ELSEVIER

Polymer 43 (2002) 7069–7074

polymer

www.elsevier.com/locate/polymer

Polymer Communication

Synthesis and properties of copolyimides containing naphthalene group

Tsu-Shang Leu[a], Chun-Shan Wang[b,*]

[a]Department of Chemical Engineering, Yung-Ta Junior College of Technology and Commerce, Ping-Tung 900, Taiwan, ROC
[b]Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan, ROC

Received 27 May 2002; received in revised form 26 July 2002; accepted 2 August 2002

Abstract

Several series of copolyimides were synthesized from various ratios of two diamines with aromatic tetracarboxylic dianhydrides through thermal imidization process to determine the effect of naphthalene ring on the physical properties of polymers. The copolyimides were characterized using inherent viscosity, differential scanning calorimetry (DSC), TGA, DMA, TMA and dielectric analyzer. DSC showed only a T_g and exhibited that the copolyimides had a low entropy, amorphous state and formed random polymers. They retained high modulus even at high temperatures by DMA, and had measured coefficients of thermal expansion in the range of 15–57 ppm by TMA. The glass transition temperatures (T_g) of all polymers were found to be 287–321 °C by DSC. Their decomposition temperatures at 10% weight loss in nitrogen atmospheres were above 556 °C. These polymer films had dielectric constants ranging from 2.9 to 3.4 with moisture absorptions of less than 2.65%. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Naphthalene structure; Copolymerization; Random polymer

---

1. Introduction

Most of the copolyimides were prepared from general monomers [1–4] few were concerned with copolyimides containing naphthalene structure. In order to improve the heat resistance of phenyl polyimide, some naphthyl polyimides have been developed, such as naphthalene pendant group [5], 1,5-bis(4-aminophenoxy)naphthalene [6]. By appropriately selecting the ratios of the dianhydride component and the diamine component, copolyimides films having desirable thermal and physical properties can be obtained [7–9]. In this study, two dianhydrides (PMDA, pyromellitic dianhydride; 6FDA, 4,4′-(hexafluoroisopropylidene)diphthalic dianhydride) and two diamines (BAPN, 2,7-bis(4-aminophenoxy)naphthalene; ODA, 4,4′-oxydianiline) are used as starting materials for homopolyimides or copolyimides and expected to find a correlation between the properties and the compositions of the polymers.

2. Experimental

2.1. Materials

2,7-Dihydroxynaphthalene (Aldrich), 4,4′-oxydianiline (ODA, Janssen), pyromellitic dianhydride (PMDA, Chriskev), 4,4′-(hexafluoroisopropylidene)diphthalic dianhydride (6FDA, Aldrich), *p*-chloronitrobenzene (TCI), hydrazine monohydrate (Katayama), potassium carbonate anhydrous (SHOWA), 10% palladium on activated charcoal (TCI), *N*,*N*-dimethylacetamide (DMAc, Ferak), *N*,*N*-dimethylformamide (DMF, Ferak), *N*-methyl-2-pyrrolidone (NMP, Ferak), dimethyl sulfoxide (DMSO, Ferak), 2-methoxyethanol (Merck), *o*-chlorophenol (Janssen), *m*-cresol (Janssen), pyridine (Ferak) were obtained from commercial sources as indicated. The dianhydrides (PMDA and 6FDA) were recrystallized from acetic anhydride to achieve the required purity. All the reaction solvents and chemicals were used as received and then stored over calcium hydride or in a dry box under reduced pressure.

2.2. Measurements

^{1}H NMR spectra were registered using a Bruker Analytik AMX-400 spectrometer using DMSO-d_6 as a solvent. The ^{1}H chemical shifts were calibrated by using tetramethylsilane (TMS). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna-520 spectrometer with KBr pellets or using 10 μm film. Spectra in the optical range of 400–4000 cm^{-1} were obtained by averaging 32 scans at a resolution of 4 cm^{-1}. Electron impact (EI) source mass spectrometric analyses were performed on a VG 70-250S

---

* Corresponding author. Tel.: +886-6-2757575; fax: +886-6-2344496.
E-mail address: cswang@mail.ncku.edu.tw (C.S. Wang).

