Preparation and characterization of organic-soluble optically transparent polyimides from alicyclic dianhydride, bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride

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Organic-soluble optically transparent polyimides were prepared from alicyclic dianhydride monomer, bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCDA). BCDA gives soluble polyimides with diamines containing at least one flexible linkage such as ether, methylene and sulfide. The polyimides have glass transition temperatures above 350°C and a thermal decomposition temperature of 450°C in an inert atmosphere. The polyimides form a tough film with an ultra-violet cut-off between 300 and 400 nm, which is comparable to that of a fluorinated polyimide.

(Keywords: soluble polyimides; optical transparency; alicyclic dianhydride)

INTRODUCTION

Wholly aromatic polyimides such as DuPont's Kapton® and Ube's Upilex® are well known for their high thermal stability and excellent mechanical properties[1]. However, fabrication of polyimides is difficult because of their poor solubility in organic solvents. Significant efforts have been made to improve solubility by designing their structure: introducing bulky pendent groups onto the backbone and increasing flexibility along the polymer chain[2–4]. In recent years, a fluorinated dianhydride monomer, i.e. hexafluoroisopropylidene 2,2-bis(phthalic acid anhydride) (6FDA), has been extensively investigated because the monomer gives highly soluble polyimides while maintaining their good thermal stability[5,6]. The fluorinated polymers are also colourless, which is advantageous for applications such as photopolymers and opto-electronics[6,7]. On the other hand, polyimides derived from an alicyclic dianhydride, i.e. bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCDA), also offer solubility in organic solvents and the attribute of being colourless[8,9]. The BCDA polyimides also showed reasonable thermal stability[8,9] and are expected to have good mechanical properties because of the rigid cyclic structure. However, there is little published literature regarding the alicyclic polyimides[8–11]. It appears worth while to investigate further the alicyclic polyimides as another class of colourless soluble polyimides. In the present paper, synthesis of BCDA polyimides was attempted with various diamines. Also, the organic solubility, and the thermal and optical properties of BCDA polyimides were examined. Several 6FDA polyimides were also examined for comparison.

Diamines used for BCDA polyimide synthesis were 4,4′-diaminodiphenyl ether (DADE), 4,4′-diaminodiphenylmethane (MDA), bis[4-(3-aminophenoxy)phenyl]sulfone (*m*-BAPS), bis[4-(4-aminophenoxy)phenyl]sulfone (*p*-BAPS), 1,3-bis(4-aminophenoxy)benzene (TPE), 1,3-bis(3-aminophenoxy)benzene (APB), 4,4′-diaminodiphenylsulfone (DDS), 4,4′-diaminodiphenyl sulfide (ASD), 4,4′-bis(aminophenoxy)biphenyl (BAPB), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (HFBAPP), 3,3′-dimethoxy-4,4′-diaminobiphenyl (FBB), 2,4,6-trimethyl-1,3-phenylenediamine (DAM), tolylene-2,4-diamine (TDA), 3,3′-dihydroxy-4,4′-diaminobiphenyl (HAB), 9,9-bis(4-aminophenyl)fluorene (FDA), *o*-toluidinesulfone (TSN), 3,3′-dimethyl-4,4′-diaminobiphenyl (DMB) and 3,3′,5,5′-tetramethylbenzidine (TMB). The chemical structures of the diamine monomers are shown in *Figure 1*, along with those of BCDA and 6FDA.

EXPERIMENTAL

Materials

BCDA was purchased from Aldrich Chemical Co. (USA). 6FDA (E-Grade) was purchased from Hoechst Celanese Corp., Short Hills, NJ (USA). TSN, DADE, MDA, ASD, DDS, TPE, *m*- and *p*-BAPS, BAPB, HFBAPP, DMB, FBB and FDA were purchased from Wakayama Seika Kogyo Co. Ltd, Wakayama (Japan). TMB and DAM were purchased from Tokyo Kasei Organic Chemicals, Tokyo (Japan). APB was purchased from Mitsui Toatsu Chemicals Inc., Tokyo (Japan). All the other chemicals (reagent grade) were purchased from Tokyo Kasei Organic Chemicals and used without further purification.

