Polymer Bulletin 54, 39–46 (2005)
DOI 10.1007/s00289-005-0363-8

Polymer Bulletin

Synthesis of copolyimide containing fluorine and naphthalene with synergizing effect on dielectric constants

Bor-Kuan Chen[1] (✉), Sun-Yuan Tsay[1], I-Chao Shih[2]

[1]Department of Polymer Materials, Kun Shan University of Technology, Tainan, TAIWAN 710
[2]Department of Chemical Engineering, National Cheng Kung University,Tainan, TAIWAN 701

E-mail: chenbk@seed.net.tw

Received: 23 January 2005 / Revised version: 22 February 2005 / Accepted: 22 February 2005

Summary

Novel copolyimides containing fluorine and naphthalene groups were synthesized from 4,4’-(Hexafluoroisopropylidene)diphthalic dianhydride (6FDA) and two diamines, 1,4-Bis(4-amino-2-trifluoromethylphenoxy) benzene (BATB) and 2,7-bis(4-aminophenoxy) naphthalene (BAPN) in various ratios via thermal imidization. The introduction of fluorinated groups into dianhydride improved transparency of copolyimides. All films are transparent. The structures and physical properties of copolyimides were characterized by FT-IR, DSC, TGA, XRD, UV-Vis and dielectric analyzer to study the effect of diamines on the physical properties of modified polymers. Copolyimides containing a higher percentage of BAPN have higher glass transition temperature and are less soluble in organic solvents. The copolyimide consisting of 50/50 mole % of BATB/BAPN has the lowest dielectric constant (2.60 at 1 KHz), reflecting the synergizing effect from both diamines.

Introduction

Electronic materials require high thermal and dimensional stabilities, low dielectric constants, and good mechanical properties. In microelectronic device circuitry, the propagation velocity of the signal is inversely proportional to the square of the dielectric constant of the propagation medium. Therefore, a low dielectric constant is essential for faster signal propagation without crosstalk. Polyimide (PI) is one of the most suitable materials [1]. PI can be synthesized via condensation from dianhydride and diamine. In order to meet the strict requirements in modern microelectronics, much research has been made to improve the heat resistance, processability, and dielectric properties of PI. Some approaches place emphasis on reducing molecular regularity, rigidity, and cohesive energy density. The introduction of fluoroalkyl groups, especially trifluoromethyl (CF_3) group has been demonstrated to ensure PI with desirable dielectric properties, excellent thermal and mechanical properties [2]. Other approaches have sought to incorporate flexible linkage groups such as ether [3] or bulky pendant groups along the polymer backbone [4-6]. Incorporating pendant groups has proven to be effective in improving PI solubility because the method enhances free volume and reduces the packing force [7]. Successful results can be achieved by using one, or a combination, of these approaches. In order to improve the heat resistance of phenyl PI, some naphthyl polyimides have been developed [8]. To obtain desirable thermal and physical properties, copolyimides can be prepared by selecting the appropriate ratios of the dianhydride component and the diamine component.

In this study, we synthesized copolyimides from 4,4'-(Hexafluoroisopropylidene) diphthalic dianhydride (6FDA) with a diamine containing fluorine, 1,4-Bis(4-amino-2-trifluoromethylphenoxy) benzene (BATB) and a diamine containing naphthalene, 2,7-bis(4-aminophenoxy) naphthalene (BAPN). The effects of various mole ratios on the soluble, thermal, transparent, and dielectric properties of PI copolymers were studied. An unexpected synergizing effect on dielectric constant from diamines was observed.