PII: S0032-3861(02)00530-X

GC/MS spectrometer with a solid inlet. Elemental analyses were carried out with Heraeus CHN-Rapid elemental analyzer. Differential scanning calorimeter (Perkin–Elmer DSC-7) measurements were used in this study. Samples of approximately 5 mg in weight were sealed in hermetic aluminum pans and scanned in the calorimeter with a heating rate of 20 °C/min in the range of 40–350 °C under N_2 atmosphere and the glass transition temperature (T_g) values were taken as the change in the specific heat in the heat flow curves. Dynamic mechanical analysis (DMA) was performed on a Perkin–Elmer DMA-7 thermal analyzer system. A sample 10 mm length (measuring system display sample height, it was decided from sample zero), 2 mm in width was used. The modulus and tan δ were studied when the sample was subjected to temperature scan mode with an extension measuring system (use stainless steel extension kit) at a programmed heating rate of 5 °C/min from 30 to 350 °C at a frequency of 1 Hz. Thermogravimetric analyses (TGA) were performed on a Perkin–Elmer TGA-7 thermal analyzer using a heating rate of 20 °C/min in N_2 at a purge pressure of 25 psi within the temperature range of 80–800 °C. The coefficient of thermal expansion (CTE) was measured with TMA mode (use quartz extension kit) of Perkin–Elmer DMA-7 thermomechanical analyzer (10 °C/min, 30–360 °C and 2 mN tension). The thermal expansion increased with temperature and the CTE values were calculated from the slope prior T_g. The inherent viscosities of the copolyimides in concentrated H_2SO_4 solutions (conc. 0.5 g/dl) were measured at 30 °C with a Ubbelohde viscometer. The amounts of moisture absorption were measured by immersing specimens in 30 °C water for 48 h, and measuring the weight difference after aging [10]. The dielectric constants were determined by the bridge method with Du pont-2970 dielectric analyzer at a frequency of 1 kHz, 300 N, and 30 °C in a N_2 atmosphere at a flow rate of 500 cm^3/min by the two parallel plate mode. The specimens were subjected to vacuum pretreatment of 1–3 mm Hg at 100 °C for 2 h to eliminate absorbed water, and an average of at least three individual determinations was used.

2.3. 2,7-Bis(4-nitrophenoxy)naphthalene (BNPN)

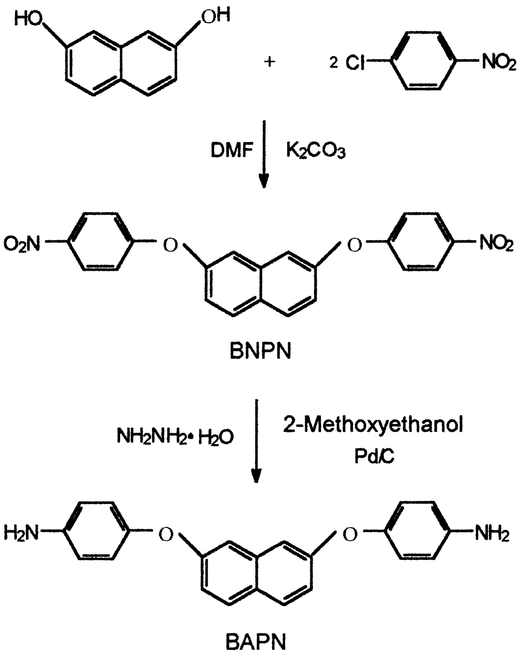
A mixture of 2,7-dihydroxynaphthalene (32.02 g, 0.2 mol), *p*-chloronitrobenzene 69.34 g (0.44 mol), potassium carbonate 55.28 g (0.4 mol), and 167 ml of DMF was refluxed at 140–142 °C for 8 h under nitrogen. After completion of the reaction, the reaction mixture was added to water to precipitate product. The resulting solid was filtered and recrystallized from 2-methoxyethanol to produce 74.77 g (93%) of green crystals. Mp 167–168 °C; IR (KBr) cm^{-1}: 1335, 1510 (NO_2 str), 1240 (C–O–C str), 3100 (aromatic C–H); MS (EI) *m/e* intensity (%): 402 (M^+, 100); ^1H NMR (400 MHz, DMSO-d_6), δ 7.1–8.2 (m, 14H, phen. H). Anal. calcd for $C_{22}H_{14}N_2O_6$: C, 65.67; H, 3.48; N, 6.97. Found: C, 65.66; H, 3.47; N, 6.92.