Polymer synthesis

All the polymers were synthesized by the thermal imidization method with phenolic solvents such as

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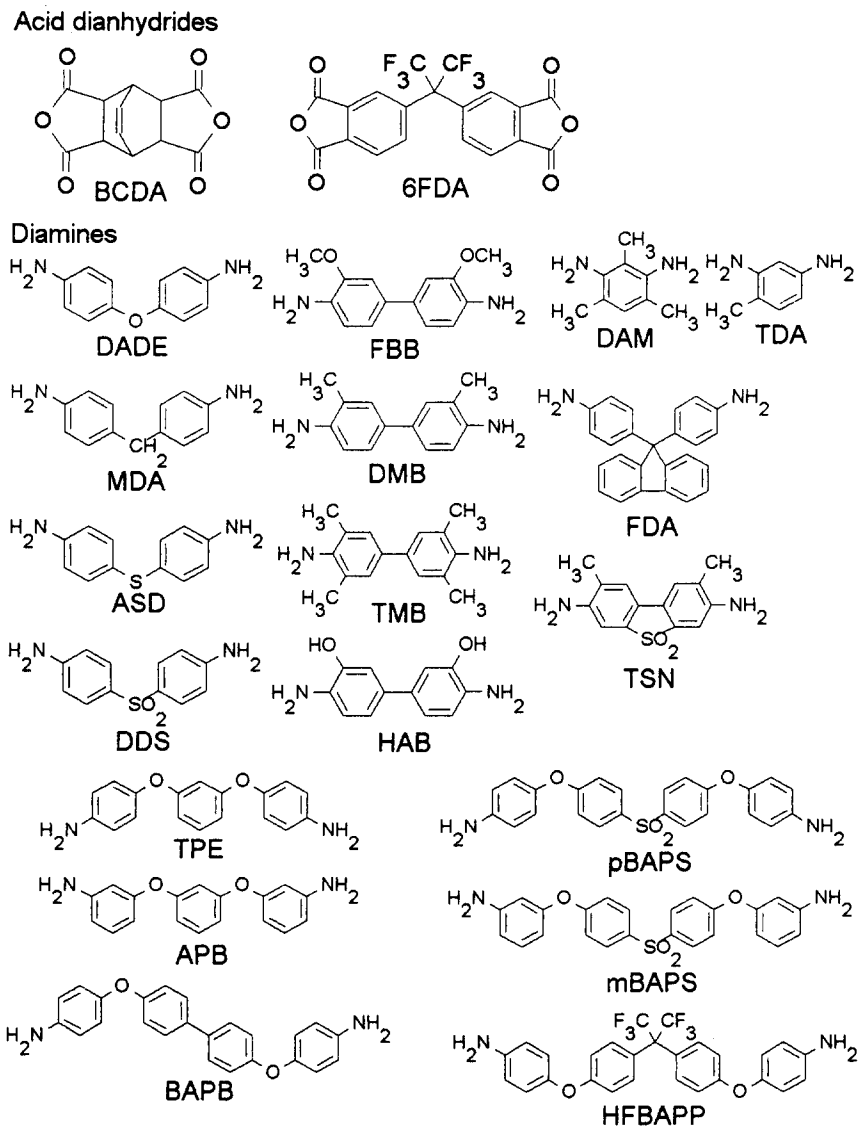

Figure 1 Chemical structures and abbreviations of monomers used for polyimide synthesis

m-cresol or a 7:3 mixture of phenol and *p*-methoxyphenol. Stoichiometric amounts of dianhydride and diamine were placed in a four-necked separation flask fitted with a mechanical stirrer, a distillation trap with a condenser, and a dry nitrogen inlet. Solid content was set to 25 wt%. About 10 vol% of toluene was also added as an azeotropic agent. A slow nitrogen flow through the flask was continuously employed throughout the reaction. The reaction solution was stirred at room temperature for 30 min and then at 180°C for 5 h. Collected water was removed from the distillation trap with toluene. After being cooled down, the solution was poured into excess methanol and homogenized with a laboratory mixer. The precipitate was filtered off and soaked in excess methanol overnight. The precipitate was again filtered and air dried. The obtained powder was finally dried in an oven at 145°C under reduced pressure for 8 h.

