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Colorless and Soluble Strictly Alternating Copolyimides Containing Aliphatic Spiro Units from 2,8-Dioxaspiro[4.5]decane-1,3,7,9-tetrone

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ABSTRACT: Strictly alternating copolyimides containing aliphatic spiro units were prepared via diimide (with five-membered rings)−dianhydrides (with six-membered rings) derived from 2,8-dioxaspiro[4.5]-decane-1,3,7,9-tetrone (TCDA) and diamines. The polymerization was conducted by the conventional two-step procedure using the diimide−dianhydrides and diamines. The resulting poly(imide−imide)s have alternating diamine components and also a head-to-head (tail-to-tail) structure in the imide ring sequence. The poly(imide−imide) films exhibited excellent colorlessness (cutoff wavelength) and transparency (UV−visible transmittance). Most of the poly(imide−imide)s were soluble in typical polar aprotic solvents such as *N*,*N*-dimethylacetamide (DMAc) and also in *m*-cresol, except for the wholly aliphatic ones. These poly(imide−imide)s had decomposition temperatures between 379 and 419 °C in a nitrogen atmosphere, and the glass transition temperatures were shown to be in the wide range of 197−315 °C depending on the combination of the two kinds of diamines.

Introduction

Wholly aromatic polyimides such as Kapton exhibit excellent thermal stability and good mechanical, optical, electrical, and chemical properties and have been widely used in a variety of fields such as aerospace and microelectronics.[1−3] However, most of them are highly colored polymers with colors ranging from yellow to brown and possess poor processability due to high glass transition or melting temperature and low solubility to commercially available solvents. Therefore, much effort has been made to improve the disadvantage and to design polyimides with the desired properties.[4−20]

One of the attempts is in the structural modification such as the incorporation of flexible bridging units,[10−12] bulky substituent groups,[13−16] and aliphatic moieties[17−20] into the polyimide backbone. However, this approach has a limitation in the preparation of new monomers with specific structures.

An alternative method is the copolymerization of either two different diamines and a dianhydride or two different dianhydrides and a diamine. Copolyimides thus prepared have a generally random sequence of the components.[21,22] Random copolyimides have some problems, including uneven distribution of monomer components and formation of insoluble homooligomers due to different reactivities of dianhydrides or diamines used. These difficulties could be overcome by copolymerization in an alternating fashion. Furthermore, strictly alternating copolyimides have the potential to create new materials with unique characteristics by the control of primary structure and the combination of desired properties and/or functions. Nevertheless, there are few reports on strictly alternating copolyimides.[23−26] In all of such attempts, the alternating copolyimides are synthesized via diimide−diamine analogues prepared by troublesome synthetic procedures in multisteps.

The authors have reported the synthesis of unsymmetric aliphatic tetracarboxylic acid derivatives having a quaternary or a spiro carbon atom and the intramolecular ring transformation with amines for the first time.[27,28] In this paper, the synthesis of colorless and soluble strictly alternating copolyimides from an aliphatic tetracarboxylic dianhydride having a spiro carbon atom with two different ring sizes (five- and six-membered anhydrides), 2,8-dioxaspiro[4.5]decane-1,3,7,9-tetrone (TCDA) (**1**), is described. The resulting copolyimides have alternating diamine components and also a head-to-head (tail-to-tail) structure in the imide ring sequence.

Experimental Section

Materials. According to the procedure described in the previous paper,[28] 2,8-dioxaspiro[4.5]decane-1,3,7,9-tetrone (TCDA) (**1**) was prepared in three steps starting from itaconic anhydride and isoprene. All diamines were commercially obtained and used after purification by usual methods. *p*-Phenylenediamine (PPD), 4,4′-methylenedianiline (MDA), 4,4′-oxydianiline (ODA), 4,4′-diaminodiphenyl sulfone (DDS), 2,2-bis(*p*-aminophenyl)hexafluoropropane (BAAF), and 1,6-hexamethylenediamine (HMDA) were purified by recrystallization and/or sublimation in vacuo. *m*-Phenylenediamine (MPD) and 1,4-cyclohexanediamine (CHDA) were distilled prior to use. The solvents, *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Other organic solvents were purified by standard procedures. Reagents used were of commercial quality unless otherwise stated.

Measurements. Melting points were measured on the Yazawa Chemical BY-1 apparatus and are uncorrected. The elemental analyses were performed on a FISONS Instruments EA1108 CHN analyzer. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 (^{1}H, 399.65 MHz; ^{13}C, 100.40 MHz; for monomers) or a JEOL JNM-LA500 (^{1}H, 500.00 MHz; ^{13}C, 125.65 MHz; for polymers) spectrometer. IR spectra were obtained using a JASCO IR-700 spectrometer. Inherent viscosities of all polymers were determined with an Ubbelohde viscometer at a concentration of 0.5 g/dL in DMAc at 30 °C. The molecular weights of polymers were estimated by gel permeation chromatography (GPC) system equipped with a JASCO 880-PU HPLC pump, a Shodex RI SE−61 detecter and Shodex GPC KF-806L columns in 0.05 M LiCl/DMF solution at 40 °C based on polystyrene standards. Wide-

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angle X-ray diffractograms were obtained on a Rigaku RINT2100 X-ray diffractometer with Cu Kα radiation (40 kV, 20 mA) in the scanning rate of 4°/min. UV−visible spectra were recorded on a JASCO Ubest-35 spectrometer. Thermogravimetric studies (TGA) were made with a Shimadzu DTG-50 analyzer in a nitrogen (50 cm^3/min) atmosphere at a heating rate of 10 °C/min. Differential scanning calorimetric studies (DSC) were carried out with a Rigaku DSC 8230 analyzer at a heating rate of 30 °C/min.

