

# Aromatic/Cycloaliphatic Polyimides and Polyamide-Imide from Trans-1,4-Cyclohexane Diisocyanate: Synthesis and Properties

MEHDI BARIKANI, SHAHRAM MEHDIPOUR-ATAEI

Iran Polymer Institute, P. O. Box 14965/115, Tehran, Iran

Received 11 January 1999; accepted 1 December 1999

**ABSTRACT:** Mixed aromatic/alicyclic polyimides were prepared by polycondensation reactions of trans-1,4-cyclohexane diisocyanate (CHDI) with pyromellitic dianhydride (PMDA), benzophenonetetracarboxylic dianhydride (BTDA), and hexafluoroisopropylidene diphthalic anhydride (6FDA). Also, polycondensation of CHDI with trimellitic anhydride led to synthesis of polyamide-imide. In order to obtain the optimized condition for polymerization reactions, model compound studying was considered. Model compound and polymers were characterized by common methods. Physical properties of polymers, including thermal behavior, thermal stability, solution viscosity, and solubility behavior, were also studied. Mild polymerization condition was the main advantage of using diisocyanate instead of diamine in synthesis of these thermally stable polymers. Furthermore, synthesis of poly(amic acid) and polyimide via nonaromatic diamine can introduce synthetic problems, but by applying nonaromatic diisocyanate a facile method for preparation of aromatic/cycloaliphatic polyimides was obtained. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1102–1107, 2000

**Key words:** polyimide; polyamide-imide; dianhydride; diisocyanate; synthesis

## INTRODUCTION

Polyimides and polyamide-imides are of high interest for many engineering applications due to their excellent thermal and mechanical properties. The aerospace, automobile, and microelectronics industries have developed many important applications.<sup>1</sup> Additionally, introduction of alicyclic moieties into the main chains of polyimides restrains the formation of intermolecular charge-transfer complexes to lower the dielectric constant, a property that is highly desirable for microelectronics applications.

In addition to low dielectric constant, some excellent properties such as good optical clarity, low

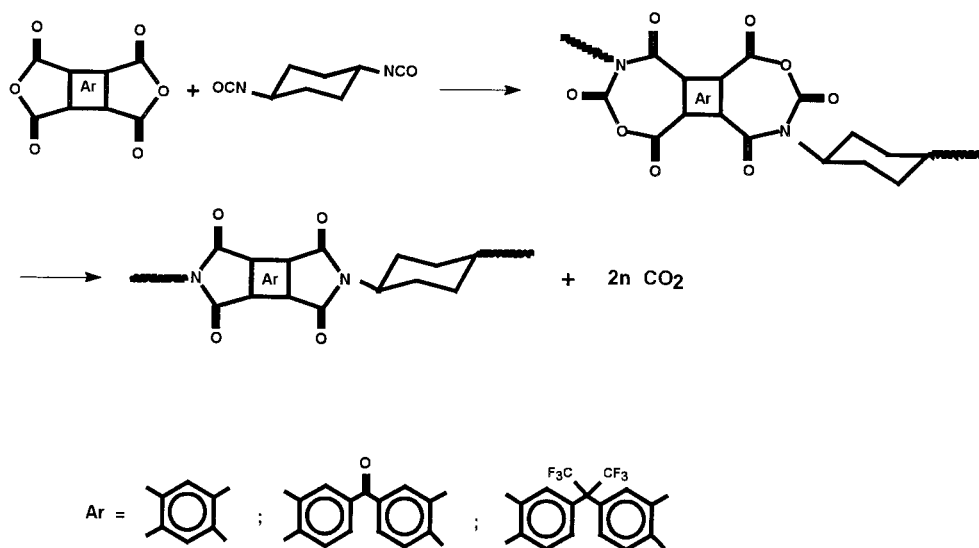
refractive index, and good mechanical properties are observed in mixed or fully nonaromatic polyimides.

Several methods have been developed for the preparation of polyimides.<sup>2</sup> Preparation of polyimides from aromatic diamines and aromatic dianhydrides is the most common method. Mixing the diamine and dianhydride in polar aprotic solvent at ambient temperatures produces a solution of poly(amic acid). Such solutions are commonly used to cast films or coatings. Poly(amic acid) on subsequent heating at elevated temperatures loses water to form the polyimide by cyclodehydration. Unlike aromatic polyimides, which are readily prepared via the mentioned two-step method, nonaromatic monomers can preclude high-molecular-weight poly(amic acid) generation, by formation of salt during the initial stages

---

Correspondence to: M. Barikani.