Imidization was confirmed by Fourier-transform infrared (*FT*i.r.) spectroscopy with the characteristic imide peaks of BCDA polyimides observed at 1777–1779 cm^{-1} (imide >C=O symmetric stretching), 1710–1714 and 1719–1725 cm^{-1} (imide >C=O asymmetric stretching), 1377–1385 cm^{-1} (C–N stretching) and 697–716 cm^{-1} (imide ring deformation). *Figure 2* shows the chemical structure of the polyimides.

Several 6FDA polyimides were also synthesized using the same procedure as described above. 6FDA/DMB, 6FDA/TMB and 6FDA/HFBAPP polyimides were synthesized via the conventional chemical imidization method using acetic anhydride and triethylamine, as described elsewhere (e.g. ref. 12). Complete imidization was also confirmed by *FT*i.r. measurements with characteristic imide peaks. The inherent viscosities of the polyimides were between 0.5 and 1.6 dl g^{-1} with conditions described later.

The polymer films were prepared by casting an *N*-methylpyrrolidone (NMP) solution of the polymers onto a clean glass plate followed by drying in a vacuum oven at 85°C for 1 h and then 145°C for 2 h. The films were peeled off from the plate and further dried in a high-vacuum chamber at 80°C for 1 h and 145°C for 3 h.

Measurements

The differential scanning calorimetry (d.s.c.) measurements were done with a Shimadzu DSC-50 apparatus at a heating rate of 10°C min^{-1} under nitrogen atmosphere. The d.s.c. was run twice consecutively, the second run being used to determine the glass transition temperature (T_g). BCDA polyimides were run up to 350°C, and 6FDA

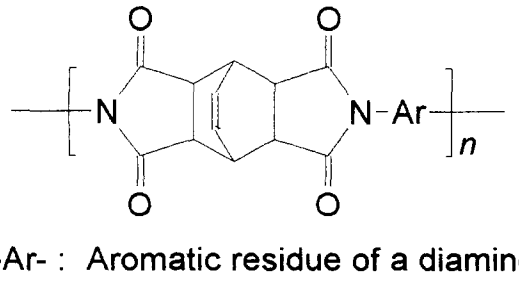

Figure 2 Chemical structure of BCDA polyimides

polyimides were run up to 420°C. The thermogravimetric analysis (t.g.a.) was done using a Shimadzu TGA-50. The t.g.a. was conducted at a heating rate of 10°C min^{-1} and a temperature up to 900°C under nitrogen atmosphere.

The ultra-violet/visible (u.v./vis.) spectra were obtained with a Hitachi U-3210 spectrophotometer. The *FT*i.r. spectra were measured with a Nicolet FTIR spectrometer. The polymer films were used for both u.v./vis. and i.r. measurements.

Inherent viscosities of the polyimides were measured using an Östwald viscometer with 0.5 g dl^{-1} NMP solution at 30°C. The solubility test procedure is described in the following. Some powdered sample (5–10 mg) was placed in a test tube, and about 5 ml of a given solvent was added. The mixture was heated to the boiling point (not higher than 180°C) of the solvent and left to stand overnight at room temperature. Solubility was determined visually.

RESULTS AND DISCUSSION

Synthesis

Of the 17 diamines, eight gave soluble polyimides and two gave partially soluble polyimides. The other seven diamines resulted in precipitation during the thermal imidization process. The diamines that gave a soluble polyimide with BCDA are DADE, MDA, ASD, *p*-BAPS, *m*-BAPS, TPE, APB and FDA. The diamines with which the polymer became insoluble upon imidization are DAM, TDA, DMB, TMB, TSN, HAB, BAPB and DDS. (It was reported in ref. 9 that DDS gave a soluble polyimide with BCDA.) FBB gave a partially soluble polyimide, and HFBAPP gelled upon thermal imidization. HFBAPP was frequently observed to cause gelation by the thermal imidization method. A soluble polyimide may be obtained with BCDA if chemical imidization is employed.