Monomer Synthesis. Diimide−Dianhydrides (5−7). A typical procedure is as follows. To a stirred solution of TCDA (**1**) 5.350 g (27.0 mmol) in dry DMF (30 mL) was added ODA 2.712 g (13.5 mmol) at room temperature. On addition of ODA, the temperature of the mixture rose to ca. 40 °C by exothermal reaction, and the reaction was continued for 1 h at ambient temperature. The reaction mixture was concentrated in vacuo and dissolved in 50 mL of acetone. The solution was poured into a mixture of chloroform (600 mL) and hexane (300 mL) to precipitate a white powder of diimide−tetracarboxylic acid (**2**). This was collected by filtration and dried overnight in vacuo. The diimide−tetracarboxylic acid (**2**) was placed in 40 mL of acetic anhydride. The mixture was heated to 100 °C with stirring. The reaction mixture gradually turned into a clear solution and then immediately separated as a solid again. Heating was continued for another hour at 100 °C. After cooling, the white solid precipitated was collected by filtration, washed with acetic anhydride and toluene, and dried overnight at 100 °C in vacuo to give the diimide−dianhydride TCDA−ODA (**5**) as a white powder (7.388 g, 98%): mp >315 °C; IR (KBr) 1806, 1790, 1764, 1712 (C═O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.36 (d, 4H, $J = 9$ Hz), 7.17 (d, 4H, $J = 9$ Hz), 3.34 (d, 4H, $J = 17$ Hz), 3.20 (d, 4H, $J = 17$ Hz), 2.85 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 179.03, 173.61, 166.08, 156.12, 129.00, 127.41, 118.87, 39.70, 39.17, 36.57. Anal. Calcd for $C_{28}H_{20}N_2O_{11}$: C, 60.00; H, 3.60; N, 5.00. Found: C, 59.72; H, 3.74; N, 5.16.

The other diimide−dianhydrides, TCDA−CHDA (**6**) and TCDA−MDA (**7**), were prepared in a similar manner from TCDA (**1**) and the corresponding diamines.

TCDA−CHDA (6). A white powder (85%): mp >315 °C; IR (KBr) 1808, 1764, 1699 (C═O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.77 (m, 2H), 3.10 (s, 8H), 2.66 (s, 4H), 2.05−1.99 (m, 4H), 1.72−1.70 (m, 4H); ^{13}C NMR (DMSO-d_6) δ 179.78, 174.25, 166.11, 49.75, 39.10, 38.75, 36.51, 26.97. Anal. Calcd for $C_{22}H_{22}N_2O_{10}$: C, 55.70; H, 4.67; N, 5.90. Found: C, 55.87; H, 4.71; N, 5.61.

TCDA−MDA (7). A white powder (99%): mp >315 °C; IR (KBr) 1808, 1763, 1709 (C═O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.35 (d, 4H, $J = 8$ Hz), 7.24 (d, 4H, $J = 8$ Hz), 4.03 (s, 2H), 3.32 (d, 4H, $J = 17$ Hz), 3.19 (d, 4H, $J = 17$ Hz), 2.84 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 179.06, 173.66, 166.17, 141.35, 130.04, 129.09, 127.17, 40.19, 39.71, 39.19, 36.60. Anal. Calcd for $C_{29}H_{22}N_2O_{10}$: C, 62.37; H, 3.97; N, 5.02. Found: C, 62.26; H, 3.82; N, 5.18.

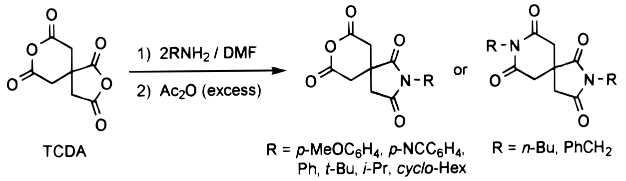
Polymer Synthesis. Preparation of Poly(imide−amic acid)s (8a−h, 9g−h, 10d). A typical polymerization procedure is as follows. To a mechanically stirred suspension of TCDA−ODA (**5**) 0.8407 g (1.500 mmol) in 5 mL of dry DMAc were added DDS 0.2974 g (1.500 mmol) and 3 mL of dry DMAc at room temperature. After several minutes, after the reaction mixture had turned into a clear solution, the temperature was elevated to 100 °C. The reaction was continued at 100 °C for 24 h. After cooling, the resulting viscous solution was slowly poured into 500 mL of methanol with stirring to precipitate poly(imide−amic acid) (**8e**). This was collected by filtration, washed with methanol, and dried overnight at room temperature in vacuo. The polymer yield was almost quantitative.

IR of **8e** (KBr): 3346 (N−H), 3500−2500 (br, O−H), 1800−1650 (br, C═O) cm^{-1}.

Other poly(imide−amic acid)s were synthesized by a similar procedure.

Preparation of Poly(imide−imide) Films (11a−h, 12g−h, 13d) by Thermal Imidization. A typical procedure for the preparation of poly(imide−imide) films by thermal imidization is as follows. The 10 wt % solution of a poly(imide−amic acid) in dry DMAc was cast on a glass plate. The poly(imide−amic acid) was converted to a poly(imide−imide) by successive heating at 80 °C for 2 h, 150 °C for 2 h, 250 °C for 2 h, and 300 °C for 1 h under argon atmosphere. Similarly, poly(imide−imide) films were cast on a quartz glass plate for UV−visible spectroscopy and on a NaCl plate for IR spectroscopy.