*Journal of Applied Polymer Science*, Vol. 77, 1102–1107 (2000)  
© 2000 John Wiley & Sons, Inc.



**Scheme 1** Synthesis of polyimides.

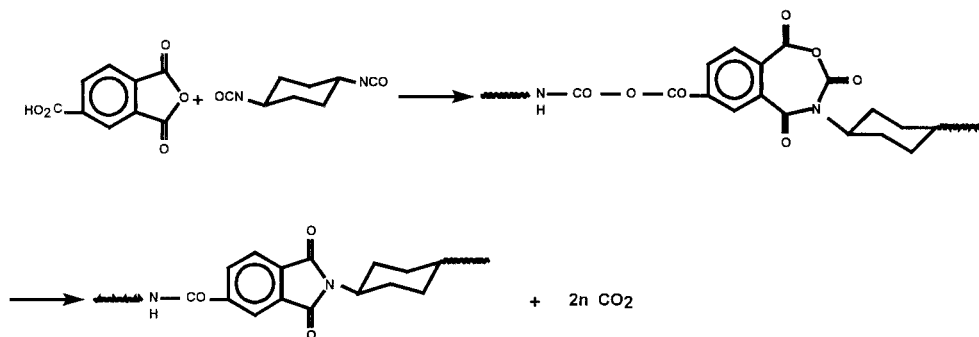
of the polymerization, and therefore form low-molecular-weight polyimide.<sup>3</sup>

Diisocyanates are important monomers for the manufacture of addition and condensation polymers. Condensation polymers obtained from diisocyanates and suitable substrates with the loss of carbon dioxide are of commercial importance. Reaction of diisocyanates with tricarboxylic acid anhydrides and tetracarboxylic acid dianhydrides gives polyamide-imides and polyimides, respectively. A group of heterocyclic polymers obtained from diisocyanates and suitable substrates, often by an addition reaction followed by a condensation step, have gained prominence in the high-performance polymer area.<sup>4</sup>

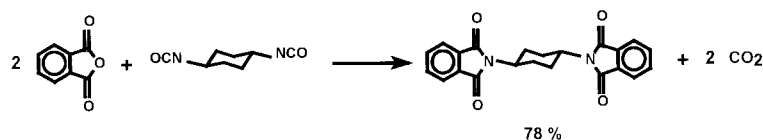
The dianhydride-diisocyanate reaction in solution and under melt-fusion conditions was first investigated by Meyers in 1969.<sup>5</sup> Since then numerous reports appeared in this field.<sup>6-8</sup> In these

polycondensation reactions, the evolved small molecule is carbon dioxide gas, which would easily bubble out of the reaction system during polymerization. Different aspects of reactions for preparation of polyimides and polyamide-imides from diisocyanates have been investigated.<sup>9-11</sup>

Our previous work with aromatic diisocyanates has focused on the preparation of fully aromatic polyimides and polyamide-imides.<sup>12</sup> The present article deals with the synthesis and properties of polyimides and polyamide-imide from *trans*-1,4-cyclohexane diisocyanate (CHDI). Polyimides were prepared by polycondensation of CHDI with aromatic dianhydrides including pyromellitic dianhydride (PMDA), benzophenonetetracarboxylic dianhydride (BTDA), and hexafluoroisopropylidene dipthalic anhydride (6FDA) (see Scheme 1). Polyamide-imide was also synthesized by re-



**Scheme 2** Synthesis of polyamide-imide.



**Scheme 3** Synthesis of model imide compound.

action of CHDI with trimellitic anhydride (see Scheme 2).

## EXPERIMENTAL

### Materials

PMDA, BTDA, 6FDA, and CHDI were purchased from Aldrich Chemical Co. Trimellitic anhydride, phthalic anhydride, and all the solvents were obtained from Merck Co. The dianhydrides were dried in a vacuum oven at 110°C for 5 h. CHDI was purified by sublimation under vacuum. The solvents were stirred overnight under nitrogen at 40–50°C over calcium hydride before vacuum distillation.