As shown in the above results, all the diamines having a phenylene or benzidine backbone gave an insoluble product, while diamines having flexible linkage(s) gave a soluble polyimide. Since BCDA has a rigid structure, a diamine containing a flexible bond is favoured owing to an entropic advantage in the solution state. Also, a longer chain diamine 'dilutes' the amount of imide groups, which reduces the cohesive energy density of the polyimides.

Thermal analysis

Figure 3 shows a typical t.g.a. curve of BCDA polyimides under nitrogen atmosphere (BCDA/ASD). As seen in *Figure 3*, decomposition of BCDA polyimides proceeds through two steps. The first decomposition occurs at 440–470°C, and the second at 580–600°C (*Table 1*). The alicyclic segment has a decomposition temperature about 100°C lower than the remaining aromatic segments. The two-stage decomposition of BCDA polyimides has been observed by Suzuki and Hojo[8] and Itamura *et al.*[9].

Itamura *et al.*[9] reported that the two-stage decomposition was observed only in air and proposed the retro Diels–Alder reaction for the first thermal decomposition of BCDA polyimides. They did not observe the two-stage decomposition under nitrogen atmosphere as compared with our observation. *Figure 4* shows the t.g.a. curve of BCDA/ASD polyimides in air. The curve appears almost identical to the one obtained in nitrogen (*Figure 3*). It is not known where the discrepancy originates from. It should be noted, however, that Suzuki and Hojo[8] and the present author used a commercial BCDA and applied a heating rate of 10°C min^{-1} for the t.g.a. analysis, while Itamura *et al.*[9] used BCDA synthesized in their own

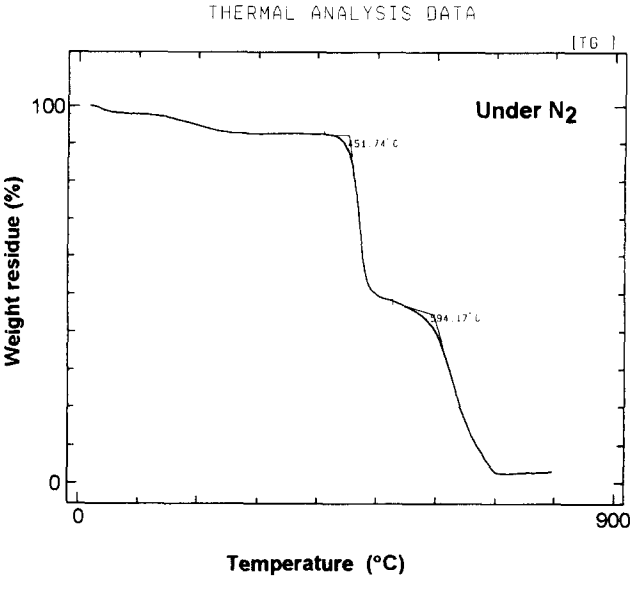

Figure 3 Thermogravimetric (t.g.a.) curve of BCDA/ASD polyimide with a 10 ml min^{-1} nitrogen flow

Table 1 Characterization of soluble BCDA polyimides

Diamine[a]	$[\eta]^b$ (dl g^{-1})	T_g^c (°C)	Decomposition temperatures[d] (°C) 1st	2nd	Literature values
DADE	1.65	>350	444	580	441 (1st), 577 (2nd) (air)[8] 415 (N_2), 330 (air)[9]
MDA	0.86	>350	455	603	422 (1st), 556 (2nd) (air)[8] 410 (N_2), 385 (air)[9]
ASD	0.86	>350	452	594	(under N_2)
			447	586	(under air)
FDA	0.34	>350	456	584	
p-BAPS	0.56	340	467	–[e]	
m-BAPS	0.50	261	469	–[e]	
TPE	1.66	297	453	–[e]	
APB	0.74	228	460	603	

[a] See *Figure 1* for the abbreviations of diamines
[b] Using 0.5 g dl^{-1} NMP solution at 30°C
[c] Determined by d.s.c. method at a heating rate of 10°C min^{-1}
[d] Onset temperatures; t.g.a. was run at a heating rate of 10°C min^{-1} under nitrogen atmosphere (refer to text for explanation of the 1st and 2nd decomposition temperatures)
[e] A clear second decomposition point could not be determined

laboratory via a new preparation process and employed a slower heating rate (5°C min^{-1}).

