Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 6571−6580
polymer
www.elsevier.com/locate/polymer

High optical transparency, low dielectric constant and light color of novel organosoluble polyamides with bulky alicyclic pendent group

Der-Jang Liaw [a,*], Wen-Hsiang Chen [a], Chi-Kuang Hu [a], Kueir-Rarn Lee [b], Juin-Yih Lai [b]

[a] *Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan*
[b] *R&D Center for Membrane Technology and Department of Chemical Engineering, Chung Yuan University, Chung-Li 320, Taiwan*

Received 21 May 2007; received in revised form 14 August 2007; accepted 17 August 2007
Available online 22 August 2007

Abstract

Novel optically transparent, low dielectric and highly organosoluble alicyclic polyamides derived from bulky alicyclic diamine containing trifluoromethyl group on either side, 1,1-bis[4-(2-trifluoromethyl-4-aminophenoxy)phenyl]-4-*tert*-butylcyclohexane (**BTFAPBC**), were prepared. The polyamides were obtained in almost quantitative yields and showed inherent viscosity values between 0.55 and 0.72 dL g^{-1} in DMAc solution. Most of the polyamides showed excellent solubility in polar solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*′-dimethyl acetamide (DMAc), *N*,*N*′-dimethyl formamide (DMF), pyridine, cyclohexanone, γ-butyrolactone and chloroform. The cut-off wavelength for polyamides ranged from 350 to 388 nm. Polyamides with alicyclic *tert*-butylcyclohexyl cardo and trifluoromethyl substituents exhibited low dielectric constants ranging from 3.29 to 3.98 (at 100 Hz) compared with commercially available polyamides [Amodel®, 4.2−5.7 at 100 Hz]. Polyamides showed glass transition temperatures in the range of 244−266 °C and possessed a coefficient of thermal expansion (CTE) of 60−75 ppm °C^{-1}. Thermogravimetric analysis data showed that the polyamides were stable up to 430 °C and the 10% weight loss temperature was found to be in the range of 437−466 °C in nitrogen atmosphere. The polyamide films had a tensile strength in the range of 66−103 MPa, elongation at break in the range of 5−8%, and tensile modulus in the range of 1.5−2.2 GPa. Due to their properties, the polyamides could be considered as engineering plastic and photoelectric materials.

Keywords: Bulky; Trifluoromethyl; *tert*-Butylcyclohexane

1. Introduction

Aromatic polyamides are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties such as mechanical properties, low flammability and chemical resistance [1−9]. Because of the interest that they have generated, considerable effort has been made to modify their chemical structure to improve their solubility with regard to a specific application such as optical transparency and light color [1−9]. Thus, for obtaining films from polyamides, it is essential to restrain the crystallization and orientation of the molecular chains of the polymers.

Polymers containing pendent trifluoromethyl or trifluoromethoxy groups are of special interest [10−16]. Incorporation of these groups serves to increase the free volume of the polymers [10−16], thereby improving various properties including solubility and optical transparency without forfeiting thermal stability.

Furthermore, improvement of the solubility, mechanical and thermal properties and enhancement of rigidity by introduction of cardo group in polymer backbone have been reported [17−24]. Our previous studies have reported that incorporation of cardo pendent group such as cyclododecylidene [17], adamantane [18,19], tricyclo[5.2.1.0^{2,6}]decane [20,21], triphenylamine [22], pyrene [23], naphthalene [24]

---

* Corresponding author. Tel.: +886 2 27376638/27335050; fax: +886 2 23781441/27376644.

E-mail addresses: liaw@ch.ntust.edu.tw, liaw6565@yahoo.com.tw, liawdj@mail.ntust.edu.tw (D.-J. Liaw).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.08.041

into the backbone of polyamides improves solubility, processability maintaining good thermal stability [15,17–20]. The cardo, *tert*-butylcyclohexylidene group, could be considered as an alicyclic group and has been incorporated into several polymer backbones to improve the processability [6,16].

In the present article, we report the syntheses of a series of novel polyamides bearing trifluoromethyl and *tert*-butylcyclohexylidene pendent groups. The optical, dielectric, thermal, physical, and mechanical properties of those polyamides were investigated and discussed in this paper.

2. Experimental section

2.1. Materials

The diol, 1,1-bis(4-hydroxyphenyl)-4-*tert*-butylcyclohexane (**BHBC**), the dinitro, 1,1-bis[4-(2-trifluoromethyl-4-nitrophenoxy)phenyl]-4-*tert*-butylcyclohexane (**BTFNPBC**), and the diamine, 1,1-bis[4-(2-trifluoromethyl-4-aminophenoxy)-phenyl]-4-*tert*-butylcyclohexane (**BTFAPBC**) were synthesized according to the method reported in the preceding studies [6,16]. 2-Chloro-5-benzotrifluoride (from ACROS), anhydrous potassium carbonate (from ACROS), hydrazine monohydrate (from MERCK), 10% palladium on activated carbon (Pd/C from MERCK) and acetic anhydride (from MERCK) were used as received. Reagent-grade aromatic dicarboxylic acids such as isophthalic acid (Ip), 5-*tert*-butylisophthalic acid (Bp), 2,6-naphthalenedicarboxylic acid (Na), 4,4′-dicarboxydiphenyl sulfone (Sb) and 2,2-bis(4-carboxyphenyl)hexafluoropropane (6F) were purified by recrystallization [19,20]. The solvents were purified according to the standard methods.

