fully characterized and the physical and thermal properties of the obtained polymer were studied. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2168–2172, 2003

Key words: poly(ester–imide); thermal stability; dianhydride; diacid chloride

INTRODUCTION

Wholly aromatic polyimides are widely used in the electronic packaging, semiconductor, and automobile industries because of their outstanding thermal stability, superior electrical-insulating property, high mechanical strength, good adhesion to commonly used substrates, and remarkable chemical stability.^{1,2} However, their intractability and inferior solubility make polyimides lack the properties essential for successful fabrication into appropriate forms. To overcome these problems, different methods have been suggested. One efficient method is copolymerization. Therefore, copolyimides such as poly(ester–imide)s, poly(urethane–imide)s, and poly(amide–imide)s have been developed.

Aromatic poly(ester–imide)s (PEIs) are an important class of thermally stable polymers and they have various commercial applications. Their main applications are in coatings for enameled wires, high-strength fibers, hot melt adhesives, heat-resistant films, and printed circuit boards.^{3–6} Several methods have been reported for the synthesis of PEIs; some of the most important ones include direct polycondensation of trimellitic anhydride with a mixture of a diamine and a diol,^{7,8} reaction of a dicarboxylic acid containing preformed imide group with a diol,^{3,4,9–11} polycondensation of a diphenol containing imide ring with a diacid chloride,¹² reaction between a dianhydride containing ester group and a diamine,^{13–15} and direct polycon-

densation of a diisocyanate containing ester linkage with a dianhydride.¹⁶

Aromatic PEIs are generally infusible and insoluble in common organic solvents, and pose processing difficulties, limiting their widespread utility.¹⁷

In our continuous interest in preparation and characterization of novel polyimides,^{18–24} we recently synthesized new diimide–dinaphthols and used them for the synthesis of poly(urethane–imide)s.²⁵ Here we wish to describe the synthesis of novel PEIs from the prepared diols containing built-in imide structure. Effects of bulky group, methylene groups, and meta-catenation in the structures were studied and the obtained properties were compared.

EXPERIMENTAL

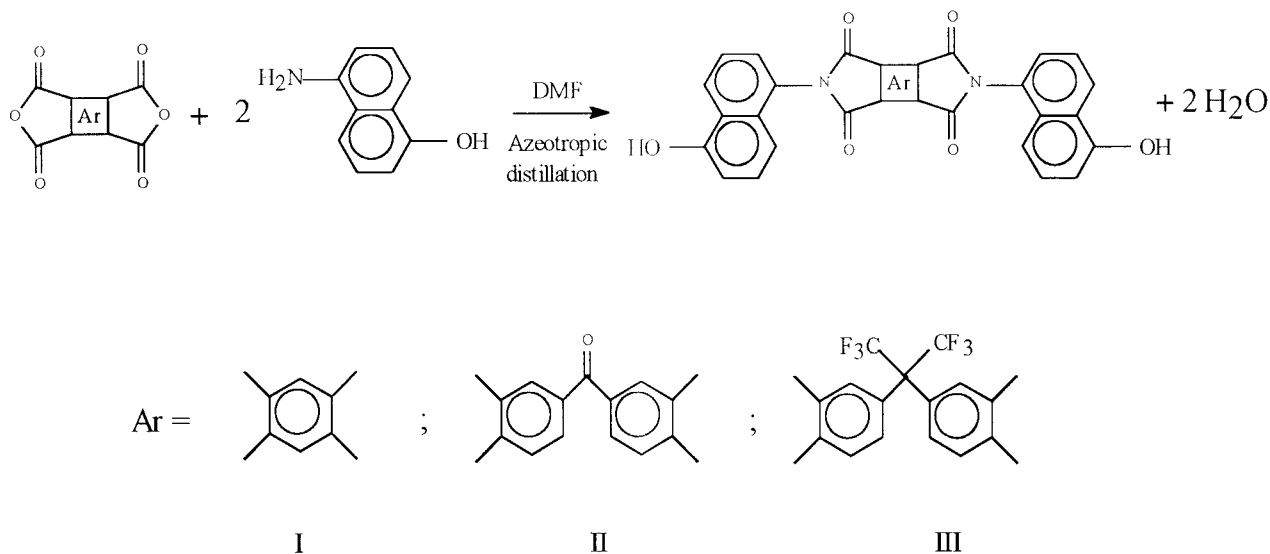
Materials

All chemicals were purchased either from Merck or Aldrich Chemical Co. Pyromellitic dianhydride (PMDA), benzophenonetetracarboxylic dianhydride (BTDA), and hexafluoroisopropylidene diphthalic anhydride (6FDA) were dried in a vacuum oven at 110 °C for 5 h. *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone (NMP) were purified by distillation under reduced pressure over CaH₂. Terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) was purified by recrystallization from dry *n*-hexane.