The characterization results of the eight soluble BCDA polyimides are summarized in *Table 1*. T_g was determined by the d.s.c. method. The BCDA polyimides with DADE, MDA, ASD and FDA do not show T_g up to 350°C. All the soluble polyimides except the polymer with FDA can form a flexible tough film.

Solubility

Table 2 shows the solubility of the BCDA polyimides in 10 common organic solvents: hexane, toluene, ethyl acetate, chloroform, acetone, dioxane, *m*-cresol, NMP, methylcellosolve (2-methoxyethanol) and dimethylsulfoxide (DMSO). The solvents' ability to dissolve or swell BCDA polyimides was found to be in the following order: NMP (11.2) ≥ *m*-cresol (11.1) ≥ DMSO (13.0) > chloroform (9.3) > 1,4-dioxane (10.0) > toluene (8.9) = ethyl acetate (8.9) = acetone (9.8) > methylcellosolve (12.1) > hexane (7.3). The solubility parameters, *SP* (cal $cm^{-3})^{1/2}$, of the solvents are shown in parentheses[14]. The polar and hydrogen-bonding factors of the Hansen parameters of the solvents are plotted in *Figure 5*. The van der Waals (dispersion) force does not vary widely among the solvents, and thus is ignored here. As seen in *Figure 5*, solvents that can dissolve or swell the polyimides are located near the hydrogen-bonding parameter of 4 (cal $cm^{-3})^{1/2}$. On the other hand, the good solvents are scattered along the polar parameter axis. Solubility of BCDA polyimides may be controlled more readily by the hydrogen-bonding factor than by the polar factor. The result suggests that a solvent having *SP* value of about 12 with hydrogen-bonding parameter of about 4 is promising to dissolve the polyimides. The tendency appears similar to that reported for organic-soluble polyimides such as 6FDA polyimides and benzophenonetetracarboxylic dianhydride (BTDA) polyimides[15].

For comparison, the solubilities of eight 6FDA polyimides are shown in *Table 3*. The T_g values of the polymers are also shown in *Table 3*. A 6FDA-based polyimide has higher solubility in organic solvents. 6FDA can give a soluble polymer with rigid diamines, such as phenylenediamines and benzidines, which failed to give organic solubility with BCDA. The high solubility of 6FDA polyimides is believed to be due to the significantly

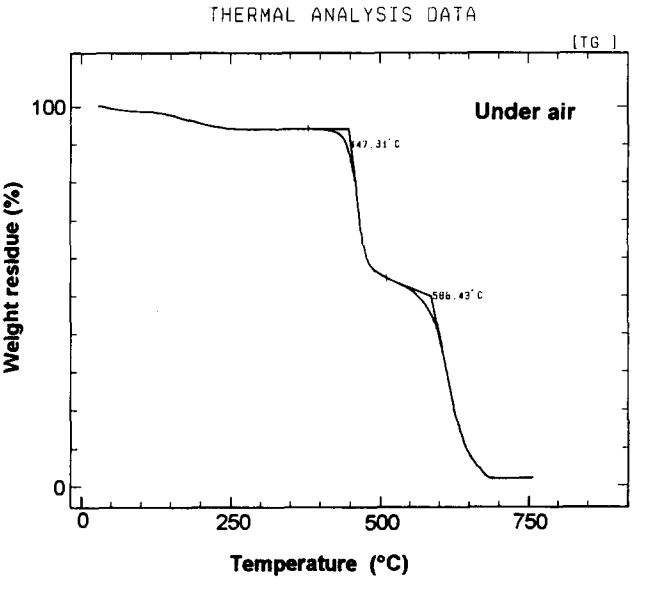

Figure 4 Thermogravimetric (t.g.a.) curve of BCDA/ASD polyimide with a 10 ml min^{-1} air flow