2.2. Preparation of polymers

2.2.1. Polyamide **PA-5**

A flask was charged with a mixture of diamine **BTFAPBC** (0.4 g, 0.6224 mmol), 2,2-bis (4-carboxyphenyl)-hexafluoropropane (244.1 mg, 0.6224 mmol), triphenyl phosphite (TPP, 0.3 mL), pyridine (0.3 mL), *N*-methyl-2-pyrrolidinone (NMP, 2 mL) and calcium chloride (0.3 g). The reaction mixture was maintained at 130 °C under argon atmosphere for 3 h. After cooling, the reaction mixture was poured into a large amount of methanol with constant stirring, producing a precipitate. The precipitate was filtered, washed with hot methanol and hot water several times, which afforded **PA-5**. All the other polyamides (**PA-1**–**PA-4**) were prepared adopting a similar procedure.

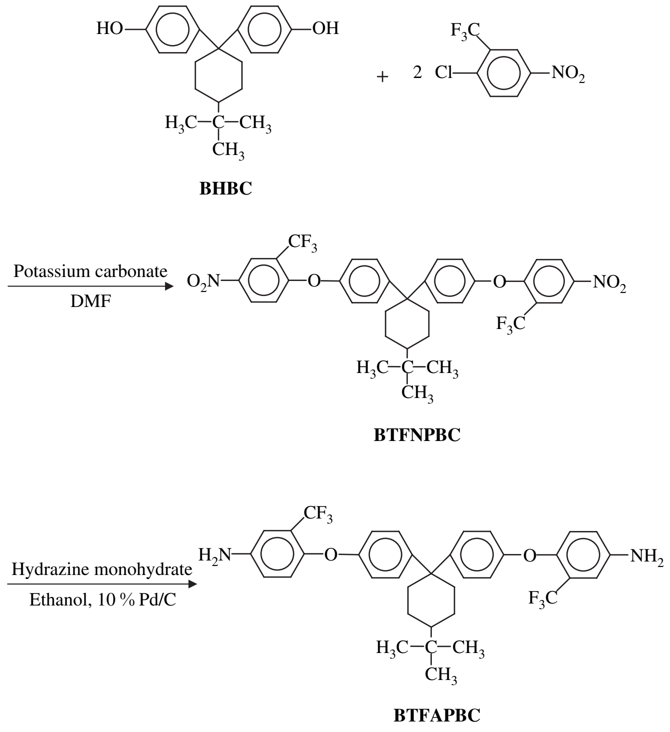
2.3. Measurements

Melting points were measured in capillaries on a Büchi apparatus (Model BUCHI 535). IR spectra were recorded in the range of 4000–400 cm^{-1} on a JASCO IR-700 spectrometer. The ^{13}C and ^{1}H NMR spectra were obtained by BRUKER AVANCE 500 NMR operated at 500 MHz for proton and 125 MHz for carbon. The inherent viscosities of all polymers were measured using Capillary Ubbelohde viscometer. Elemental analyses were conducted on a Perkin–Elmer 2400 instrument. Thermogravimetric analyses were obtained on a Du Pont 2100 at a heating rate of 10 $°C\,min^{-1}$ in the range of ambient temperature to 800 °C under nitrogen and air flowing condition of flow rate of 60 $cm^3\,min^{-1}$. Onset temperatures (PDT) were evaluated as 10% weight loss. Char yield (Y_c) was recorded at 800 °C in nitrogen atmosphere. Differential scanning calorimetry (DSC) analyses were performed on a TA instruments DSC 2010 differential scanning calorimeter at a heating rate of 10 $°C\,min^{-1}$ under air atmosphere. Glass transition temperatures were measured from the inflection point in the DSC heating thermogram. The temperature was calibrated with indium. The samples were encapsulated in hermetically sealed aluminum pans, with a typical sample weight of approximately 2 mg. Tensile properties were determined from stress–strain curves obtained with a Orientec Tensilon with a load cell of 10 kg_f. A gauge of 2 cm and a strain rate of 2 $cm\,min^{-1}$ was used for this study at room temperature. Measurements were performed at ambient temperature with film specimens of dimensions 4 mm wide, 5 cm long, and *ca.* 0.1 mm thick. The in-plane linear coefficient of thermal expansion (CTE) was obtained from a TA TMA-2940 thermomechanical analyzer (10 $°C\,min^{-1}$ from 25 to 300 °C, 10 mN). The CTE value on the temperature scale between 50 and 150 °C was recorded after an initial conditioning step (heating to 300 °C, holding for 5 min and cooling). Dielectric constants were measured by the parallel plate capacitor method using a dielectric analyzer (TA instruments DEA 2970) on thin films. Gold electrodes were vacuum deposited on both surfaces of dried films, followed by measuring at 25 °C in a sealed chamber maintained under nitrogen atmosphere. UV–vis spectra of the polymer films were recorded on a JASCO V-550 spectrophotometer at room temperature in air. A cut-off wavelength is defined here where the transmittance decreased below 1% in the spectrum.

3. Results and discussion

3.1. Synthesis of monomers and polymers

Scheme 1 outlines the synthetic route applied for the preparation of the diamine compound **BTFAPBC**. The diol compound **BHBC** was synthesized from the reaction of 4-*tert*-butylcyclohexanone with excess phenol in the presence of 3-mercaptopropionic acid as a catalyst. Compound **BHBC** was reacted with 2-chloro-5-nitrobenzotrifluoride in the presence of potassium carbonate and afforded the dinitro compound **BTFNPBC**. The catalytic hydrogenation of compound **BTFNPBC** to diamine compound **BTFAPBC** was accomplished by using hydrazine monohydrate as a reducing agent under Pd/C catalysed conditions. The results of the IR and elemental analyses are presented in Section 2. The ^{1}H, ^{13}C and HMQC NMR spectra of the dinitro (**BTFNPBC**)



Scheme 1. Synthesis of diamine, 1,1-bis[4-(2-trifluoromethyl-4-amino-phenoxy)phenyl]-4-*tert*-butylcyclohexane (**BTFAPBC**).

and diamine (**BTFAPBC**) compounds are shown in Figs. 1a, b and 2a–c, respectively. Assignments of peaks in spectrum are given in these figures. These results clearly confirm that the dinitro and diamine prepared are consistent with the proposed structure.