2.4. 2,7-Bis(4-aminophenoxy)naphthalene (BAPN)

To a dinitro of BNPN (40.2 g, 0.1 mol) in 2-methoxyethanol (200 g) was added 0.20 g of 10% Pd/C, and hydrazine monohydrate (85%, 50 ml) was charged to the stirred mixture dropwise at 100 °C over 1 h. After addition was completed, the mixture was stirred at 100 °C for another 4 h. The solution was then filtered to remove Pd/C. The product was recrystallized again from 2-methoxyethanol to produce pale-orange crystals, and then dried in vacuo (80 °C). The yield was 32.5 g (95%), mp 166–167 °C; IR (KBr) cm^{-1}: 3395, 1630 (NH str and deformation), 1210 (C–O–C str); MS (EI) *m/e* intensity: 342 (M^+, 100); ^1H NMR (400 MHz, DMSO-d_6), 5.0 ppm (4H, NH_2, s), 6.5–7.8 ppm (14H, ph-H, m). Anal. calcd for $C_{22}H_{18}N_2O_2$: C, 77.19; H, 5.26; N, 8.19. Found: C, 76.97; H, 5.26; N, 8.18. The reaction is shown in Scheme 1.

2.5. Polymer synthesis and film casting

For the polymerization the mole ratio of the two diamines was varied from 0/100 to 100/0% in increments of 25%. A three-necked flask was equipped with an addition funnel and a high-purity N_2 inlet was charged with a solution of diamine in DMAc, then dianhydride was added to the aforementioned solution in four portions of 90, 5, 3 and 2% within an effective time period. In general, polyimides were synthesized based on mole ratio diamine/-dianhydride of 1:1 and solid content of 10–15 wt%, respectively. In this study, diamine/dianhydride ratio of 1:1.03 and 15 wt% solid content were chosen to control the molecular weight in polymerization to yield the desired molecular weight polyimide. The reaction mixture (ca.



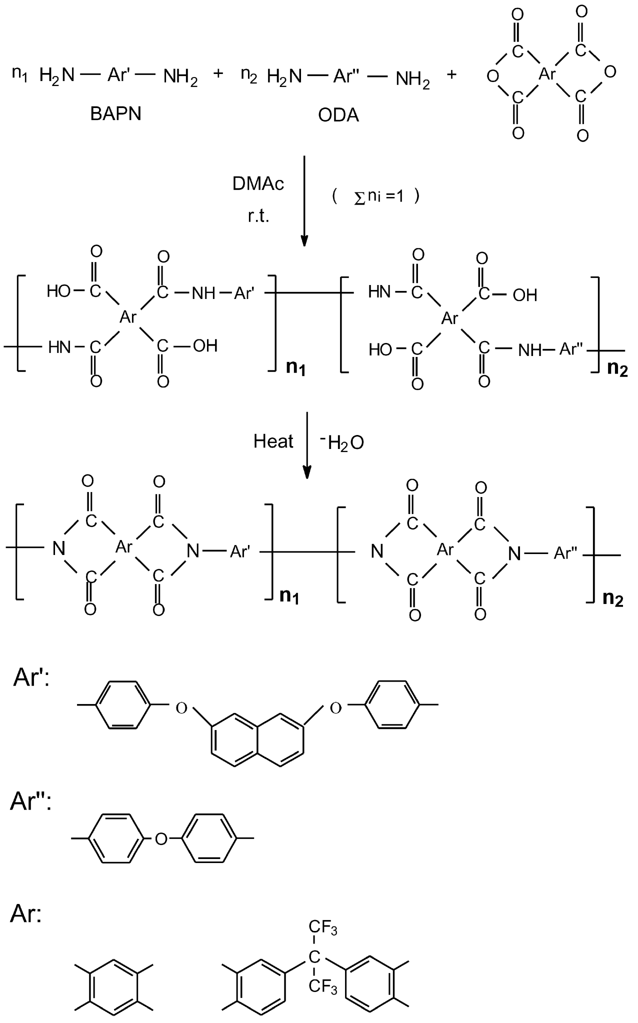
Scheme 1.