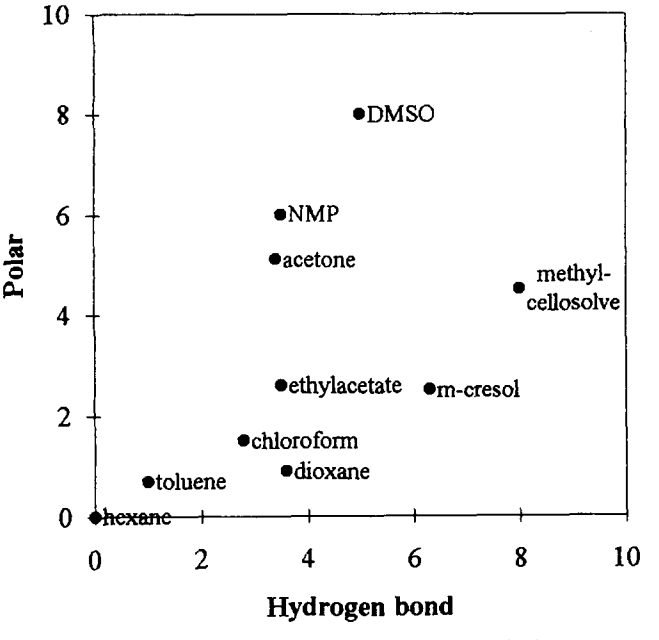

Figure 5 Polar and hydrogen-bonding factors ((cal $cm^{-3})^{1/2}$) of Hansen parameters of solvents studied[13]

Table 2 Solubility of BCDA polyimides[a]

Diamine[b]	DADE	MDA	ASD	FDA	*p*-BAPS	*m*-BAPS	APB
SP value[c]	12.3	12.1	12.5	12.3	n.a.[d]	n.a.[d]	12.1
Hexane	−	−	−	−	−	−	−
Toluene	−	−	−	−	−	−	−
Ethyl acetate	−	−	−	−	−	−	−
Chloroform	−	+	−	+	+	+	+
Acetone	−	−	−	−	−	−	+
1,4-Dioxane	−	−	−	−	−	+	+
m-Cresol	++	+++	+++	+++	+++	+++	+++
NMP	+++	+++	+++	+++	+++	+++	+++
Methylcellosolve	−	−	−	−	−	−	−
DMSO	+++	++	+++	+++	++	+++	+++

[a] Solubility: (−) unchanged besides colouring of solvents, (+) swollen, (++) strongly swollen and/or partially dissolved, (+++) dissolved
[b] See *Figure 1* for the abbreviations of diamines
[c] Solubility parameter ((cal $cm^{-3})^{1/2}$) calculated according to Fedors[13] group contribution method
[d] Value is not given because sulfonyl ($-SO_2-$) group is not available in the literature[13]

Table 3 Solubility of 6FDA polyimides[a]

Diamine[b]	FDA	DDS	DAM	TSN	FBB	DMB[e]	TMB[e]	HFBAPP[e]
T_g(°C)[c]	378	347	388	>420	348	378	394	257
SP value[d]	11.7	n.a.[f]	10.3	n.a.[f]	11.4	11.3	9.9	10.6
Hexane	−	−	−	−	−	−	−	−
Toluene	+	−	−	−	−	−	−	+++
Ethyl acetate	−	−	++	−	−	+	−	+++
Chloroform	+++	+	+++	+	+++	++	+	+++
Acetone	+	−	+++	+++	++	+	+	+++
1,4-Dioxane	+++	+	+++	+	+++	+++	++	+++
m-Cresol	+++	++	+++	+++	+++	+++	++	+++
NMP	+++	+++	+++	+++	+++	+++	++	+++
Methylcellosolve	−	−	−	−	−	−	−	−
DMSO	+++	+++	+++	+++	+++	+++	+	+++

[a] Solubility: (−) unchanged besides colouring of solvents, (+) swollen, (++) strongly swollen and/or partially dissolved, (+++) dissolved
[b] See *Figure 1* for the abbreviations of diamines
[c] Determined by d.s.c. method at a heating rate of 10°C min^{-1}
[d] Solubility parameter ((cal cm^{-3})$^{1/2}$) calculated according to Fedors[13] group contribution method
[e] Note that the polyimides were prepared by the chemical imidization method. Therefore, the solubility is not strictly comparable to that of the other polymers
[f] Value is not given because sulfonyl (–SO_2–) group is not available in the literature[13]

lower cohesive energy of the 6FDA segment than that of the other dianhydrides*.