Scheme 1



IR of **11e** (film): 1787, 1711, 1695 (C═O) cm^{-1}.

Preparation of Poly(imide−imide)s (11a−h) by Chemical Imidization. A typical procedure for the preparation of poly(imide−imide)s by chemical imidization is as follows. To a stirred solution of a poly(imide−amic acid) (0.50 mmol) in 5 mL of dry DMAc were added 5 mL of acetic anhydride and 2 mL of dry pyridine at room temperature. The mixture was stirred at room temperature for 1 h in argon atmosphere and then heated at 120 °C for 4 h. After cooling, the solution was poured into 250 mL of methanol to precipitate a poly(imide−imide). This was collected by filtration and dried overnight at 100 °C in vacuo.

11e (97%): IR (KBr) 1788, 1713, 1694 (C═O) cm^{-1}; ^1H NMR (DMSO-d_6, 100 °C) δ 8.06 (d, 4H, $J = 8.6$ Hz), 7.45 (d, 4H, $J = 8.6$ Hz), 7.41 (d, 4H, $J = 8.9$ Hz), 7.18 (d, 4H, $J = 8.9$ Hz), 3.29 (d, 4H, $J = 17$ Hz), 3.24 (d, 4H, $J = 17$ Hz), 2.97 (s, 4H); ^{13}C NMR (DMSO-d_6, 100 °C) δ 178.30, 172.79, 169.32, 155.79, 140.19, 140.01, 129.79, 128.36, 127.55, 127.31, 118.39, 39.83, 39.43, 39.34.

Results and Discussion

Monomer Synthesis. According to the reported method,[28] aliphatic tetracarboxylic dianhydride having a spiro carbon atom with two different rings (five- and six-membered anhydrides), 2,8-dioxaspiro[4.5]decane-1,3,7,9-tetrone (TCDA) (**1**), was prepared in three steps starting from itaconic anhydride and isoprene.

Recently, we have reported the characteristic reaction of TCDA (**1**) with various amines.[28] The reaction with primary amines and subsequent dehydration gave either imide (with five-membered ring)−anhydride (with six-membered ring) or diimide (with five- and six-membered rings), depending on the hydrocarbon moiety of the amines used (Scheme 1). In particular, in the cases of amines with aryl or *sec*-alkyl or *tert*-alkyl group, such as aniline, *p*-anisidine, *tert*-butylamine, isopropylamine, and cyclohexylamine, the imide−anhydrides were exclusively obtained because of the mechanism via intramolecular ring transformation.

On the basis of this knowledge, novel anhydride-capped diimides, diimide (with five-membered rings)−dianhydrides (with six-membered rings) (**5**−**7**), were prepared in high yields by the reaction of TCDA (**1**) with 4,4′-oxydianiline (ODA), *trans*-1,4-cyclohexanediamine (CHDA), and 4,4′-methylenedianiline (MDA), respectively, and the subsequent dehydration of the resulting diimide (with five-membered rings)−tetracarboxylic acids (**2**−**4**) (Scheme 2). The structures of the diimide−dianhydrides (**5**−**7**) were confirmed by IR, ^1H NMR, and ^{13}C NMR spectroscopy and elemental analyses, referring to the characterization of analogous imide−anhydrides. In the IR spectra, two peaks due to six-membered anhydrides were observed at 1806−1808 and 1763−1764 cm^{-1}, and no peaks were found at higher than 1840 cm^{-1} due to five-membered anhydrides. In the ^1H NMR spectra, a singlet peak due to the methylene protons in