### Instruments

Infrared measurements were performed on a Bruker-IFS 48 FTIR spectrometer. The H-NMR spectrum was recorded on a Varian FT-80 A. The mass spectrum was recorded on a Shimadzu GC-MS-QP 1100 EX. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)

were recorded in air at heating rate of 10°C/min on a Stanton Redcraft STA-780. Differential thermogravimetric (DTG) traces were recorded on a Polymer Lab TGA-1500. Dynamic mechanical thermal analysis (DMTA) was recorded on a Polymer Lab DMTA. Measurement were performed in tension mode with film specimens. Films (5.0 cm long, 0.5 cm wide, and about 0.2 mm thick) were prepared by doctor blading the seven-membered ring intermediate solutions and subsequent programmed heating of the samples to final cure temperature (at 50°C for 3 h, 100°C for 1 h, 175°C for 1 h, 200°C for 1 h, and then 250°C for 1 h in vacuum). Inherent viscosities were measured by using an Ubbelohde viscometer.

### Model Compound Synthesis

Model imide compound was prepared according to the following procedure. Into a 100-mL, three-necked, round-bottomed flask equipped with a thermometer, nitrogen gas inlet tube, a reflux condenser, oil bath, and a magnetic stirrer was placed 0.01 mol CHDI and about 25 mL of dry dimethylacetamide (DMAc), and 0.02 mol

**Table I** Reactants, Structures, and Properties of the Polymers

No.	Reactants	Structure	Isolated Yield (%)	Inherent Viscosity (dL/g) <sup>a</sup>
I	CHDI + PMDA		88	0.452
II	CHDI + BTDA		90	0.433
III	CHDI + 6FDA		92	0.441
IV	CHDI + Trimellitic		95	0.408

<sup>a</sup>Measured at a concentration of 0.5 g/dL in H<sub>2</sub>SO<sub>4</sub> at 30°C.

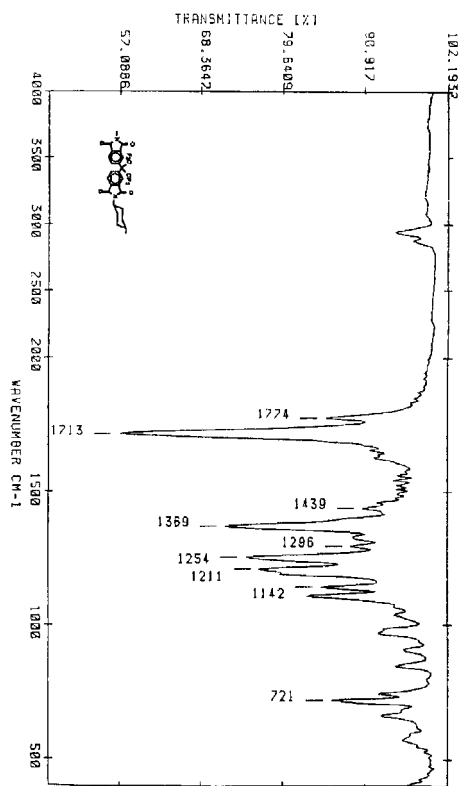


Figure 1 IR spectrum of polymer CHDI-6FDA.

phthalic anhydride was added into the reaction flask in small quantities over a period of 15–20 min at 0°C with vigorous stirring.

The solution was stirred at 0°C for 0.5 h and then slowly heated to 40°C and held for 2.5 h at this temperature. The reaction mixture was further heated to 90°C and maintained for 2 h; carbon dioxide gas evolution was observed at this temperature. The reaction mixture was heated to 130°C and kept for 20 h. The model compound was precipitated by pouring the flask content into water; it was then filtered, washed, and dried.

#### Polymer Synthesis

A typical procedure for preparation of polyimide is as follows. Into a 100-mL, three-necked, round-

bottomed flask equipped with a thermometer, nitrogen gas inlet tube, a reflux condenser, oil bath, and a magnetic stirrer was placed 0.01 mol CHDI and dissolved in about 30 mL of dry DMAc, and 0.01 mol dianhydride was added in small quantities over a period of 15–20 min at 0°C with vigorous stirring.

The solution was stirred at 0°C for 0.5 h and then slowly heated to 40°C and held for 2.5 h at this temperature. The reaction mixture was further heated to 90°C and maintained for 2 h; carbon dioxide gas evolution was observed at this temperature. The reaction mixture was heated to 130°C and kept for 20–25 h. During this time, carbon dioxide continued to evolve from the solution, but at a slower rate. Nitrogen atmosphere was maintained in the reaction flask throughout the course of reaction.

The obtained polymer was precipitated by pouring it into water; it was then filtered, washed several times with hot methanol, and dried in vacuum oven at 110°C overnight.

The same procedure was applied for preparation of polyamide-imide by using trimellitic anhydride instead of dianhydride.