Ultra-violet/visible spectroscopy

St Clair *et al.* have demonstrated that fluorinated 6FDA polyimides show optical transparency over a broad range[16] compared with other aromatic polyimides. The lack of colour of the 6FDA polyimides is due to the hexafluoroisopropylidene group between the phenyl groups. Hasegawa *et al.* reported that the longest-wavelength absorption band in aromatic biphenyltetracarboxylic dianhydride (BPDA) polyimides is due to the π–π^* transition of the biphenyl bisimide group[17]. In 6FDA polyimides, however, the perfluorinated group breaks up the electron conjugation between the phenyl groups as well as hindering electronic interactions between the polymer chains. The effects result in the high optical transparency of 6FDA polyimides. According to the above discussions, it is natural to expect that BCDA polyimides would also be colourless because the polyimides do not have a biphenyl bisimide group. In addition, the aliphatic bicyclo structure of BCDA is not sterically favourable for the electronic interaction. Indeed, the prepared BCDA polyimide films were found to be as colourless as the 6FDA polyimide films also prepared in our laboratory.

Figure 6 shows u.v./vis. spectra of the BCDA/DADE polyimide film and the 6FDA/DADE polyimide film. The BCDA/DADE film shows a u.v. cut-off wavelength near 300 nm, while the 6FDA counterpart film shows a cut-off between 400 and 500 nm. The BCDA film has its u.v. cut-off wavelength almost 100 nm lower than that of the 6FDA film and correspondingly high optical transparency over a wider range.

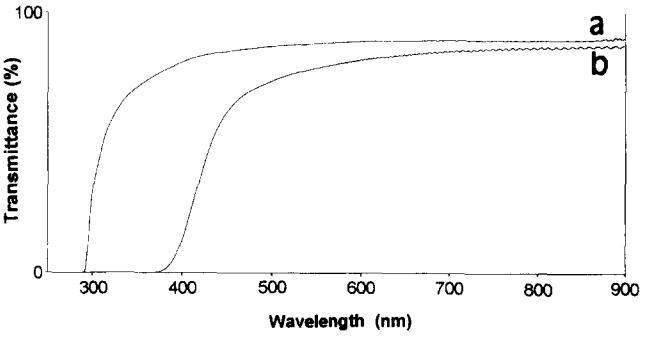

Figure 6 Ultra-violet/visible spectra of (a) BCDA/DADE (21.9 μm thickness) and (b) 6FDA/DADE (24.0 μm thickness) polyimide films

The u.v./vis. spectra of the other four BCDA polyimide films (13.4–24.0 μm thickness) are shown in *Figure 7* along with that of the 6FDA/HFBAPP polyimide film (20.8 μm thickness) for comparison. As seen in *Figure 7*, the u.v. cut-off wavelengths of the BCDA polyimides vary with the diamines used. The cut-off wavelength of BCDA/*m*-BAPS is lower than that of BCDA/*p*-BAPS, confirming that the *meta* linkage disturbs the extended electron conjugation along the chain. All the BCDA polyimides showed lower u.v. cut-off wavelength than fluorinated 6FDA/HFBAPP polyimides. It can be concluded that BCDA is more effective than 6FDA in making colourless polyimides.

CONCLUSION

Organic-soluble polyimides derived from BCDA show solubility in limited organic solvents in spite of their high T_g values. At least one flexible linkage, e.g. ether, sulfide, or methylene, in a diamine is necessary to make BCDA polyimides soluble. The thermal decomposition temperatures of BCDA polyimides with aromatic diamines are 440–470°C, which is reasonably high for an aliphatic polyimide owing to its bicyclic structure. The soluble BCDA polyimides have u.v. cut-off wavelengths lower than that of the 6FDA counterpart, suggesting that BCDA is a promising component to design colourless polyimides.