Instrument

Infrared (IR) measurements were performed on a Bruker-IFS 48 Fourier transform infrared (FTIR) spectrometer. The H-NMR spectra were recorded in di-

Correspondence to: Shahram Mehdipour-Ataei (s.mehdipour@proxi.ipi.ac.ir).



Scheme 1 Preparation of diimide-dinaphthols.

methyl sulfoxide (DMSO- d_6) solution using a Bruker Avance DPX 250-MHz instrument. A CHN-O-Rapid Heraeus elemental analyzer performed elemental analyses.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780. Inherent viscosities were measured by using an Oswald viscometer. Wide angle X-ray diffraction patterns were performed at room temperature on an X-ray diffractometer (Siemens model D 5000) using Ni-filtered Cu $K\alpha$ radiation (40 kV, 25 mA) with scanning rate of $3^\circ/\text{min}$.

Monomer synthesis

A typical procedure was as follows: A three-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, a dropping funnel, and a Dean-Stark condenser was charged with 0.02 mol of 5-amino-1-naphthol (3.18 g) and 6 mL of dry DMF. To the stirred solution, an aromatic dianhydride (0.01 mol) dissolved in 10 mL of dry DMF was added dropwise over a period of 0.5 h at $0-5^\circ\text{C}$. The mixture was stirred further for 2 h. Then 7 mL of dry toluene was added to the mixture and it was heated for 2.5 h at 110°C . Heating was continued for 2.5 h at 140°C and the liberated water was removed from the mixture by azeotropic distillation.

When PMDA was used as dianhydride, the reaction mixture was poured into water-ice solution and stirred. Then it was isolated by filtration, washed with distilled water and DMF, and dried under vacuum at 100°C .

When BTDA and 6FDA were used as dianhydride, the reaction mixture was cooled to room temperature and poured slowly with stirring into 20 mL of 1N HCl

solution and kept for 10 h. Then it was filtered, washed repeatedly with water and acetone, and dried at 100°C under vacuum.

Polymer synthesis

A typical example of polycondensation reaction for the preparation of PEIs was as follows: In a round-bottomed flask equipped with a stirrer, nitrogen inlet tube, HCl outlet tube, and condenser was placed 5 mmol of bisimidenaphthol, 0.08 g of triethylamine hydrochloride, and 10 mL of 1,2-dichlorobenzene. The mixture was heated to 180°C under nitrogen flow and a solution of 5 mmol diacid chloride in 10 mL of 1,2-dichlorobenzene was added dropwise through a funnel. The mixture was heated until the evolution of hydrogen chloride ceased, a period of about 4 h. After cooling, the polymer was precipitated in hexane and washed with alcohol and water successively. Yield of the reaction was above 87%.

RESULTS AND DISCUSSION

Direct polycondensation reaction of a diphenol containing preformed imide group and a diacid chloride has been known as a general method for the preparation of poly(ester-imide)s.¹⁰ According to this, we used reaction of aromatic dianhydride (PMDA, BTDA, and 6FDA) with 5-amino-1-naphthol for the preparation of diols containing imide structures (Scheme 1).

In this way, bulky naphthyl group was introduced into the backbone of diols. Structures of the prepared diimide-dinaphthols were characterized by common spectroscopic methods. FTIR spectra of the diols showed characteristic bands at about 3410 cm^{-1} (O-H), 1770, 1710, 1370, and 715 cm^{-1} (imide bands).