Scheme 2

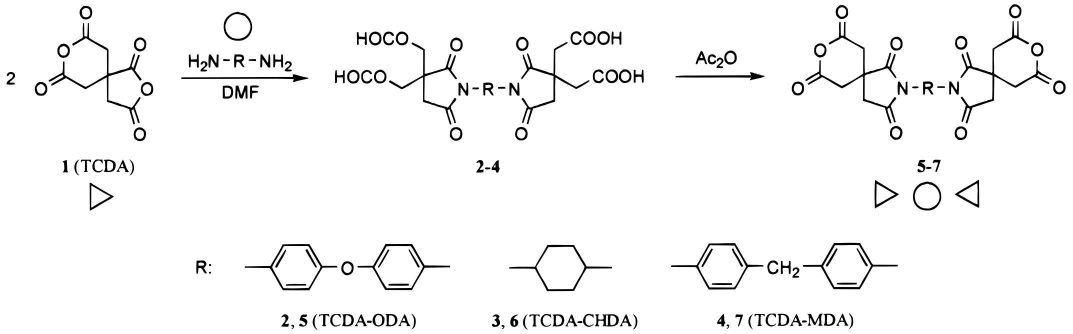
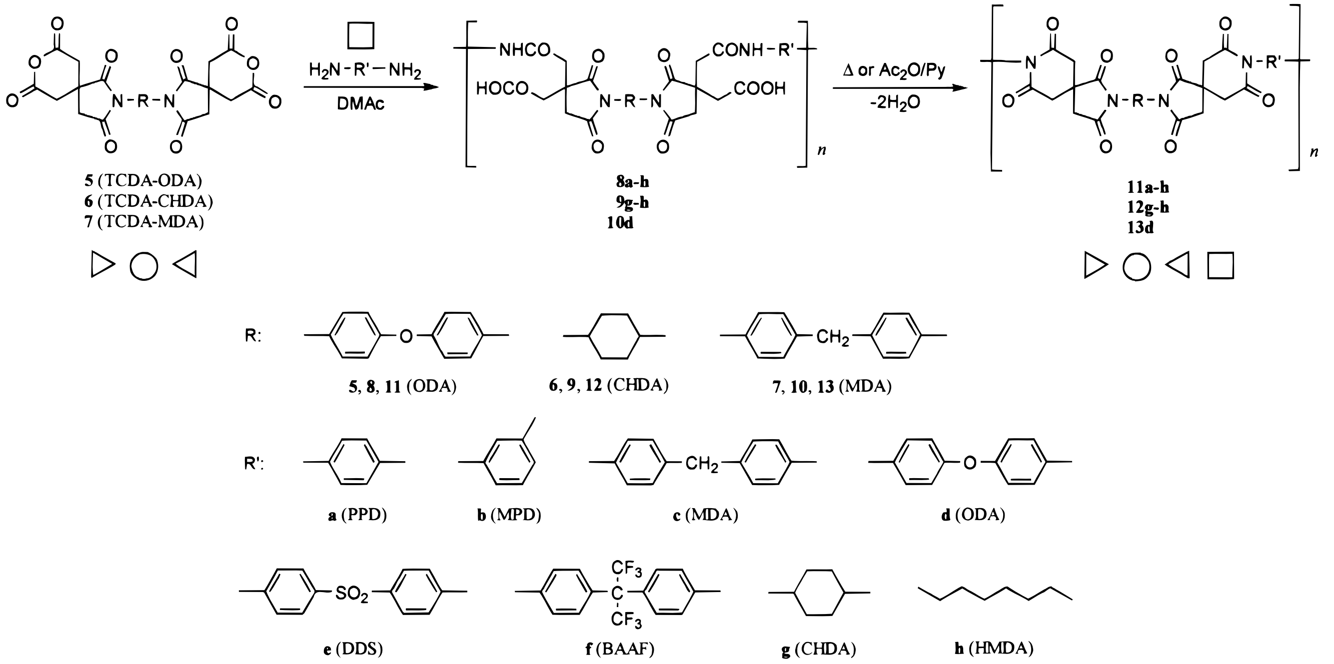


Table 1. Yields and Solubility[a] of Diimide−Dianhydrides

no.	diimide−dianhydride	yield (%)	solvents[b]						
			DMSO	DMF	DMAc	NMP	THF	Acetn	$CHCl_3$
5	TCDA−ODA	98	++	+	+	+	−	−	−
6	TCDA−CHDA	85	++	++	++	++	−	−	−
7	TCDA−MDA	99	++	++	+	++	−	−	−

[a] Solubility: ++, easily soluble; +, soluble; −, insoluble. [b] DMF: *N*,*N*-dimethylformamide. DMAc: *N*,*N*-dimethylacetamide. NMP: *N*-methyl-2-pyrrolidone. DMSO: dimethyl sulfoxide. THF: tetrahydrofuran. Acetn: acetone. $CHCl_3$: chloroform.

Scheme 3



five-membered rings and two doublet peaks due to geminal protons of the methylene groups in six-membered rings proved the noncoplanar spiro structure of diimide−dianhydrides. A further purification procedure was not conducted because of the difficulty in recrystallization of the diimide−dianhydrides, but the purity of the materials was confirmed by elemental analyses and the spectral data. As shown in Table 1, all the diimide−dianhydrides (**5**−**7**) were soluble in *N*,*N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP), which were the typical solvents used in the preparation of poly(amic acid)s, followed by thermal or chemical conversion to polyimides.

Polymer Synthesis. Strictly alternating copolyimides containing aliphatic spiro units in the polymer backbone were prepared by the conventional two-step procedure using the diimide−dianhydrides and diamines (Scheme 3). The resulting copolyimides have alternating diamine components and also a head-to-head (tail-to-tail) structure in the imide ring sequence:

▷○◁□

Hitherto, there was no report on the synthesis of strictly alternating copolyimides via diimide−dianhydride derivatives. This method is a facile synthetic procedure to prepare strictly alternating copolyimides by an optional combination of two kinds of diamines. There is a larger variety of choices in diamines than in dianhydrides. The diimide−dianhydrides and diamines used are also listed in Scheme 3. The poly(imide−imide)s from TCDA−ODA (**5**) or TCDA−MDA (**7**) have both aromatic and aliphatic moieties, and those from TCDA−CHDA (**6**) have only aliphatic moieties.