The synthesis methodology for these new polyamides (**PA-1**–**PA-5**) by Yamazaki reaction conditions [25] is shown in Scheme 2. All the polymerizations in NMP proceeded and afforded homogeneous solutions, indicating that the polymers possessed good solubility in the polymerization medium. The polyamides were obtained in almost quantitative yields and the inherent viscosities between 0.55 and 0.72 $\mathrm{dL\,g^{-1}}$ in DMAc solution are summarized in Table 1. The structure of polyamides was confirmed by elemental analysis, IR and NMR spectroscopies. The results of the elemental analyses of these polyamides are presented in Table 2. They were almost in good agreement with the calculated values of the proposed structures. The values of carbon were lower than the calculated values of the proposed structures. This finding may be attributed to the hygroscopic characteristics of the amide group [26]. The amount of absorbed water of these PAs was in the range of 1.74–2.70% and is presented in Table 2. Fluorine and hydrophobic substitution almost universally results in lower water absorption. **PA-2** and **PA-5** had the lower values for water absorption. The hydrophobic nature imparted by the *tert*-butyl and trifluoromethyl groups renders **PA-2** and **PA-5** less water absorbing as compared to other polymers [26,27]. The IR spectrum of the polyamides showed the characteristic absorptions around 3297 and 1658 $\mathrm{cm^{-1}}$, which are characteristic of N–H stretching and carbonyl stretching (C=O), respectively. A strong absorption band was observed around 1250 $\mathrm{cm^{-1}}$ due to the C–O–C linkage. The ^{1}H and ^{13}C NMR spectra of the polyamide (**PA-2**) compound are shown in Fig. 3a and b, respectively. Assignments of peaks in spectrum are also given in these figures. These results clearly confirm that the prepared polyamide (**PA-2**) is consistent with the proposed structure.

3.2. Polymer characterization

The solubilities of the polyamides in various organic solvents at 3.0% ($\mathrm{mg\,mL^{-1}}$) are summarized in Table 1. Most polyamides showed excellent solubility in polar solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethyl acetamide (DMAc), *N*,*N*-dimethyl formamide (DMF), pyridine, cyclohexanone, γ-butyrolactone and chloroform, but they are soluble on heating at 60 °C in tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO). Comparing the solubility of polyamides without trifluoromethyl group, in general, the incorporation of trifluoromethyl group improves the solubility of polyamides in organic solvents [11,12]. The bulky alicyclic *tert*-cardo group probably hinders packing of the polyamide chains; consequently, the solvent molecules can easily penetrate to solubilize the chain. It indicated that the *tert*-butylcyclohexane group effectively improves the solubility of polyamides.

The thermal behaviors of the polyamides were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). There were no melting peaks (T_m) detected in DSC and the absence of peak in DSC supported the generally amorphous nature of the polymers. The DSC thermograms of polyamides obtained from the second heating trace showed T_g transition in the range of 244–266 °C (Table 3). The increasing order of T_g generally corresponds to the stiffness and bulkiness of the dicarboxylic acid moiety [2,28]. The T_g of **PA-2** (256 °C) is higher than **PA-1** (244 °C) due to the presence of bulky *tert*-butyl group in the polymer chain (**PA-2**). Polyamide **PA-4**, containing a sulfone group, exhibited a higher T_g value (266 °C) because of its higher polar interactions between sulfonyl groups in the main chain [29,30]. The 10% weight loss temperature (PDT) and the char yield (Y_c) at 800 °C in nitrogen atmosphere, measured by TGA, are also summarized in Table 3. All the polymers exhibited excellent thermal stability. Polyamides were stable up to 430 °C and the 10% weight loss temperature was between 437–466 °C in nitrogen atmosphere.

All the polyamides including those containing aliphatic group in the backbone exhibited good thermal stability. This implies that the solubility of polyamides is improved by incorporation of bulky aliphatic group in the polymer backbone without compromising the good thermal stability.

The CTE (the coefficient of thermal expansion) values of polyamides were between 60 and 75 $\mathrm{ppm\,°C^{-1}}$. Polyamides containing flexible ‘spacer’ links, such as –O–, $-C(CF_3)_2-$