TABLE I
Characteristic Features of Diimide-Dinaphthols

Compound	Reactants	Yield (%)	IR (cm ⁻¹ ; KBr)	NMR (ppm; DMSO-d ₆)
I	PMDA + 5-amino-1-naphthol	79	3425, 1771, 1715, 1370, 715	10.08 (s,2H) 8.38–8.24 (m,2H) 7.63–6.98 (m,12H)
II	BTDA + 5-amino-1-naphthol	83	3410, 1767, 1710, 1365, 710	10.05 (s,2H) 8.36–8.21 (m,6H) 7.61–6.96 (m,12H)
III	6FDA + 5-amino-1-naphthol	81	3415, 1770, 1712, 1368, 712	10.06 (s,2H) 8.38–8.21 (m,6H) 7.60–6.96 (m,12H)

H-NMR spectra of the diimide-dinaphthols showed absorption at about δ 10.05 (O—H), δ 8.35–8.20 (aromatic hydrogens of dianhydride), and δ 7.60–6.95 (aromatic hydrogens of naphthalene). Table I shows the characteristic features of the prepared diimide-dinaphthols.

High temperature solution polycondensation reactions of the obtained diols with aromatic diacid chlorides including TPC and IPC yielded fully aromatic PEIs. Also, polycondensation of the diols with aliphatic diacid chloride (ie: sebacoyl chloride (SEB)) resulted in preparation of aromatic-aliphatic PEIs (Scheme 2).

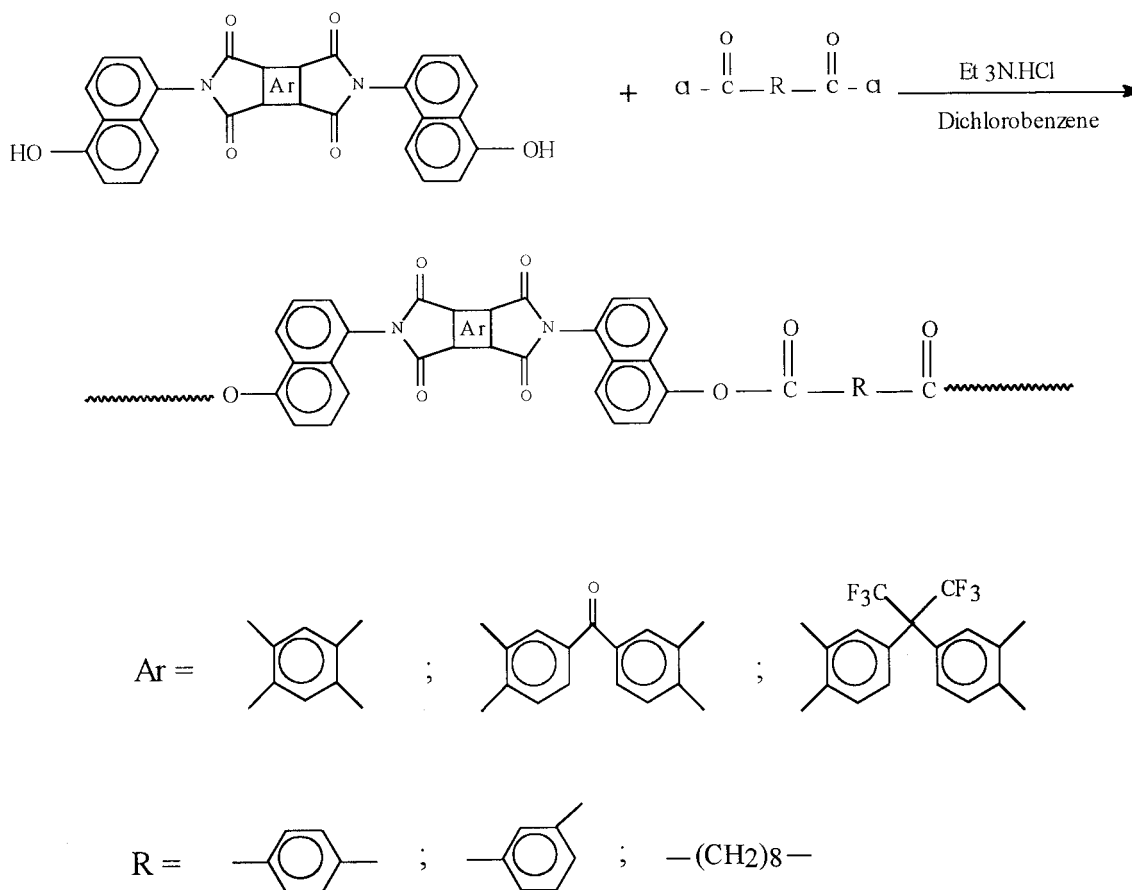
It is worth mentioning that interfacial polycondensation reaction afforded PEIs in low yield.