Polymerization was conducted in dry DMAc at 100 °C for 24 h, which conditions gave the highest yield and

Table 2. Preparation of Poly(imide−amic acid)s[a] and the Corresponding Poly(imide−imide)s

		poly(imide−amic acid)		poly(imide−imide)					
diimide−dianhydride	diamine	no.	η_{inh}^{e} (dL/g)	no.	η_{inh}^{e} (dL/g)	$M_n^{g} \times 10^{-4}$	$M_w^{g} \times 10^{-4}$	M_w/M_n^{g}	film quality
TCDA−ODA	PPD	**8a**[b]	0.24	**11a**	0.30	4.34	5.70	1.31	flexible
	MPD	**8b**[c]	0.20	**11b**	0.21	6.97	8.44	1.21	flexible
	MDA	**8c**[b]	0.54	**11c**					flexible
	ODA	**8d**[b]	0.33	**11d**					flexible
	DDS	**8e**[b]	0.16	**11e**	0.21	2.93	3.68	1.25	brittle
	BAAF	**8f**[c]	0.17	**11f**	0.28	4.50	6.07	1.35	flexible
	CHDA	**8g**[c]	0.34	**11g**	0.26	3.29	4.65	1.41	flexible
	HMDA	**8h**[d]	0.26	**11h**					flexible
TCDA−CHDA	CHDA	**9g**[c]	0.20[f]	**12g**					brittle
	HMDA	**9h**[d]	0.15	**12h**					flexible
TCDA−MDA	ODA	**10d**[b]	0.29	**13d**					flexible
(PMDA)	(ODA)			Kapton					flexible

[a] The reactions were carried out with diimide−dianhydride (1.50 mmol) and diamine (1.50 mmol) in DMAc (8 mL) at 100 °C for 24 h. [b] Precipitated by MeOH. [c] Precipitated by CH_2Cl_2. [d] Precipitated by Et_2O. [e] Measured in DMAc on 0.5 g/dL at 30 °C. [f] Partially insoluble in DMAc. [g] Estimated by GPC based on polystyrene standards.

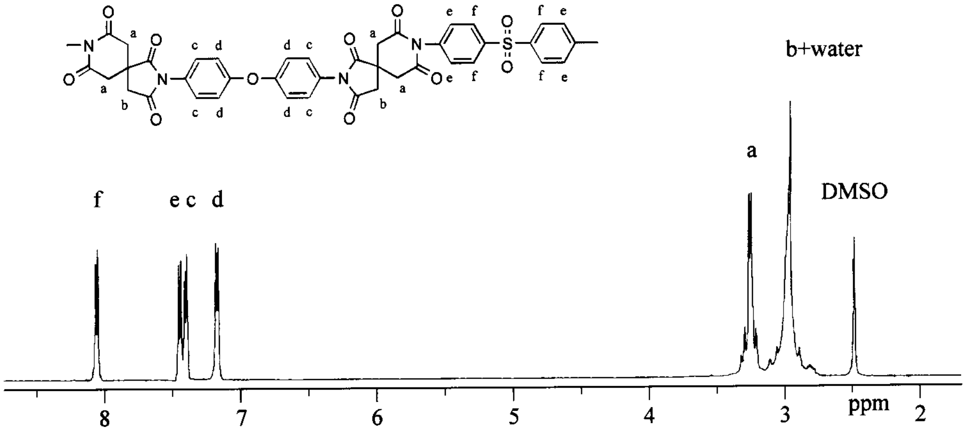


Figure 1. 500 MHz ^{1}H NMR spectrum of a poly(imide−imide), TCDA−ODA−DDS (**11e**), in DMSO-d_6 at 100 °C.

inherent viscosity in the polymerization of TCDA−ODA (**5**) with MDA. The polymerization, even at a high temperature under aerobic conditions, did not bring about an adverse effect on the color of the resulting poly(imide−amic acid)s. In the preparation of poly(amic acid)s from dianhydrides and diamines in a polar solvent, the process of monomer addition plays an important role to achieve a successful polymerization and the good properties.[11,29,30] Although the yield and inherent viscosity were little affected by the monomer addition mode, the addition mode of adding solid diamines to the solution of diimide−dianhydrides resulted in less coloration of poly(imide−amic acid)s than the reversed addition mode. Therefore, the former addition mode was adopted.

The coloration and transparency of polyimide films are influenced by the curing temperature and atmosphere.[17] Poly(imide−imide)s cured in argon were less colored than in air, and the weight loss due to the thermal dehydration of the poly(imide−amic acid)s was observed around 250 °C by thermogravimetry. Therefore, the thermal imidization of the poly(imide−amic acid)s was carried out by stepwise heating to 300 °C under argon atmosphere as described in the Experimental Section. The completion of the imidization was confirmed by IR spectroscopy and thermogravimetry.

As shown in Table 2, the inherent viscosities of the poly(imide−amic acid)s precipitated with poor solvents were in the range 0.15−0.54 dL/g. The higher molecular weight poly(imide−amic acid) was yielded by the polymerization of TCDA−ODA (**5**) with MDA. The inherent viscosities of the soluble poly(imide−imide)s (**11a**−**b**, **e**−**g**) were in the range 0.21−0.30 dL/g and were generally higher than those of the corresponding poly(imide−amic acid)s (**8a**−**b**, **e**−**g**). The number- and weight-average molecular weights (M_n and M_w) of the soluble poly(imide−imide)s (**11a**−**b**, **e**−**g**) were in the ranges 29300−69700 and 36800−84400, respectively. The cast films of all poly(imide−imide)s were flexible except those of TCDA−ODA−DDS (**11e**) and TCDA−CHDA−CHDA (**12g**), which became brittle during the thermal imidization process.

The crystallinity of the poly(imide−imide)s for as-cast film was evaluated by their wide-angle X-ray diffraction patterns with 2θ ranging from 5 to 50°. All of the poly(imide−imide) films showed almost the same pattern with no distinctive peaks and were proved amorphous.