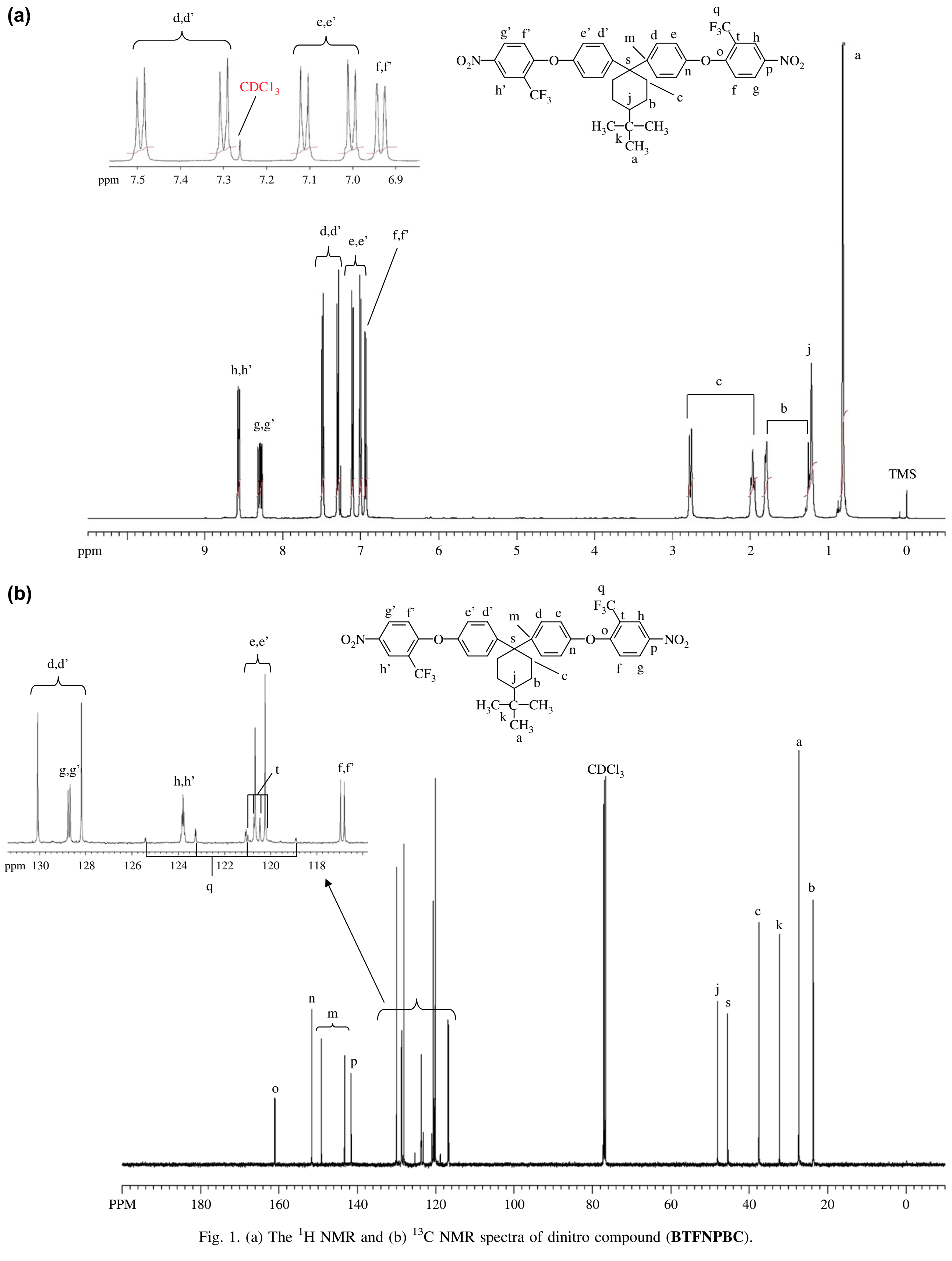


Fig. 1. (a) The ^{1}H NMR and (b) ^{13}C NMR spectra of dinitro compound (**BTFNPBC**).