Experimental

Materials

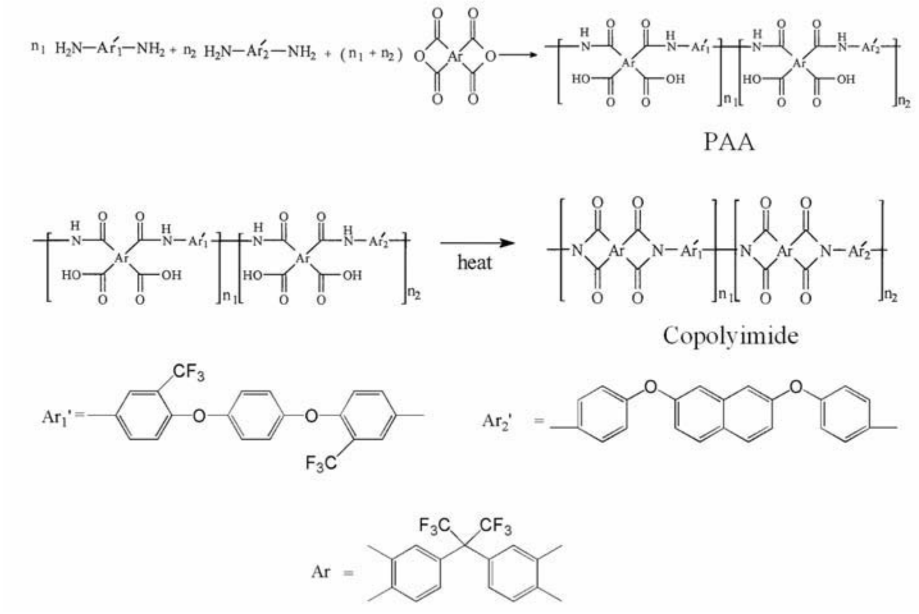
4,4'-(Hexafluoroisopropylidene)diphthalic dianhydride (6FDA) was purchased from Lancaster, UK and was recrystallized from acetic anhydride and vacuum dried before use. 1,4-Bis(4-amino-2-trifluoromethylphenoxy)benzene (BATB) was prepared by the catalytic reduction of 1,4-bis(4-nitro-2-trifluoromethyl phenoxy)benzene (BNTB) with hydrazine hydrate and Pd/C catalyst in refluxing ethanol [6]. BNTB was synthesized from 1,4-hydroquinone and coupled with 2-chloro-5-nitrobenzotrifluoride in the presence of K_2CO_3 in DMAc. 2,7-bis(4-aminophenoxy) naphthalene (BAPN) was prepared according to a procedure described in the literature [8]. 2,7-dihydroxy naphthalene was reacted with *p*-chloro nitrobenzene via aromatic nucleophilic substitution in the presence of potassium carbonate. The resulting dinitro compound was subsequently reduced with hydrazine as the reducing agent and palladium as the catalyst to produce BAPN. *N*-methyl-2-pyrrolidone (NMP) was purchased from Tedia and purified by distillation under reduced pressure and stored over 4Å molecular sieves. The other reagents were used as received.

Synthesis of copolyimides

Copolyimides were synthesized by reacting BATB and BAPN with 6FDA as shown in Scheme 1. The reactor was purged with dry nitrogen for 30 min. Different mole ratios of BATB and BAPN were charged into the reactor through an addition funnel (the amount used is listed in the Table 1). NMP (solid content 30%) was then charged. Until complete dissolution of diamines, 6FDA was added to the reactor in two portions, 80% and 20% respectively, through another addition funnel within one hour. In this study, 6FDA/diamine ratio of 1.03:1 was chosen to control the molecular weight in polymerization to yield the desired molecular weight PI. After 6FDA was charged, residual NMP was added into the reactor to dilute the reaction mixture (solid content 15%). The reaction mixture was stirred at room temperature in N_2 atmosphere resulting in a viscous copolyamic acid (PAA) solution after 3 h. The PAA solution was spread on a glass plate using a spin-coater to obtain PAA film. The films were thermally dried at 60°C for 2 h to remove most of the solvent in a forced air oven and were converted to the copolyimide with a heating program of 110°C for 2 h followed by 1 h each at 200 and 300°C. The films were cooled to room temperature, soaked in water and stripped from the plates. After drying the aforementioned films at 110°C for 24 h in vacuum, the copolyimide films **PI**$_1$~**PI**$_5$ were obtained.

Table 1. Monomer compositions

Polymer Code	BATB/BAPN (mol %)	BATB (mmole)	BAPN (mmole)	6FDA (mmole)	Inherent viscosity
PI$_1$	100/0	2.57	0.0	2.64	0.72
PI$_2$	75/25	1.83	0.61	2.51	0.76
PI$_3$	50/50	1.15	1.15	2.39	0.79
PI$_4$	25/75	0.55	1.65	2.27	0.83
PI$_5$	0/100	0.0	2.11	2.17	1.04



Scheme 1. Copolymerization of 6FDA with BATB and BAPN.

Characterization

Physical and chemical properties

^{1}H NMR spectra were performed on a Bruker AMX-400 spectrometer with dimethyl sulfoxide (DMSO-d_6) or $CDCl_3$ as the solvent. Fourier transfer infrared (FTIR) spectra were recorded on a Bio-Rad FTS-40A spectrometer. The inherent viscosities were measured with NMP as solvent and an Ubbelohde viscometer (Schott Gerate AVS-310) at 30°C and at a concentration of 0.5 g/dL. The solubility of the copolymers was determined for the film samples in various solvents. UV–vis spectra of the polymer films (~30μm thickness) were recorded on a Perkin-Elmer Lambda 10 spectrophotometer at room temperature. Wide-angle X-ray diffractograms (XRD) were obtained at room temperature with film specimens about 0.2 mm thick on a

Rigaku Geiger Flex D-Max IIIa x-ray diffractometer, using Ni-filtered CuK_α radiation (40kV, 15mA).