NMR Studies. To confirm that the poly(imide−imide)s have alternating diamine components and a head-to-head (tail-to-tail) structure in the imide ring sequence, the NMR studies of the soluble poly(imide−imide) TCDA−ODA−DDS (**11e**) were performed. The ^{1}H NMR and ^{13}C NMR spectra of **11e** are shown along with the assignments in Figures 1 and 2, respectively. In the ^{1}H NMR spectrum, a singlet peak (b) due to the methylene protons in five-membered rings and two doublet peaks (a) due to geminal protons of the methylene groups in six-membered rings proved the noncoplanar spiro structure of the TCDA moiety. Four doublet peaks (c−f) due to para-substituted aromatic protons in two kinds of diamine moieties were also found. In the ^{13}C NMR spectrum, three peaks (1, 4, 6) due to the carbonyl carbons in the TCDA moiety, eight peaks (7−14) due to the aromatic carbons in the diamine moieties,

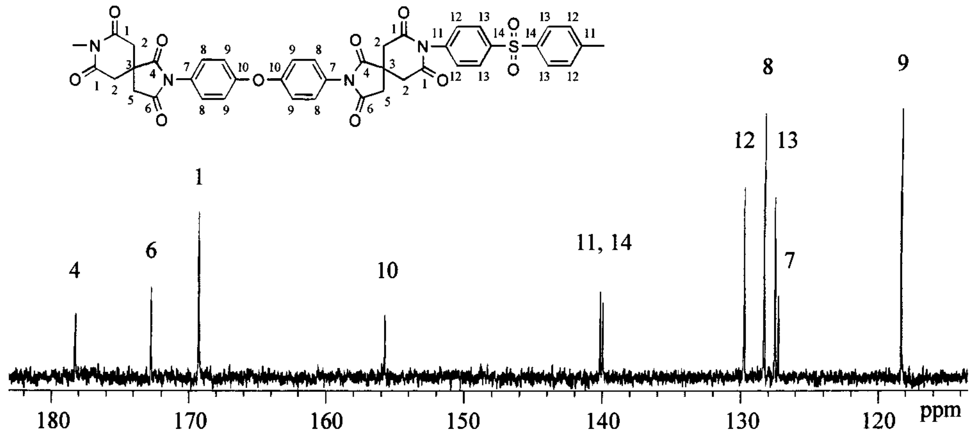


Figure 2. 126 MHz ^{13}C NMR spectrum of a poly(imide−imide), TCDA−ODA−DDS (**11e**), in DMSO-d_6 at 100 °C.

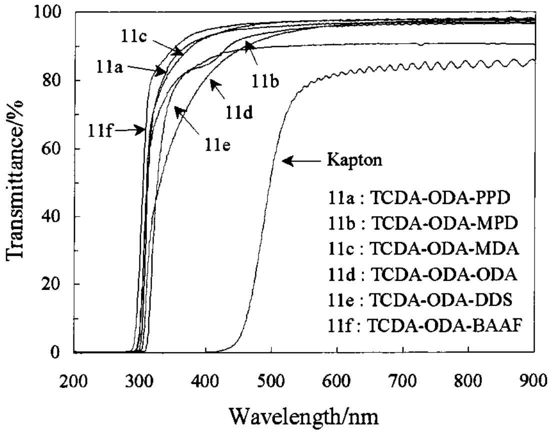


Figure 3. UV−visible spectra of 10−33 μm thick poly(imide−imide) films (**11a**−**f**) prepared from aromatic diamines and TCDA−ODA (**5**).

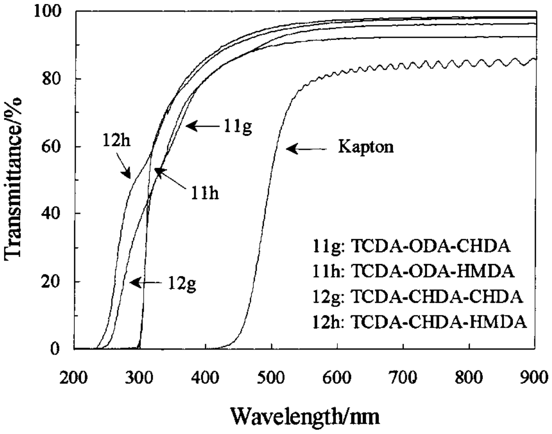


Figure 4. UV−visible spectra of 18−24 μm thick poly(imide−imide) films (**11g**−**h**, **12g**−**h**) prepared from aliphatic diamines and TCDA−ODA (**5**) or TCDA−CHDA (**6**).

Table 3. Optical Properties of Poly(imide−imide) Films

no.	film thickness[a] (μm)	cutoff wavelength (nm)	transparency[b] (%)	normalized transparency[c] (%)
11a	18	298	96	98
11b	19	294	95	97
11c	10	293	97	97
11d	23	302	94	97
11e	33	308	90	97
11f	15	287	97	98
11g	24	296	93	97
11h	18	297	95	97
12g	19	244	90	95
12h	20	235	96	98
13d	16	303	92	95
Kapton	10	421	63	63

[a] Measured using a micrometer. [b] Average transmittance in the visible region (400−780 nm). [c] Evaluated by assuming that all poly(imide−imide) films have the same thickness (10 μm).

and three peaks (2, 3, 5) due to the methylene carbons and the spiro carbon in the TCDA moiety were observed. Furthermore, a peak at 169.3 ppm due to the carbonyl carbons in six-membered rings shifted significantly as compared with the 166.1 ppm peak of TCDA−ODA (**5**). These results demonstrated that the newly formed imides were six-membered imides and no intramolecular ring transformation took place during the polymerization and subsequent imidization; that is, the copolyimides with the definite structure and sequence were provided by the synthetic strategy via diimide−dianhydrides without side reactions and randomization.