8 ml) was stirred at room temperature in N_2 atmosphere affording a viscous poly(amic acid) solution after 4 h. The solution was spread (with film casting apparatus) on a heatproof glass plate and dried at 80 °C for 4 h in a forced air oven. The film on glass were then converted to the polyimide by heating in air at 120, 150, 180 and 300 °C each for 1 h, respectively. The film was cooled to room temperature, and stripped from the plate by soaking in water, as shown in Scheme 2.

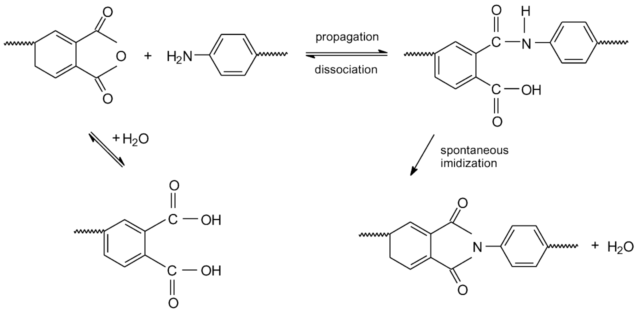
3. Results and discussion

3.1. Monomer synthesis and preparation of polymers

The high yield of monomers (dinitro and diamine, reduction of the dinitro compound to an amino compound can be carried out in a number of ways [11]) could be attributed to the dipotassium salt of 2,7-dihydroxynaphthalene was a good nucleophile, and the electron-withdrawing effect of NO_2 group in *p*-chloronitrobenzene also increases its reactivity. The structures of monomers were confirmed by ^{1}H NMR spectrum, mass spectrometry, IR spectrum and elemental analysis. A series of copolyimides were synthesized by the conventional two-step method starting with diamines and a aromatic tetracarboxylic dianhydride through ring-opening polyaddition and subsequent thermal cyclodehydration imidization. In general, the two-stage method (bulk thermal-imidization) suffer from imidization problems due to their diffusion/mobility [12]. The system undergoes a viscosity increase and changes from viscous liquid through gel to glass; a final cure temperature above the glass transition temperature of the fully imidized material is needed to provide the adequate chain mobility required for a high degree of imidization. Poly(amic acid) formation is actually a very complex situation which includes the competition between propagation and hydrolysis [13]. The reaction is shown in Scheme 3. Scheme 2 shows the polymerization results and structure of the synthesized copolymers. Although the preferred structure of copolymers is shown in Scheme 2 as the dyad (two mers) configuration, however, it may contain a small percentage of triad (three mers). The composition of the repeat unit differs from the two mers (monomeric units) by the elements of water.



Scheme 2.



Scheme 3.

This section treats cases where whole polymer chains are linked together to form for larger polymer structures. Stated mathematically, the probability of finding a sequence $\cdots AB\cdots$ of repeat units A, B, …, which can be written

$$P(\cdots \mathrm{AB} \cdots) = P(\mathrm{A})P(\mathrm{B}) = \prod_i P(i) \qquad i = \mathrm{A}, \mathrm{B}, \ldots \qquad (1)$$

where $P(\mathrm{A}), P(\mathrm{B})$, and so on are the unconditional probabilities of the occurrence of the various repeat units. If Eq. (1) is considered, some of the possible copolymers will be represented by

Long sequence : polyA–block–polyB

Short sequence : poly(A–ran–B)

The term –ran– was used to indicate a random copolymer. Table 1 summarizes the resulted polymers (homopolyimides and copolyimides). Polymers (PI-6–PI-10) had inherent viscosities between 0.53 and 0.56, which were lower than those of the polymers (PI-1–PI-5).