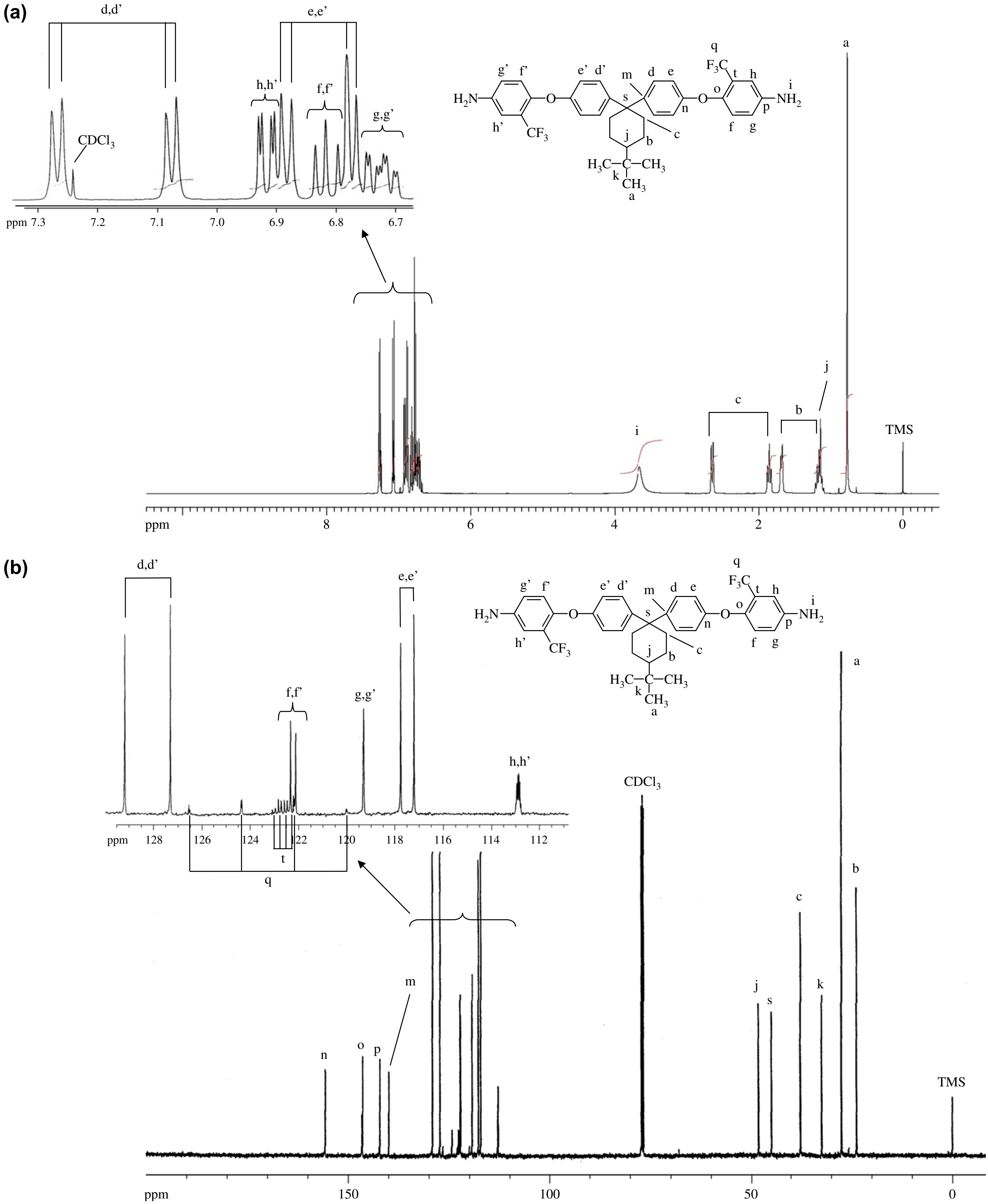


Fig. 2. (a) The ^{1}H NMR, (b) ^{13}C NMR, (c) HMQC spectra of diamine compound (**BTFAPBC**).

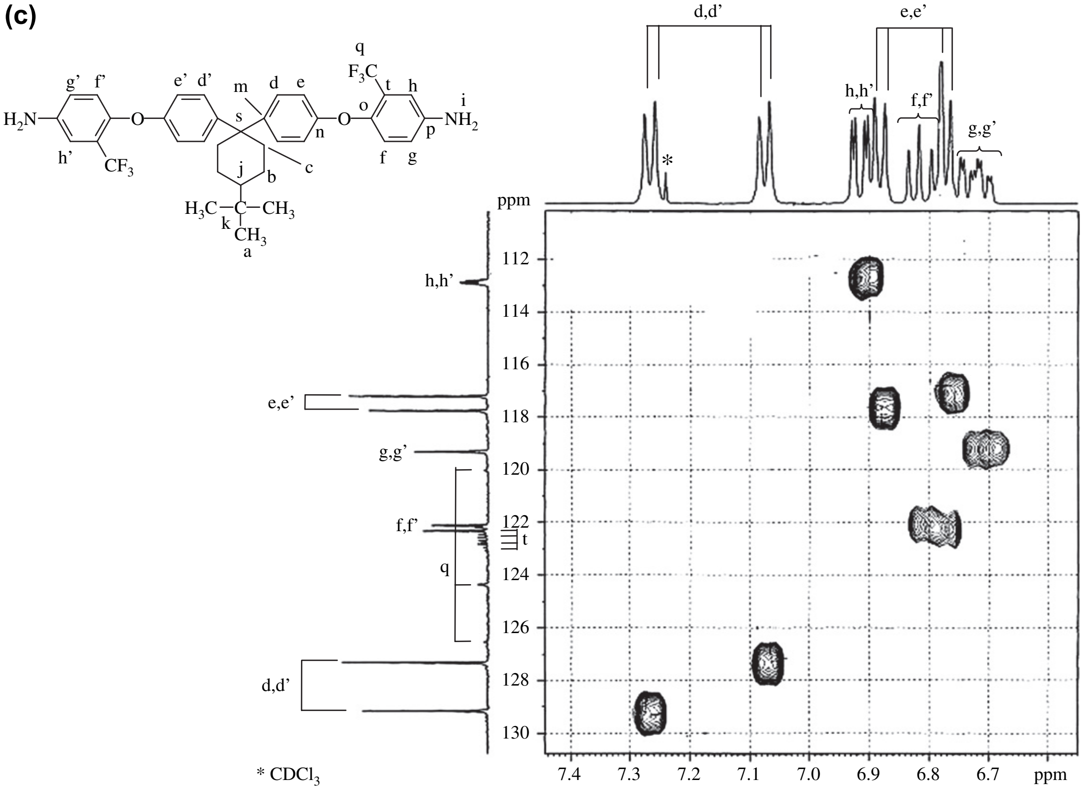
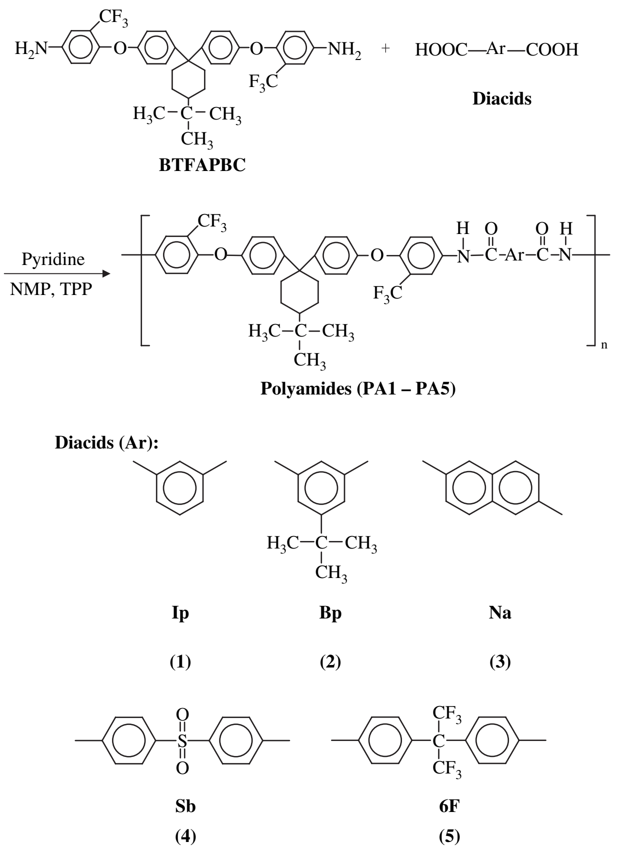


Fig. 2. *Continued.*



Scheme 2. Synthesis of polyamides derived from diamine **BTFAPBC**.

and $-SO_2-$ tend to have higher CTE values (60–75 ppm °C^{-1}) than those of commercially available polyamides [31].