UV−Visible Spectroscopic Studies. The cast films of the resulting poly(imide−imide)s were entirely colorless or slightly pale yellow. The transmission UV−visible spectra of the 10−33 μm thick poly(imide−imide) films are shown in Figures 3−5. All of the spectra of the poly(imide−imide) films show cutoff wavelengths shorter than approximately 300 nm and no distinct peak maxima. The cutoff wavelengths of the poly(imide−imide)s are far shorter than that of Kapton (421 nm). In particular, wholly aliphatic poly(imide−imide)s (**12g**−**h**) show cutoff wavelengths (244 and 235 nm) far shorter than those (**11a**−**h**) from TCDA−ODA (Figure 4). The transmittances of the flexible poly(imide−imide) films in plateau are excellent (>95%) and are much higher than that of Kapton (80−85%). The films of TCDA−ODA−BAAF (**11f**), TCDA−ODA−MDA (**11c**), and TCDA−ODA−PPD (**11a**) have nearly complete optical transparency (>95%) at wavelengths longer than 400, 430, and 440 nm, respectively. The optical properties of the poly(imide−imide) films are summarized in Table 3. The transparency of the poly(imide−imide) films was evaluated by the average transmittance of the poly(imide−imide) films in the visible region (400−780 nm). Normalized transparency was also evaluated by assuming that all poly(imide−imide) films have the same thickness (10 μm). The normalized transparency of all the poly(imide−imide) films was excellent (95−98%). A remarkable difference between TCDA−ODA−MDA (**11c**) and TCDA−MDA−ODA (**13d**) due to the reversed combination of diamine components should be notable (Figure 5).

Table 4. Solubility[a] of Poly(imide−imide) Films

	solvents[b]									
no.	DMF	DMAc	NMP	DMSO	H_2SO_4	Cresol	Py	THF	Acetn	$CHCl_3$
11a	++	++	++	++	++	+	+−	−	−	−
11b	++	++	++	++	++	+	+−	−	−	−
11c	+−	+−	+−	+−	+−	+−	+−	−	−	−
11d	+−	+−	+−	+−	+−	+−	+−	−	−	−
11e	++	++	++	++	++	+	+	−	−	−
11f	++	++	++	++	++	+	++	+−	+−	−
11g	++	++	+−	+−	+	+−	+−	−	−	−
11h	+−	+−	+−	+−	+	+−	+−	−	+−	−
12g	+−	+−	+−	+−	+−	+−	+−	−	−	−
12h	−	−	−	−	−	−	−	−	−	−
13d	+−	+−	+−	+−	+−	+−	+−	−	−	−
Kapton	−	−	−	−	++	−	−	−	−	−

[a] Solubility: ++, soluble at room temperature; +, soluble by heating; +−, swelling; −, insoluble. [b] DMF: *N*,*N*-dimethylformamide. DMAc: *N*,*N*-dimethylacetamide. NMP: *N*-methyl-2-pyrrolidone. DMSO: dimethyl sulfoxide. H_2SO_4: concentrated sulfuric acid. Cresol: *m*-cresol. Py: pyridine. THF: tetrahydrofuran. Acetn: acetone. $CHCl_3$: chloroform.

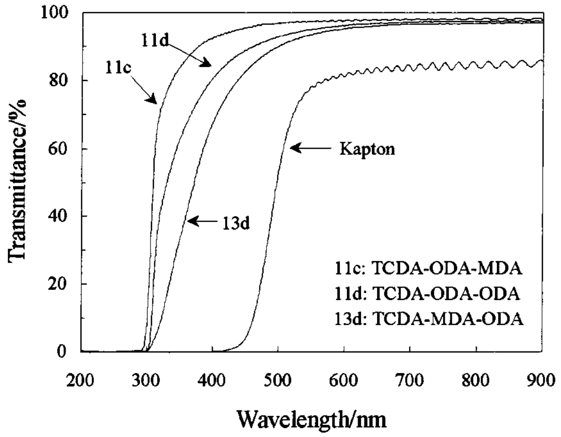


Figure 5. UV−visible spectra of 10−23 μm thick poly(imide−imide) films of TCDA−ODA−MDA (**11c**), TCDA−ODA−ODA (**11d**), and TCDA−MDA−ODA (**13d**).

The colored nature of conventional polyimides is due to the presence of intra- and intermolecular charge transfer (CT) interactions and electron conjugation.[31−35] The good optical transparency of the resulting poly(imide−imide) films resulted from the decrease in the intramolecular CT interaction and electron conjugation by the aliphatic structure of the TCDA moiety. In addition, the intermolecular CT interaction was also suppressed because the noncoplanar spiro structure of the TCDA moiety increased the intermolecular stacking distance between poly(imide−imide) chains.