Three approaches were applied to the synthesis of PEIs with modified structures: (1) the introduction of

a large substituent along the polymer backbone; (2) the disruption of symmetry and regularity of the repeating unit; (3) the incorporation of flexible or kinked linkages in the backbone.

The infrared (IR) spectra of the PEIs showed the presence of the imide bands at about 1780, 1720, 1370, and 720 cm⁻¹. Bands of ester group appeared at about 1220 (C—O—C) and 1720 cm⁻¹ (C=O) which was overlapped with one of the absorption of imide ring. Elemental analyses of the polymers showed good agreement with the calculated values. The inherent viscosity of the polymers, as a measure of molecular weight, was in the range of 0.40–0.57 dL/g, which showed reasonable molecular weight. The obtained results were summarized in Table II.

Thermal behavior and thermal property of the polymers were studied by recording their DSC and TGA



Scheme 2 Preparation of PEIs.

TABLE II
Structure and Properties of the Polymers

Reactants	Structure	Elemental Analysis						Yield (%)	Inherent ^a viscosity (dL/g)
		Calculated			Found				
		C	H	N	C	H	N		
PMDA + TPC		72.38	2.86	4.44	72.23	2.90	4.48	90	0.40
PMDA + IPC		72.38	2.86	4.44	72.43	2.89	4.40	87	0.42
PMDA + SEB		72.07	4.50	4.20	71.98	4.63	4.31	92	0.52
BTDA + TPC		72.57	3.00	3.81	72.73	2.93	3.88	89	0.47
BTDA + IPC		72.57	3.00	3.81	72.67	3.05	3.68	91	0.48
BTDA + SEB		73.25	4.42	3.64	73.37	4.33	3.79	95	0.57
6FDA + TPC		65.89	2.57	3.27	65.79	2.53	3.36	90	0.51
6FDA + IPC		65.89	2.57	3.27	65.97	2.63	3.39	93	0.52
6FDA + SEB		65.92	3.81	3.14	65.99	2.69	3.09	93	0.55

^a Measured at a concentration of 0.5 g/dL in NMP at 30 °C

graphs. The measurements were carried out in air at a heating rate of 10°C/min. The results were collected in Table III.

In order to obtain reliable results from the DSC technique, thermal behavior of the poly(ester-imide)s was studied by heating the polymers up to 350°C, cooling, and heating again. Accordingly, T_g values were taken as the midpoint of the change in slope of the baseline in DSC traces. Polymers based on IPC and SEB monomers showed a step transition corresponding to a T_g in the range of 152–189°C. Also, no endothermic peak related to the melting temperature (T_m) was detected for them. These results indicated that these polymers possess an amorphous characteristic, which was confirmed by wide-angle X-ray scattering (WAXS) measurements.

In another experiment, DSC traces were studied after all the polymers annealed at 200 °C for 8 h. The observed results for the thermal behavior of the polymers were almost similar to the previous experiment.

The temperature for 10% gravimetric loss (T_{10}) is an important criterion for evaluations of thermal stability in these heat resistant PEIs. It was found that more rigid structures were more heat resistant so PMDA-derived polymers were more stable than BTDA-derived polymers, which were more stable than 6FDA-derived PEIs. Also the thermal stability of TPC-derived polymers were higher than the IPC-derived polymers. On the other hand, fully aromatic PEIs were more stable than corresponding aromatic-aliphatic PEIs, which was obviously due to the presence of the weak linkages in the aliphatic moieties.

TABLE III
Thermal Properties of the Polymers^a

Polymer	T_g (°C)	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	Char yield at 600°C
PMDA + TPC	^b	385	480	530	53
PMDA + IPC	189	390	465	525	47
PMDA + SEB	166	255	330	490	45
BTDA + TPC	^b	370	465	540	39
BTDA + IPC	173	380	460	560	35
BTDA + SEB	154	235	305	460	32
6FDA + TPC	^b	320	420	550	55
6FDA + IPC	175	300	410	500	52
6FDA + SEB	152	220	295	435	47

^a T_g : glass transition temperature; $T_{10\%}$: temperature for 10% weight loss; T_{max} : maximum decomposition temperature; char yield: Weight of polymer remained.