* Thermal analysis of the 6FDA model imide compound showed an extremely low melting temperature and low enthalpy of fusion compared with other acid dianhydride model compounds. The result implies that 6FDA has lower cohesive energy density. On the other hand, the entropy of fusion of the 6FDA model was comparable to or even lower than that of the other dianhydride models, which indicates hindered rotation around the hexafluoroisopropylidene group. According to these results, the high solubility of 6FDA polyimides is exclusively due to its low cohesive energy. The thermal analysis of the imide model compounds will be submitted elsewhere

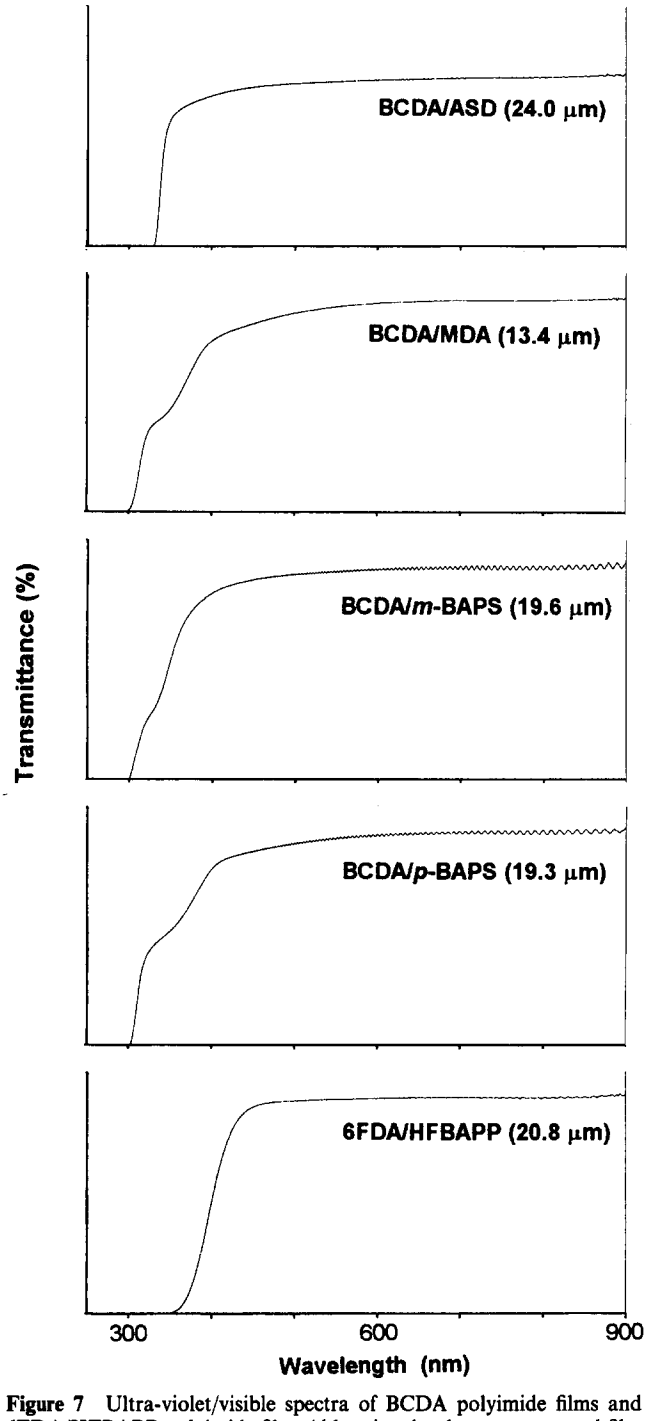

Figure 7 Ultra-violet/visible spectra of BCDA polyimide films and 6FDA/HFBAPP polyimide film. Abbreviated polymer names and film thicknesses in parentheses are shown in the figure

BCDA polyimides having organic solubility with high T_g values above 350°C can offer both fabrication ability and good thermomechanical properties. Also, their wide range of optical transparency and the reactive double bond may provide ample opportunity for applications such as optoelectronic devices and photopolymeric materials.

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