Table 1
Synthesis of polymers from various component systems

Polymer	Diamine (mol%)	BAPN (mmol)	ODA (mmol)	PMDA (mmol)	6FDA (mmol)	Solid[a] (wt%)	η_{inh}[b] (dl/g)
PI-1	ODA(100)		2.649	2.728		0.15	0.80
PI-2	BAPN(25)/ODA(75)	0.611	1.833	2.517		0.15	0.78
PI-3	BAPN(50)/ODA(50)	1.135	1.135	2.337		0.15	0.75
PI-4	BAPN(75)/ODA(25)	1.588	0.529	2.181		0.15	0.77
PI-5	BAPN(100)	1.984		2.044		0.15	0.79
PI-6	ODA(100)		1.711		1.762	0.15	0.56
PI-7	BAPN(25)/ODA(75)	0.406	1.217		1.672	0.15	0.54
PI-8	BAPN(50)/ODA(50)	0.772	0.772		1.590	0.15	0.55
PI-9	BAPN(75)/ODA(25)	1.104	0.368		1.516	0.15	0.53
PI-10	BAPN(100)	1.407			1.449	0.15	0.54

[a] For solid content in solvent:

$$\frac{m[(\sum X_i M_i)_{\text{diamine}} + 1.03 M_{\text{dianhyd.}}] \times 10^{-3}}{\rho_s V_s} = 0.15$$

where m is mmol, X_i, mole fraction of component i, M_i molecular weight of component i, ρ_s density of solvent, and V_s volume of solvent.

[b] 0.5 g/dl in concentrated H_2SO_4 at 30 °C.

3.2. Characterization of polymers

In this study, the systems of the homopolyimides and the copolyimides with incremental increase in the content of naphthalene structure was investigated. The thermal properties of polymers were investigated by DSC and TGA, as shown in Figs. 1 and 2. Both the T_g and T_d (10 wt% degradation temperature) change gradually with an increase in the BAPN fraction, and the copolyimide's T_g is only slightly higher than that of the homopolyimides, indicating that the stiff linkage in the backbone structure. The plot does show a linear dependence, and no significant differences in the thermostabilities of copolymers are observed. This result indicates that the contribution of BAPN to the rigidity of the resulting polyimide is a simple upward relationship. The linear dependence implies the weak existence of intermolecular interactions between the constituent components. Therefore, this relationship can be best described by

$$T_g = X_A T_{g_A} + X_B T_{g_B} \tag{2}$$

and

$$T_d = X_A T_{d_A} + X_B T_{d_B} \tag{3}$$

X_i and T_{g_i} or T_{d_i} are the mole fraction and glass transition

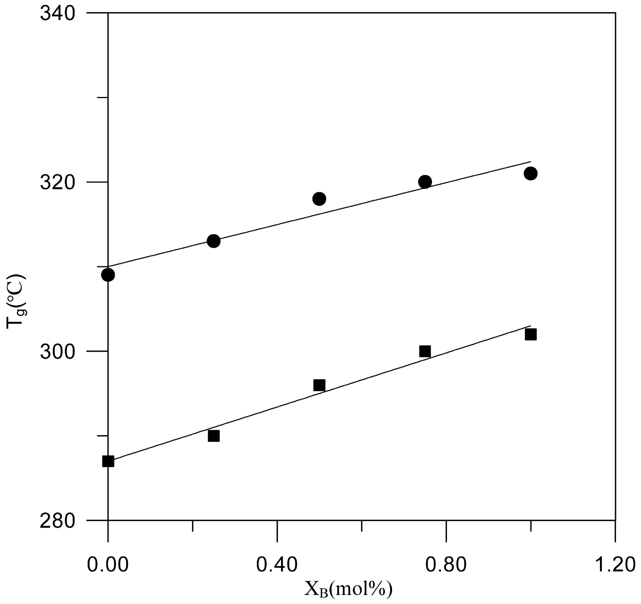


Fig. 1. Glass transition temperature of the diamine BAPN/ODA mixture as functions of composition X_B (B: BAPN) for two different dianhydrides (●: PMDA; ■: 6FDA), comparison between experimentally determined T_g (symbols) and the lines evaluated from the regression analysis.