The optical properties of the PA films are evaluated by UV–vis spectroscopy. The various transmission wavelengths are used to evaluate the transparency of these films. The UV–vis spectra of trifluoromethyl-based polyamides films are displayed in Fig. 4. Onset wavelengths for polyamides range from 350 to 388 nm. UV data of polyamides at various wavelengths are also shown in Table 4. The polyamide film **PA-2** derived from Bp exhibited high transparency, and might be attributed to the bulky *tert*-butyl group in the diacid units, which separated the chromophoric groups and interrupted the intramolecular conjugation [11].

The dielectric constants of the PA films were measured by the parallel plate capacitor method using a dielectric analyzer (TA Instruments DEA 2970) and results are listed in Table 5. The lowest value of dielectric constant of 3.29 (100 Hz, **PA-2**) was obtained for the polyamide containing the bulky *tert*-butyl group diacid. It may be speculated that the PAs containing the bulky *tert*-butyl group have higher bulk density resulting in larger free volume [32]. In addition, the PAs having the bulky *tert*-butyl group increase the free volume of polymer and further decrease the number of polarizable groups per unit volume, resulting in lower values for dielectric constant of atomic and dipolar [33,34]. In general, changing the diamine monomer from non-fluorinated to fluorinated **BTFAPBC** and having the substituted side trifluoromethyl groups could improve optical transparent nature and decrease

Table 1
Inherent viscosity and solubility of various polyamides derived from diamine **BTFAPBC**

Polymer code	η_{inh}[a] ($dL\,g^{-1}$)	Solvent[b]							
		NMP	DMAc	DMF	DMSO	Pyridine	THF	Cyclohexanone	γ-Butyrolactone
PA-1	0.67	++	++	++	+	++	+	++	+
PA-2	0.62	++	++	++	+	++	++	++	+
PA-3	0.55	++	++	++	+	++	+	++	+
PA-4	0.72	++	++	++	+	++	++	++	++
PA-5	0.59	++	++	++	+	++	++	++	+

Abbreviations: NMP, *N*-methyl-2-pyrrolidinone; DMAc, *N*,*N*-dimethyl acetamide; DMF, *N*,*N*-dimethyl formamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

[a] Measured in DMAc at a concentration of $0.5\ g\,dL^{-1}$ at 30 °C.

[b] Measured at 3.0% (w/v). The symbols represent the following: ++, soluble at room temperature; +, soluble on heating at 60 °C.

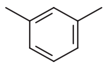
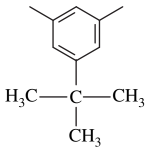
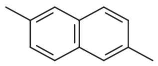
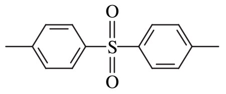
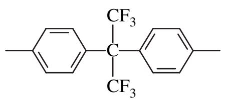
dielectric constant of polymers [11,12,16]. Upon comparison of commercially available polyamides [Amodel® (Solvay Advanced Polymers, 4.2–5.7 at 100 Hz)] [31], it was observed that the polyamides containing bulky alicyclic *tert*-butylcyclohexane and trifluoromethyl groups can effectively decrease dielectric constant of the polyamides (3.29–3.98 at 100 Hz).

The tensile properties of the polyamide films are summarized in Table 6. The polyamide films had tensile strength in the range of 66–103 MPa, elongation at break in the range of 5–8%, and tensile modulus in the range of 1.5–2.2 GPa. Most of the polyamide films exhibited high tensile strength; thus they could be considered as strong materials.

4. Conclusions

In the present study, we successfully prepared a series of new organosoluble alicyclic polyamides containing trifluoromethyl and *tert*-butylcyclohexyl groups by polycondensation. The obtained polyamides exhibit excellent solubility in most of the common organic solvents. The decomposition temperatures of polymers were over 430 °C in nitrogen. The novel alicyclic polyamides derived from diamine (**BTFAPBC**) exhibited amorphous nature, excellent optical properties, good solubility, good thermal stability, as well as mechanical properties. Most of the polyamide films exhibited excellent mechanical properties; thus they could be considered as strong materials.

Table 2
Elemental analyses of various polyamides derived from diamine **BTFAPBC**

Polymer code	Diacids	Elemental analyses (%)				Fraction of absorbed water[a] (%)
			C	H	N	
PA-1		Calcd	68.39	4.96	3.63	2.34
		Found	67.17	4.76	3.79	
		Corrtd[b]	68.78	4.87	3.88	
PA-2		Calcd	69.55	5.59	3.38	1.74
		Found	68.15	5.50	4.08	
		Corrtd[b]	69.35	5.59	4.15	
PA-3		Calcd	70.07	4.90	3.40	2.70
		Found	69.79	4.59	3.29	
		Corrtd[b]	71.73	4.72	3.38	
PA-4		Calcd	65.78	3.94	3.07	2.56
		Found	64.40	4.32	3.60	
		Corrtd[b]	66.09	4.43	3.70	
PA-5		Calcd	63.73	4.24	2.80	1.91
		Found	61.69	3.76	3.18	
		Corrtd[b]	62.89	3.83	3.24	

[a] Fraction of absorbed water (%) = (the mass of samples at room temperature − the mass of samples after drying under vacuum at 100 °C)/the mass of samples at room temperature.

[b] Corrected value = found value/(1 − fraction of absorbed water); fraction of absorbed water (%) = $(W_2 - W_1)/W_1$, where W_2 is the weight of the film samples after immersion in water and W_1 is the initial weight of the samples.