Solubility. The solubility of the poly(imide−imide) films was qualitatively tested in various solvents. The results are summarized in Table 4. Most of the poly(imide−imide)s prepared from aromatic diamines exhibited good solubility to typical polar aprotic solvents such as *N*,*N*-dimethylformamide (DMF), DMAc, NMP, and dimethyl sulfoxide (DMSO), and to *m*-cresol and concentrated H_2SO_4. Moreover, the poly(imide−imide)s (**11e**−**f**) derived from DDS or BAAF were also soluble in pyridine. Since the solubility of the poly(imide−imide)s showed a tendency to decrease with increasing molecular weight, the lower solubility of **11c**−**d** and **13d** may be due to the higher molecular weight. The wholly aliphatic poly(imide−imide)s (**12g**−**h**) obtained from aliphatic diamines revealed poor solubility to most of common organic solvents, contrary to our expectation. No difference in solubility between TCDA−ODA−MDA (**11c**) and TCDA−MDA−ODA (**13d**) due to the reversed combination of diamine components was observed at all.

Table 5. Thermal Properties of Poly(imide−imide) Films

no.	T_g[a] (°C)	T_5[b] (°C)	T_d[c] (°C)	Y_c[d] (%)
11a	294	318	379	27
11b	261	331	379	17
11c	255	384	414	26
11d	272	393	419	38
11e	283	378	401	18
11f	274	381	412	25
11g	260	361	394	4
11h	197	375	401	17
12g	315	356	390	0
12h	220	389	409	0
13d	282	373	410	20
Kapton	362	444	555	25

[a] From DSC on the second heating at a heating rate of 30 °C/min in air. [b] Temperature at which 5% weight loss was recorded by thermogravimetry at a heating rate of 10 °C/min in N_2. [c] Temperature at which 10% weight loss was recorded by thermogravimetry at a heating rate of 10 °C/min in N_2. [d] Char yield recorded by thermogravimetry at a heating rate of 10 °C/min from room temperature to 800 °C.

Thermal Properties. The physical state and morphology of polyimides and its precursors (powder, film, bulk, etc.) have an effect on the thermal properties such as thermal stability and glass transition temperature.[36,37] In particular, the film thickness affects the degradation rate of the film.[37,38] Thus, to be compared directly with Kapton film (10 μm), the poly(imide−imide) films of same thickness by thermal imidization were used as the samples for thermal analyses. The thermal behavior of the poly(imide−imide) films was evaluated by thermogravimetry (TGA) and differential scanning calorimetry (DSC). These results are summarized in Table 5.

The 5% weight loss temperatures (T_5) and the decomposition temperatures (T_d) in a nitrogen atmosphere by TGA were observed in the ranges 318−393 and 379−419 °C, respectively, depending on the combination of two kinds of diamine components. The homopolyimide (**11d**) containing only ODA as the diamine component exhibited the highest thermal stability. The wholly aliphatic poly(imide−imide)s (**12g**−**h**) had the thermal stability similar to the poly(imide−imide)s prepared from aromatic diamines. Although it is known that spiro polymers as well as ladder polymers are thermally stable, the poly(imide−imide)s containing a spiro unit in this paper had a lower thermal stability than conventional aromatic polyimides such as Kapton. The residual char yield (Y_c) at 800 °C in a nitrogen stream by TGA revealed 17−38% in the poly(imide−imide) films (**11a**−**f**, **13d**) prepared from aromatic diamines.

Most of these poly(imide−imide) films had Y_c higher than that of Kapton measured under the same conditions. The glass transition temperatures (T_g) of most of the poly(imide−imide)s were observed in the range of 255−315 °C in air by DSC. The poly(imide−imide)s (**11h**, **12h**) derived from HMDA had relatively low T_g values of 197 and 220 °C because of the incorporation of the linear hexamethylene structure.

It should be noted that a slight difference in thermal stability (T_d) and a significant difference in thermal resistance (T_g) between TCDA−ODA−MDA (**11c**) and TCDA−MDA−ODA (**13d**) prepared by the reversed combination of diamine components were observed. It was suggested that such differences were induced by the strictly controlled structure of these poly(imide−imide)s.

Conclusions

Strictly alternating copolyimides containing aliphatic spiro units in the polymer backbone were prepared via diimide (with five-membered rings)-dianhydrides (with six-membered rings). The diimide−dianhydrides (**5**−**7**) were exclusively synthesized from 2,8-dioxaspiro[4.5]-decane-1,3,7,9-tetrone (TCDA) (**1**) and diamines and had good solubility in the typical polymerization solvents such as *N*,*N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP). The polymerization was carried out by the conventional two-step procedure using the diimide−dianhydrides and diamines. It was confirmed by NMR studies that the resulting copolyimides had alternating diamine components and also a head-to-head (tail-to-tail) structure in the imide ring sequence:

▷○◁□

The poly(imide−imide) films were colorless or slightly pale yellow, and the excellent colorlessness (cutoff wavelength) and transparency (UV−visible transmittance) were revealed by the UV−visible studies. Most of the poly(imide−imide) films were soluble in various solvents such as DMAc, NMP, and *m*-cresol, but the wholly aliphatic poly(imide−imide)s (**12g**−**h**) were insoluble in most common organic solvents. These poly(imide−imide) films had decomposition temperatures between 379 and 419 °C in a nitrogen atmosphere and the wholly aliphatic poly(imide−imide)s (**12g**−**h**) exhibited a thermal stability similar to that of the poly(imide−imide)s prepared from aromatic diamines. The fair thermal stability of the aliphatic spiro structure in the poly(imide−imide) backbone was also proved. The glass transition temperatures were shown in the wide range of 197−315 °C depending on the combination of two kinds of diamines. It was suggested that these properties were created and enhanced by the aliphatic spiro units and the strictly alternating structure of the poly(imide−imide)s. It was also noticed that some differences in these properties due to the reversed combination of diamine components were observed.

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References and Notes

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