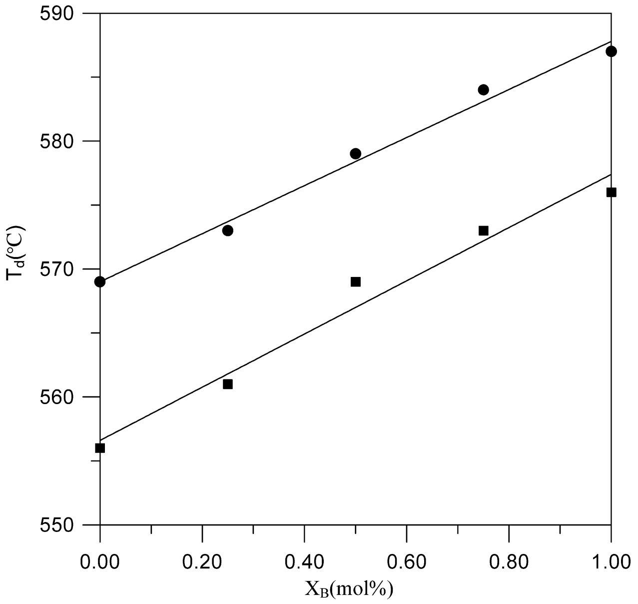


Fig. 2. Temperature of decomposition (10% weight loss) of the diamine BAPN/ODA mixture as functions of composition X_B (B: BAPN) for two different dianhydrides (●: PMDA; ■: 6FDA), comparison between experimentally determined T_d (symbols) and the lines evaluated from the regression analysis.

Table 2
Solubility of polymers

Polymer	DMF	DMAc	NMP	DMSO	Solvent			
					o-Chlorophenol	*m*-Cresol	Pyridine	H_2SO_4 (conc.)
PI-1	–	–	–	–	–	–	–	++
PI-2	–	–	+h	–	+h	−h	−h	++
PI-3	–	–	+h	–	+h	−h	−h	++
PI-4	–	–	+h	–	+h	−h	−h	++
PI-5	–	–	–	–	–	–	–	++
PI-6	–	–	−h	–	+h	–	–	++
PI-7	−h	−h	++	−h	++	+h	+h	++
PI-8	−h	−h	++	−h	++	+h	+h	++
PI-9	−h	−h	++	−h	++	+h	+h	++
PI-10	–	–	−h	–	+h	–	–	++

(–) insoluble in hot solvent, (−h) slightly soluble in hot solvent (100 °C/10 min), (+h) soluble in hot solvent, (++) soluble at room temperature, measured at a concentration of 0.5 g/dl).

temperature or degradation temperature of the component *i*, respectively. Eqs. (2) and (3) were used to describe the T_g and T_d were the composition relationship in copolyimides of ODA/PMDA–BAPN/PMDA or ODA/6FDA–BAPN/6FDA, respectively.

The DSC scan of polymers exhibited only one T_g, indicating that the various repeating units are randomly distributed along the polymer chain, and form a random copolymer structure. In addition, no endothermic peaks above their glass transition temperatures were observed in DSC scans, which may be attributed to the amorphous molecular structure for all polymers, and curing (thermal imidization) reaction for all samples can be safely completed below 350 °C without decomposition during curing. The solubilities of polymers in various solvents were investigated and the results are summarized in Table 2. All polymers are soluble in concentrated sulfuric acid at room temperature. In polar aprotic and common organic solvents, they exhibited somewhat limited solubility, while copolyimides showed better solubility compared to the homopolyimides. In addition, the polymers possessing hexafluoroisopropylidene unit [14] between two phthalimide units exhibited high solubility, because of the hexafluoroisopropylidene unit which hindered the interaction between neighboring molecules.