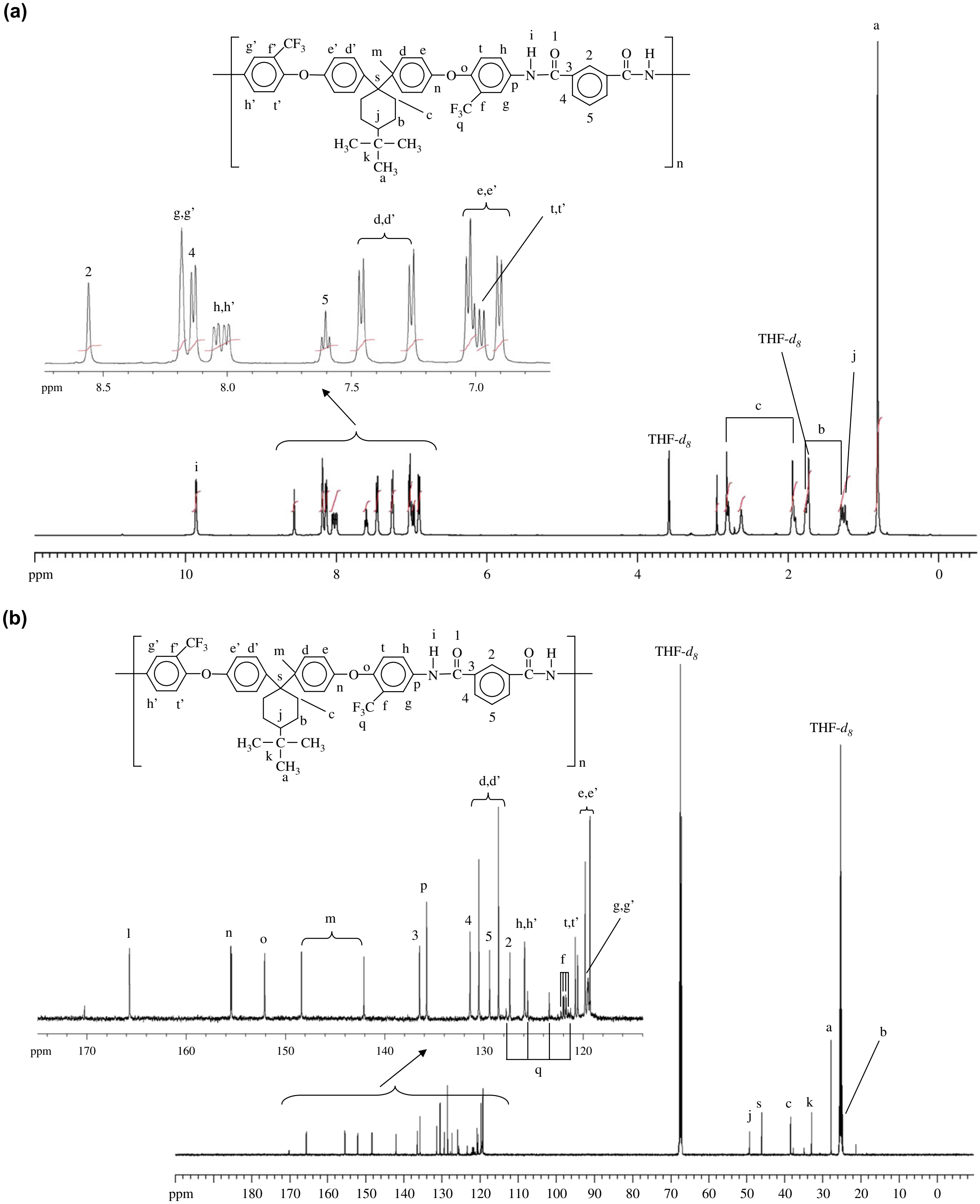


Fig. 3. (a) The ^{1}H NMR and (b) ^{13}C NMR spectra of polyamide (**PA-1**).

Table 3
Thermal properties of various polyamides derived from diamine **BTFAPBC**

Polymer code	T_g[a] (°C)	PDT[b] (°C)		Y_c[c] (%)	CTE[d] (ppm °C^{-1})
		In N_2	In Air		
PA-1	244	466	451	48	75
PA-2	256	437	424	28	74
PA-3	243	449	435	64	73
PA-4	266	466	452	48	60
PA-5	254	447	441	47	72

[a] From DSC measurements conducted at a heating rate of 10 °C min^{-1}.

[b] Temperature at 10% weight loss (PDT) was determined by TGA in nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

[c] Char yield (Y_c) at 800 °C in nitrogen atmosphere.

[d] The CTE value was obtained on the temperature scale between 50 and 150 °C.

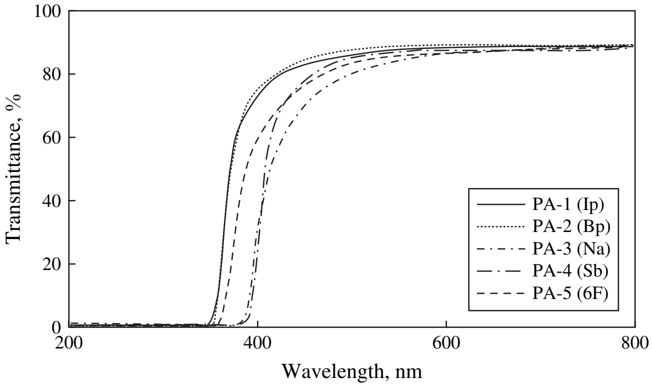


Fig. 4. Percent transparency of various polyamide films derived from diamine **BTFAPBC**.