Thermal analysis

Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA-7 thermal analyzer at a heating rate of 20°C/min in nitrogen within the temperature range of 30-800°C. Differential scanning calorimetry (DSC) data were obtained from a Perkin-Elmer DSC-7. Samples of ~5 mg were sealed in hermetic aluminum pans and scanned in the calorimeter at a heating rate of 10°C/min in the range of 50-350°C under N_2 atmosphere. The T_g values were taken as the change of the specific heat in the heat flow curves.

Dielectric constant

The dielectric property of the polymer films was tested by the IM6 of ZAHNER-elektrik GmbH & Co. KG at a frequency of 1 KHz with AC amplitude of 5mV rms. The sample holder of IM6 has two stainless steel circular plates and its diameter is 1.0 cm. Polymer films were pressed between the two circular plates when measuring the dielectric constant of polymers.

Results and Discussion

Monomer and polymer synthesis

The structure of diamines, BATB and BAPN were confirmed by IR and ^{1}H NMR. For BATB, IR (KBr) 3449 cm^{-1}, 3477 cm^{-1} (Ar-NH_2), 1248 cm^{-1} (C-O-C), 1350-1120 cm^{-1} (CF_3). ^{1}H NMR ($CDCl_3$) δ 6.945 (Ha, 2H), 6.889 (Hd, 4H), 6.753 (Hc, 2H), 6.746 (Hb, 2H), 3.707 (He, 4H). For BAPN, IR 3395 cm^{-1}, 3444 cm^{-1} (Ar-NH_2), 1220 cm^{-1} (C-O-C str). ^{1}H NMR (DMSO-d_6) δ 7.77 (2H, Hc), 7.06 (2H, Hb), 6.95 (2H, Ha),

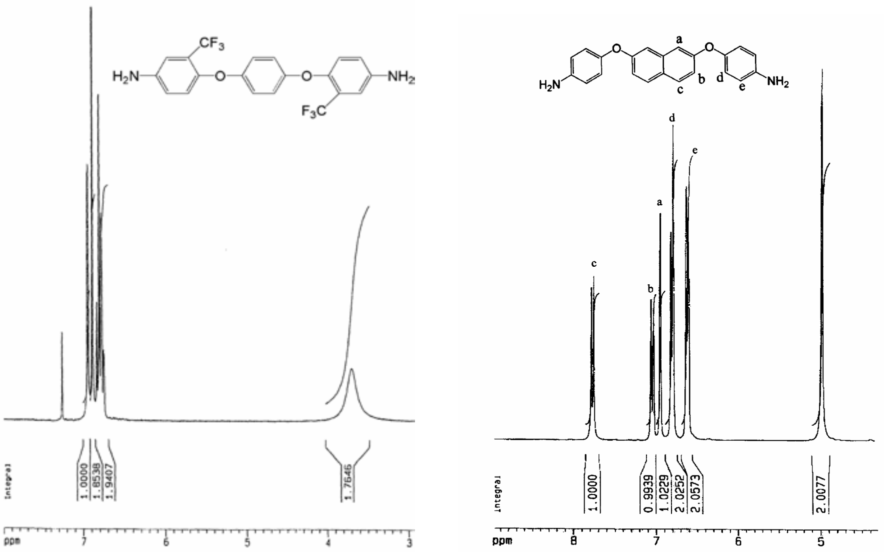


Figure 1. ^{1}H NMR spectra of (a) BATB and (b) BAPN.

6.82(4H, Hd), 6.63 (4H, He), 5.0 (4H, NH_2). Figure 1 shows the ^{1}H NMR spectrum of BATB and BAPN. All of the spectroscopic data obtained were in good agreement with the proposed structure.

The inherent viscosities of the intermediate polyamic acids of $\mathbf{PI}_1$~$\mathbf{PI}_5$ ranged from 0.72~1.04 dLg^{-1} (listed in Table 1), with PAA of $\mathbf{PI}_1$ had lowest viscosity. This can be explained by the steric hindrance effect from CF_3 group on the phenyl ring of diamine that reduced the degree of polymerization. The FT-IR spectrum of the copolyimide $\mathbf{PI}_4$ is shown in Figure 2. It exhibits characteristic imide group absorptions at 1780 and 1720 cm^{-1} (typical of imide carbonyl asymmetrical and symmetrical stretch), at 1380 cm^{-1} (C-N stretching), and at 720 cm^{-1} (C-N bending).