Table 3
Physical and mechanical properties polymers

Polymer	CTE[a] (ppm)	MA[b] (%)	DC[c]	Modulus (GPa)
PI-1	49	2.65	3.37	2.26
PI-2	42	1.82	3.33	2.91
PI-3	34	0.91	3.28	3.50
PI-4	23	0.52	3.21	3.89
PI-5	15	0.33	3.16	4.48
PI-6	57	2.56	3.19	1.33
PI-7	51	1.77	3.12	1.52
PI-8	42	0.84	3.04	1.81
PI-9	30	0.43	2.98	1.93
PI-10	21	0.21	2.91	2.10

[a] CTE, coefficient of thermal expansion.
[b] MA, moisture absorptions.
[c] DC, dielectric constant.

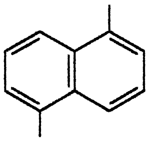
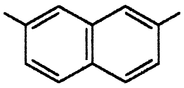
Physical and mechanical properties of the polymers were shown in Table 3. Moisture absorptions of naphthalene containing copolyimides were noticeably low. Furthermore, for the same composition, the fluoropolymers exhibited lower moisture absorptions than polymers without fluorine. Dielectric constants were also noticeably low for naphthalene and fluorine containing polymers. CTE was taken from the glassy state below T_g. Copolyimides with planar naphthalene structure showed low CTE values. Moreover, the dianhydride also had an effect on the CTE were observed, the rodlike dianhydride yielded lower CTEs. The modulus values observed in these polymers were consistent with stiff structures, and because of this high stiffness they provide films with high in-plane orientation.

The thermal, physical and mechanical properties of the 2,7-naphthalene-containing polyimide, is compared with 1,5-naphthalene-containing polyimide [6], and the results are listed in Table 4. The results suggest a higher thermal stability and better physical properties for the 2,7-naphthalene-containing polyimide than that of 1,5-naphthalene-containing polyimide. This may be attributed to the structure of 2,7-naphthalene-containing polyimide which is more symmetric than that of 1,5-naphthalene-containing polyimide.

4. Conclusions

The copolyimides containing naphthalene have a higher glass transition temperature, thermal stability and modulus; lower coefficient of thermal expansion, dielectric constant and moisture absorption than that of the homopolyimide systems and the effect is additive depending on the amount of naphthalene in the structure. The positive effect can be attributed to the planar, rigid and thermally stable structure of naphthalene ring.

Table 4
The properties of the 2,7-naphthalene-containing polyimide is compared with 1,5-naphthalene-containing polyimide

Diamine backbone structure	η_{inh} (dl/g)	T_g (°C)	T_d wt% loss in N_2 (°C)	Char yield 800 °C (%)	CTE (ppm)	Modulus (GPa)
	0.81	310 (TMA)	574	62	28.5	2.31
	0.79	321 (DSC)	587	68.4	15	4.48

Acknowledgements

Financial support of this work by the National Science Council of the Republic of China is gratefully appreciated.

References

[1] Jeon JY, Tak TM. J Appl Polym Sci 1996;61:529.

[2] Furukawa N, Yuasa M, Kimura Y. J Polym Sci Polym Chem 1998;36:2237.

[3] Feld WA, Ramalingam B, Harrris FW. J Polym Sci Polym Chem 1983;21:319.

[4] Babu GN, Samant S. Macromolecules 1982;183:1129.

[5] Wang CS, Leu TS. Polymer 2000;41:3581.

[6] Yang CP, Chen WT. J Polym Sci Polym Chem 1993;31:2799.

[7] Litauszki L, Karasz FE, Grünberg K, Berger W. J Polym Sci Polym Chem 1992;30:1227.

[8] Inoue H, Sasaki Y, Ogawa T. J Appl Polym Sci 1996;62:2303.

[9] Shiang WR, Woo EP. J Polym Sci Polym Chem 1993;31:2081.

[10] Wang CS, Leu TS, Hsu KR. Polymer 1998;39(13):2921.

[11] Wang CS, Lin CH. J Appl Polym Sci 1999;74:1635.

[12] Kim WG, Hay AS. Macromolecules 1993;26(20):5275.

[13] Leu TS, Wang CS. J Polym Sci Polym Chem 2001;39(23):4139.

[14] Feiring AE, Auman BC, Wonchoba ER. Macromolecules 1993;26:2779.