^b T_g was not detected in the DSC traces.

To study the crystalline characteristics of the poly-(ester-imide)s, WAXS measurements at room temperature in the region of $2\theta = 5^\circ\text{--}70^\circ$ were performed. According to the results, TPC-derived polymers containing rigid and symmetric moieties showed high crystallinity. This may be due to the better packing of their polymer backbone.

On the other hand, polymers derived from IPC monomer exhibited semicrystalline patterns (about 12–17% crystallinity). Also, SEB-derived polymers showed amorphous patterns that could be explained in terms of the presence of the flexible methylene groups. These observations confirmed the results of DSC experiments.

Fully aromatic PEIs were soluble in polar solvents such as NMP, DMAc, and DMF up to 0.7 g/dL. The solubility of the aromatic-aliphatic PEIs, due to the incorporation of flexible linkages, was increased up to 1.5 g/dL in the mentioned solvents.

Polymer films were prepared by casting the solution and temperature programming heating. The prepared films had a brittle nature in most cases.

CONCLUSIONS

Diols containing preformed imide groups were prepared by the reaction of 5-amino-1-naphthol with aromatic dianhydrides. High temperature solution polycondensation reactions of the prepared diimide-dinaphthols with aromatic and aliphatic diacid chloride led to the preparation of PEIs in good yields. Physical properties of the polymers including thermal property and solubility were investigated and structure-property relations were studied.

References

- Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. *Polyimide*; Chapman & Hall: New York, 1990.
- Ghosh, M. K.; Mittal, K. L. *Polyimide: Fundamentals and Applications*; Marcel Dekker: New York, 1996.
- Maiti, S.; Das, S. *J Appl Polym Sci* 1981, 26, 957.
- Maiti, S.; Das, S. *Angew Makromol Chem* 1980, 86, 181.
- Lienert, K. *Adv Polym Sci* 1999, 141, 45.
- Kricheldorf, H. R. *Adv Polym Sci* 1999, 141, 83.
- Dolui, S. K.; Pal, D.; Maiti, S. *J Appl Polym Sci* 1985, 30, 3867.
- Shen, D. C. U.S. Pat. 4,363,861, 1982.
- Maros, C. L.; de Abajo, J. *Angew Makromol Chem* 1976, 55, 73.
- Yang, C. P.; Liou, G. S.; Chen, R. S.; Yang, C. Y. *J Polym Sci, Part A: Polym Chem* 2000, 38, 1090.
- Li, C. H.; Chen, C. C.; Chen, K. M.; Chang, T. C. *J Appl Polym Sci* 1995, 55, 747.
- Sasaki, S.; Hasuda, Y. *J Polym Sci Lett Ed* 1987, 25, 377.
- Loncrini, D. F. *J Polym Sci* 1966, 4, 1531.
- Malvaney, J. G. *J Polym Sci, Part A: Polym Chem* 1986, 24, 613.
- Koton, M. M. *Vysokomol Soedin, Ser A* 1973, A 15, 310.
- Avadhani, C. V.; Wadgaonkar, P. P.; Vernekar, S. P. *Polym Bull* 1992, 28, 143.
- Kricheldorf, H. R.; Huner, R. *Makromol Chem Rapid Commun* 1990, 11, 211.
- Mehdipour-Ataei, S.; Barikani, M. *J Polym Sci, Part A: Polym Chem* 1999, 37, 2245.
- Mehdipour-Ataei, S.; Barikani, M. *Iranian Polym J* 1999, 8, 3.
- Barikani, M.; Yeganeh, H.; Mehdipour-Ataei, S. *Polym Int* 1999, 48, 1264.
- Mehdipour-Ataei, S.; Barikani, M. *J Polym Sci, Part A: Polym Chem* 2000, 38, 1487.
- Yeganeh, H.; Mehdipour-Ataei, S. *J Polym Sci, Part A: Polym Chem* 2000, 38, 1528.
- Barikani, M.; Mehdipour-Ataei, S. *J Appl Polym Sci* 2000, 77, 1102.
- Barikani, M.; Mehdipour-Ataei, S. *J Polym Sci, Part A: Polym Chem* 2001, 39, 514.
- Mehdipour-Ataei, S.; Keshavarz, S. Submitted for publication.