## RESULT AND DISCUSSION

Polyimides are generally prepared by reaction of a diamine and a dianhydride in a polar solvent to provide a viscous poly(amic acid) intermediate. Subsequent high temperature heating of poly(amic acid) will evolve the small water molecules resulting in preparation of polyimide.

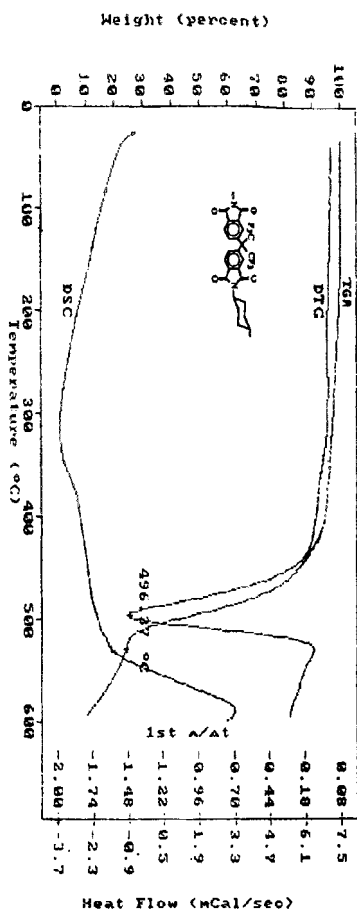
It is worth noting that polyaddition reactions with alicyclic diamines take more time than those for aromatic diamines. Also, polycondensation reactions of linear aliphatic diamines and aromatic dianhydrides were reported only at high temperatures under high pressure.<sup>13</sup>

The advantages of using diisocyanate instead of diamine are that formation of imide groups

Table II T<sub>g</sub>, T<sub>0</sub>, T<sub>10</sub>, T<sub>max</sub>, and Char Yield of the Polymers

Polymer	T <sub>g</sub> (°C)	T <sub>0</sub> (°C)	T <sub>10</sub> (°C)	T <sub>Max</sub> (°C)	Char yield at 600°C
I	—	360	430	510	18
II	250	355	425	475	24
III	350	340	420	495	10
IV	230	300	365	495	10

T<sub>g</sub>, glass transition temperature; T<sub>0</sub>, initial decomposition temperature; T<sub>10</sub>, temperature of 10% weight loss; T<sub>Max</sub>, maximum decomposition temperature; char yield, weight of polymer remained.



**Figure 2** DSC, TGA, and DTG of polymer CHDI-6FDA

happens at a lower temperature and polymerization occurs under mild condition. In addition, the evolved small molecule is carbon dioxide, which would easily bubble out of the reaction system.

### Model Compound

Reaction of CHDI with phthalic anhydride was studied as model reaction. Useful structural and analytical information was obtained by investigation of the reaction (see Scheme 3).

Structure of model compound was confirmed by the spectral data. Fourier transform infrared (FTIR) spectrum was 1767, 1710, 1377, and 717  $\text{cm}^{-1}$  for imide structure. H-NMR spectrum (dimethylsulfoxide [DMSO]- $d_6$ ) was  $\delta$  7.50–8.20 (8H, aromatic); 1.20–2.25 (8H,  $\text{CH}_2$ ); 2.75 (2H, CH). Mass spectrum was  $m/z$  374.

### Polymers

According to the obtained results, three different polyimides and one polyamide-imide were pre-

pared. Table I summarizes the results of polymerization.

FTIR spectra of polyimides show the presence of imide bands at about 1774, 1712, 1370, and 725  $\text{cm}^{-1}$  and bands at about 3330, 1774, 1705, 1628, 1377, and 729  $\text{cm}^{-1}$  were observed for polyamide-imide structure. Typical IR spectrum is shown in Figure 1.

The presence of seven-membered ring intermediate during polymerization reaction was confirmed by IR spectroscopy. IR spectra of the intermediate and that of the corresponding polymer were similar, with the exception that the band at 1650–1670  $\text{cm}^{-1}$  was intense in the spectrum of the intermediate due to the presence of additional carbonyl group. During synthesis of polyimide, carbon dioxide is released, and the intensity of the band at 1650–1670  $\text{cm}^{-1}$  decreases.

Thermal properties of polymers were studied by DSC. Transition related to softening or melting was not detected by DSC traces. The glass transition temperature ( $T_g$ ) was measured by DSC and the result is brought in Table II.