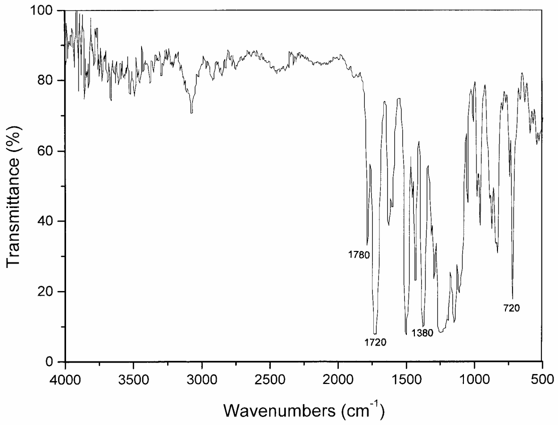


Figure 2. FT-IR spectrum of copolyimide $\mathbf{PI}_4$.

Solubility

Introducing bulky pendant groups into PI backbone has proved to be an effective approach to modify the solubility of aromatic polyimides [4,7]. The qualitative solubility of the polymers in various solvents is shown in Table 2. $\mathbf{PI}_1$ contained most fluorine and was soluble in organic solvents. With the increase of naphthalene content, $\mathbf{PI}_4$ and $\mathbf{PI}_5$ were only soluble in hot solvents, such as NMP, THF and pyridine. Therefore, the introduction of CF_3 group can effectively improve the solubility of copolymers because of the unique properties associated with fluorine (e.g., high electronegativity, high C—F bond energy, low intermolecular cohesive energy), which enhanced free volume and caused loss of chain packing.

Table 2. Solubility behavior of copolyimides*.

	Acetone	DMAc	NMP	THF	DMF	Pyridine	Dioxane	DMSO
$\mathbf{PI}_1$	++	++	++	++	++	++	+h	+h
$\mathbf{PI}_2$	++	++	++	++	++	++	+h	+h
$\mathbf{PI}_3$	++	++	+h	++	++	++	-h	-h
$\mathbf{PI}_4$	+h	—	+h	+h	-h	++	—	—
$\mathbf{PI}_5$	+h	—	+h	+h	—	++	—	—

* ++: soluble at 30°C; +h: soluble in hot solvent (80°C); -h: slightly soluble in hot solvent; —: insoluble.

Thermal properties

The thermal properties of polymers were investigated using TGA and DSC, as tabulated in Table 3. T_g gradually changes with an increase in the BAPN fraction indicating stiff linkage in the backbone structure of PI. The measured T_g values are similar to but slightly lower than those calculated by the Fox equation [9] for copolymers,

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{1}$$

where W_i and T_{gi} are the weight fraction and glass transition temperature of the component i, respectively. The DSC scan of polymers exhibited only one T_g, indicating that the various repeating units were randomly distributed along the polymer chain, which formed a random copolymer structure [8]. This is confirmed by the XRD curves of **PI**$_{1\sim5}$ as shown in Figures 3. The curves show no peak, indicating an amorphous polymer structure. The thermal decomposition temperatures at 10% weight loss ($T_{d,10\%}$) in a nitrogen atmosphere were between 534-576°C. Both the T_g and $T_{d,10\%}$ increased gradually with an increase in the BAPN fraction. Since CF_3 group is easily decomposed thermally, the char yield is lower when the BATB content is higher.

Table 3. Thermal properties of copolyimides.

Copolyimide	T_g (DSC) [°C]	T_g (calc.) [°C]	ΔT_g [°C]	$T_{d,10\%}$ [°C]	Char yield* (%)
PI$_1$	249	249	—	534	50.5
PI$_2$	253	255	+2	542	54.1
PI$_3$	258	262	+4	546	54.3
PI$_4$	270	270	+0	554	55.1
PI$_5$	280	280	—	576	59.4

*residual weight at 800°C in nitrogen.

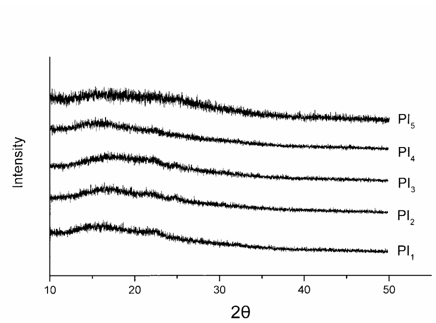


Figure 3. XRD of copolyimides.