Table 4
Optical properties of various polyamide films derived from diamine **BTFAPBC**

Polymer code	Transparency[a] (%)					
	400 nm	500 nm	600 nm	700 nm	800 nm	Cut-off (nm)
PA-1	73	87	89	90	90	352
PA-2	76	89	90	90	91	350
PA-3	28	79	86	87	88	384
PA-4	21	85	88	88	89	388
PA-5	58	85	88	90	91	360

[a] The wavelength range of UV measurement was from 200 to 800 nm.

Table 5
Dielectric properties of various polyamide films derived from diamine **BTFAPBC**

Polymer code	Film thickness (μm)	Dielectric constant					
		1 Hz	10 Hz	100 Hz	1000 Hz	10 kHz	100 kHz
PA-1	73	3.57	3.54	3.47	3.39	3.32	3.29
PA-2	74	3.40	3.33	3.29	3.23	3.18	3.14
PA-3	82	3.79	3.67	3.54	3.46	3.35	3.25
PA-4	77	4.23	4.12	3.98	3.87	3.76	3.68
PA-5	70	3.64	3.54	3.48	3.34	3.23	3.14

Table 6
Tensile properties of polyamide films derived from diamine **BTFAPBC**

Polymer code	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
PA-1	73	6	1.7
PA-2	75	6	1.5
PA-3	66	5	1.7
PA-4	103	8	2.2
PA-5	82	6	1.8

Acknowledgments

The authors thank National Science Council of the Republic of China for the financial support of this work.

References

[1] Cassidy PE. Thermally stable polymer. New York: Marcel Dekker; 1980 [chapter 4].
[2] Spiliopoulos IK, Mikroyannidis JA, Tsivgoulis GM. Macromolecules 1998;31:522.
[3] St. Clair TL. In: Wilson D, Stenzenberger HD, Hergenrother PM, editors. Polyimides. New York: Blackie; 1990. p. 58–78 [chapter 3].
[4] Negi YS, Suzuki YI, Kawamura I, Kakimoto MA, Imai Y. J Polym Sci Part A Polym Chem 1996;34:1663.
[5] Liaw DJ, Liaw BY, Chen JR, Yang CM. Macromolecules 1999;32:6860.
[6] Liaw DJ. In: Ueyama N, Harada A, editors. Macromolecular nanostructured materials. Berlin, Tokyo: Springer, Kodansha; 2004. p. 80–100 [chapter 2.2].
[7] Varma IK, Kumar R, Bhattacharyya AB. J Appl Polym Sci 1990;40:531.
[8] Wu SC, Shu CF. J Polym Sci Part A Polym Chem 2003;41:1160.
[9] Liaw DJ, Liaw BY, Yang CM. Macromolecules 1999;32:7248.
[10] Manerjee S, Madhra MK, Salunke AK, Maier G. J Polym Sci Part A Polym Chem 2002;40:1016.
[11] Liaw DJ, Huang CC, Chen WH. Polymer 2006;47:2337.
[12] Liaw DJ. J Polym Sci Part A Polym Chem 2005;43:4559.
[13] Vora RH, Goh SH, Chung TS. Polym Eng Sci 2000;40:1318.
[14] Li F, Ge JJ, Honigfort PS, Fang S, Chen JC, Harris FW, et al. Polymer 1999;40:4987.
[15] Matsuura T, Hasuda Y, Nishi S, Yamada N. Macromolecules 1991;24:5001.
[16] Liaw DJ, Chen WH, Huang CC. In: Mittal KL, editor. Polyimides and other high temperature polymers, vol. 2. Utrecht: VSP; 2003. p. 47–70.
[17] Liaw DJ, Liaw BY. Polymer 1999;40:3183.
[18] Liaw DJ, Liaw BY, Chung CY. Acta Polym 1999;50:135.
[19] Liaw DJ, Liaw BY. Macromol Chem Phys 1999;200:1326.
[20] Liaw DJ, Liaw BY, Chung CY. Macromol Chem Phys 1999;200:1023.
[21] Liaw DJ, Liaw BY, Chung CY. J Polym Sci Part A Polym Chem 1999;37:2815.
[22] Liaw DJ, Hsu PN, Chen WH, Lin SL. Macromolecules 2002;35:4669.
[23] Liaw DJ, Wang KL, Chang FC. Macromolecules 2007;40:3568.
[24] Liaw DJ, Chang FC, Wang KL, Lee KR, Lai JY. J Polym Sci Part A Polym Chem 2007;45:2367.
[25] Yamazaki N, Matsumoto M, Higashi F. J Polym Sci Polym Chem Ed 1975;13:1373.
[26] Liaw DJ, Liaw BY. J Polym Sci Part A Polym Chem 1998;36:2301.
[27] Hougham G, Tesoro G, Shaw J. Macromolecules 1994;27:3642.
[28] Liaw DJ, Liaw BY, Tseng JM. J Polym Sci Part A Polym Chem 1999;37:2629.

[29] Liaw DJ, Liaw BY, Li LJ, Sillion B, Mercier R, Thiria R, et al. Chem Mater 1998;10:734.
[30] Bruma M, Mercer F, Fitch J, Cassidy P. J Appl Polym Sci 1995;56:527.
[31] Amodel® Polyphthalamide design guide, Solvay Advanced Polymers. L.L.C., <http://www.solvayadvancedpolymers-us.com>.
[32] Wang YC, Huang SH, Hu CC, Li CL, Lee KR, Liaw DJ, et al. J Membr Sci 2005;248:15.
[33] Simpson JO, St. Clair AK. Thin Solid Films 1997;308–309:480.
[34] Liaw DJ, Chang FC, Leung MK, Chou MY, Muellen K. Macromolecules 2005;38:4024.