Temperature for zero, 10%, and maximum weight losses, and also char yields for a given polymer as calculated from TGA curves are brought in Table II.  $T_{\text{max}}$  was derived from the DTG curves.  $T_{10}$  is an important criterion for evaluating the thermal stability from TGA data. According to the obtained results, PMDA-derived polyimide is more stable than corresponding BTDA-derived polyimide, which is in turn more stable than corresponding 6FDA-derived polyimide (I > II > III). On the other hand, thermal stability of polyimide is higher than corresponding polyamide-imide (I > IV). Typical DSC, TGA, and DTG are shown in Figure 2.

Thermal stabilities of the obtained polymers and the nature of prepared films were similar to the same polymers that have been prepared earlier by related diamines.<sup>14,15</sup> Because of the brittle nature of polymer I and II films, the mechanical properties were measured for polymers III and IV. The tensile modulus and elongation at break in air at 200°C for polymer III were 2.8 GPa and 13% and for polymer IV were 2.4 GPa and 16%, respectively.

The incorporation of cycloaliphatic components into the polymer backbone led to the preparation of different polyimides with various properties. By comparison of thermal and mechanical properties it was revealed that the CHDI-6FDA polyimide comprised a particularly nice balance of properties.

The solubility of polymers were studied in different solvents. Solubility was measured at a concentration of 1g/dL at ambient temperature. All polymers were easily soluble in concentrated H<sub>2</sub>SO<sub>4</sub>. Polyimides were partially soluble in N-methyl-2-pyrrolidone (NMP), DMAc, dimethylformamide (DMF), and dimethylsulfoxide (DMSO) after a few hours stirring. (Polyimides II and III showed more solubility than polyimide I in NMP). Polyamide-imide was soluble in mentioned polar aprotic solvents after a few hours stirring. It is noteworthy that the reaction medium in polymerization reactions was homogeneous and no precipitation was observed during polymerization. After isolation and drying of polymers the solubility in polar aprotic solvents was decreased.

## CONCLUSION

Three different polyimides were prepared by polycondensation reactions of CHDI with aromatic dianhydrides. Polyamide-imide was also prepared by polymerization of CHDI with trimellitic anhydride. These aromatic/cycloaliphatic polymers showed high thermal stability. Using CHDI instead of trans-1,4-diaminocyclohexane resulted in easier preparation of the same polymers with similar properties. Performance of polymerization at lower temperature and under milder condition, and also generation of carbon dioxide gas as by-product were the main advantages of using diisocyanate instead of diamine in preparation of these polymers.

We wish to express our thanks to Dr. H. Yeganeh for valuable discussions. We also appreciate the assistance of Eng. M. Nouri and Eng. S. M. Mohaghegh.

## REFERENCES

1. Bowden, M.; Turner, S. R. *Polymers for High Technology, Electronics and Photonics*, ACS Symp Series 1987, 346, 428.
2. Cassidy, P. E. *Thermally Stable Polymers*; Marcel Dekker: New York, 1980.
3. Koton, M. M. *Polym Sci USSR* 1971, Series A, 13 (6), 1513.
4. Ulrich, H. *J Polym Sci Macromol Rev* 1976, 11, 93.
5. Meyers, R. A. *J Polym Sci Part A: Polym Chem* 1969, 7, 2757.
6. Carleton, P. S.; Farrissey, W. J.; Rose, J. S. *J Appl Polym Sci* 1972, 16, 2983.
7. Alvino, W. M.; Edelman, L. E. *J Appl Polym Sci* 1975, 19, 2961.
8. Ghatge, N. D.; Mulik, U. P. *J Polym Sci Part A: Polym Chem* 1980, 18, 1905.
9. Chapin, J. T.; Onder, B. K.; Farrissey, W. J. *Polym Prepr* 1980, 21 (2), 130.
10. Kilic, S.; Mohanty, D. K.; Yilgor, I.; McGrath, J. E. *Polym Prepr* 1986, 27 (1), 318.
11. Nien, K. E.; Yang, M. H.; Chu, T. J. *J Polym Eng* 1997, 1 (17), 23.
12. Barikani, M.; Ataei, S. M. *J Polym Sci Part A: Polym Chem* 1999, 37, 2245.
13. Sroog, C. E. *J Polym Sci Macromol Rev* 1976, 11, 161.
14. Q. Jin, T. Yamashita, K. Horie, R. Yokota, and I. Mita, *J Polym Sci Part A: Polym Chem* 1993, 31, 2345.
15. Volksen, W.; Cha, H. J.; Sanchez, M. I.; Yoon, D. Y. *Reac Func Polym* 1996, 30, 61.