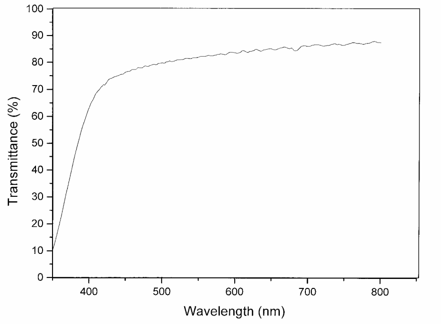


Figure 4. UV–vis spectra of the **PI**$_1$.

Transmittance

For the transmittance of visible light, all films are transparent. **PI**$_{1\sim5}$ have transmittance above 80%; **PI**$_1$ has 85% transmittance as shown in Figure 4. Based on the data, one can determine that the introduction of fluorinated groups is the primary reason for improved transparency of aromatic PIs [10]. This is consistent with the finding in an earlier report [11].

Dielectric constant

The dielectric constant of commercially available PI is typically 3.15~3.5[12]. The measurement results of the dielectric constant of copolyimides **PI**$_{1\sim5}$ are shown in Figure 5. All have values under 3 at a frequency of 1 KHz. The addition of bulky groups, such as naphthalene, limits chain packing and has been proven to enhance free volume and lowed dielectric constants in PI [13]. The incorporation of —CF_3 group prohibits close packing of the polymer chains and reduces inter-chain charge transfer of highly polar dianhydride groups [14], therefore decreasing the dielectric constant. Both naphthalene and CF_3 groups contribute to the low dielectric constant. An interesting synergizing effect on dielectric constant from two diamine groups is elucidated in Figure 5.

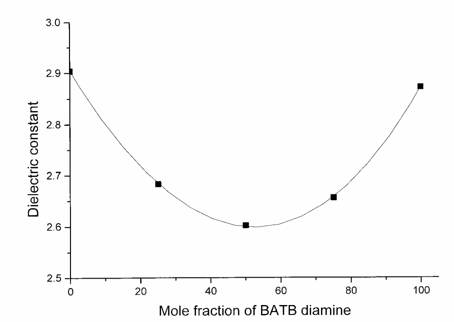


Figure 5. The synergizing effect on dielectric constant in copolyimides **PI**$_{1\sim5}$.

Conclusion

Copolyimides were synthesized from dianhydride 6FDA and two diamines, BATB, (containing naphthalene) and BAPN (containing fluorine) via thermal imidization. Copolyimides containing more BAPN are less soluble in organic solvents. Both the T_g and T_d rose gradually with an increase in the BAPN fraction. All films are transparent due to the introduction of -CF_3 group which improved transparency of copolyimides. The copolyimide containing BATB/BAPN with mole % of 50/50 has lowest dielectric constant. This synergizing effect on the decreased dielectric constant might be attributed to the presence of bulky naphthalene and CF_3 groups from both diamines, which resulted in less efficient chain packing and increased free volume.

Acknowledgements. We are grateful to the National Science Council of Taiwan for the support of this research work (Grant NSC93-2216-E168-002). Assistance from the Instrument Center of National Cheng Kung University in the characterization of polymer samples is greatly appreciated.

References

1. Ghosh MK, Mittal KL (1996) Polyimides, Fundamentals and Applications. Marcel Dekker, New York
2. Xie K, Zhang SY, Liu JG, He MH, Yang SY (2001) J Polym Sci, Part A: Polym Chem 39:2581
3. Feld WA, Ramalingam B, Harris FW (1983) J Polym Sci, Polym Chem Ed 21:319
4. Matsuura T, Hasuda Y, Nishi S, Yamada N (1991) Macromolecules 24: 5001
5. Chen BK, Chiu TM, Tsay SY (2004) J Appl Polym. Sci 94:382
6. Tsay SY, Tsai MF, Chen BK (2005) J Appl Polym Sci 95:321
7. Ayala D, Lozano AE, Abajo JD, Campa JG (1999) J Polym Sci, Part A: Polym Chem 37:805
8. Leu TS, Wang CS (2002) Polymer 43:7069
9. Fox TG (1956) Bull Am Phy Soc 1:123
10. St.Clair AK, St.Clair TL (1986) US. Patent 4,603,061
11. Yang CP, Hsiao SH, Chen KH (2002) Polymer 43:5095
12. Vora RH, Krishnan PSG, Goh SH, Chung TS (2001) Adv Funct Mater 11:361
13. Hougham G, Tesoro G, Viehbeck A (1996) Macromolecules 29:3453
14. Simpson JO, St.Clair AK (1997) Thin Solid Films 308-309:480