NOTES

Soluble Polyimides and Copolyimides Based on Alicyclic Dianhydride Having Cyclohexene and Tetralin Moieties

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Polyimides exhibit excellent thermal and mechanical properties, and have extensive engineering and microelectronics applications.[1] Aromatic polyimides such as pyromellitic polyimides are prepared from aromatic diamines and aromatic tetracarboxylic dianhydrides *via* poly(amic acid)s. Since conventional aromatic polyimides are insoluble, these polymers are usually processed as the corresponding soluble poly-(amic acid) precursors, and then either thermally or chemically imidized. However, owing to the instability of poly(amic acid)s and the liberation of water in the imidization process, problems can arise. Extensive research has been recently carried out to improve the solubility of polyimides.[2–20] We have reported the synthesis and characterization of soluble polyimides and copolyimides based on 2,3,5-tricarboxycyclopentyl acetic dianhydride (TCA-AH) and aromatic diamines.[21,22] Conventional tetracarboxylic dianhydrides such as 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) and alkyldiaminobenzophenone having long-chain linear alkyl groups with 9–14 carbon atoms (ADBP-9–14),[23] and BTDA and alkyloxy-diaminobenzene having long-chain linear alkyl groups with 10–14 carbon atoms (AODB-10–14) have also been used.[24] The recent our paper has described the soluble polyimides having dendric moieties on their side chain.[25]

Alicyclic polyimides are soluble in organic solvents in most cases, and these are useful functional polymers for the alignment films of liquid crystal display and low dielectric materials. Recent topics concerning with alicyclic polyimides were well reviewed by Matsumoto.[26] 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (cyclohexene-DA) known as Epiclon B 4400 and 4-(2,5-dioxotetrahydrofuran-3-yl)-tetralin-1,2-dicarboxylic anhydride (tetralin-DA) are representative commercially available aliphatic tetracarboxylic dianhydrides for the synthesis for soluble polyimides. Although there have been many patent literature describing polyimides based on cyclohexene-DA and tetralin-DA, there have been a few scientific publications describing polyimides[27] or poly(amide imide)s[28] based on these monomers. This paper describes the detail explanation of soluble polyimides and copolyimides based on cyclohexene-DA and tetralin-DA and the results are discussed in comparison with those based on TCA-AH.

EXPERIMENTAL

Materials

5-(2,5-Dioxotetrahydrofuryl)-3-methyl-3-cyclohexane-1,2-dicarboxylic anhydride (cyclohexene-DA) and 4-(2,5-dioxotetrahydrofuran-3-yl)-tetralin-1,2-dicarboxylic anhydride (tetralin-DA), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), and 4,4′-diaminodiphenylether (DDE) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI) and purified by following method; cyclohexene-DA, mp

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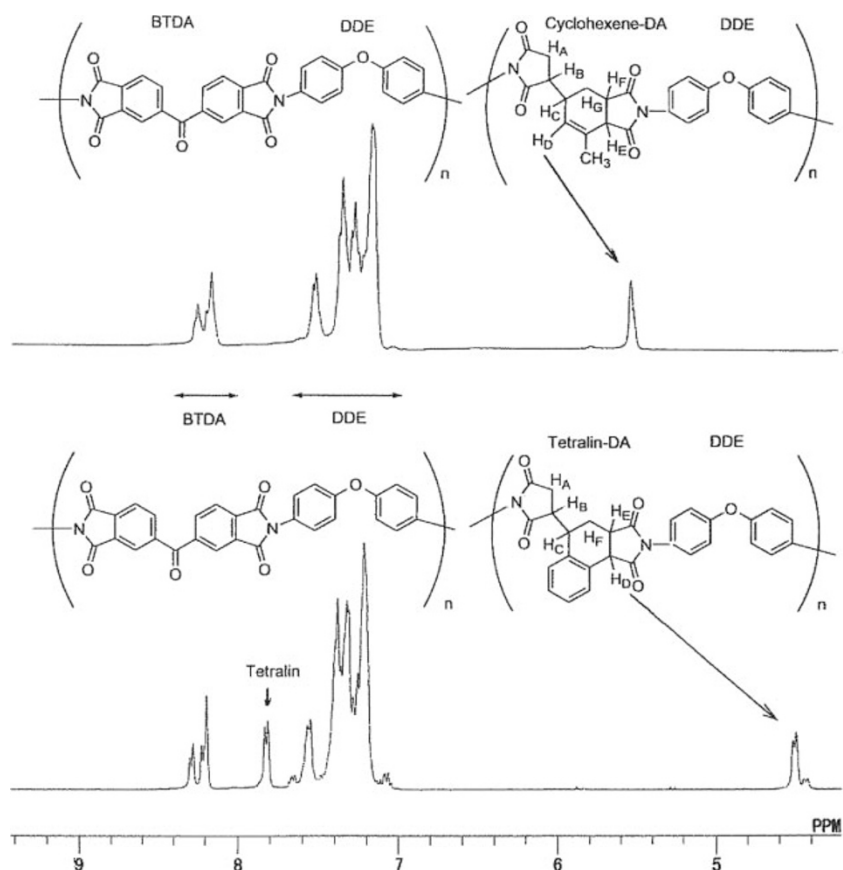
Figure 1. ^{1}H NMR spectrum of a representative copolyimides based on cyclohexene-DA and tetralin-DA. Upper; cyclohexene-DA/BTDA/DDE (80/20/100), lower; tetralin-DA/BTDA/DDE (80/20/100).

175.1 °C, recrystalized from acetic anhydride; tetralin-DA, mp 205.9 °C, recrystalized from acetic anhydride; DDE, mp 193.6 °C, recrystalized from ethanol; BTDA, mp 229.2 °C by vacuum sublimation. N-Methyl-2-pyrrolidone (NMP) (Mitsubishi Chemicals) was distilled under reduced pressure from 4 Å molecular sieves. Other conventional reagents were purchased from TCI or Wako Pure Chemical Industries, Ltd. and used as received.

Measurements

The inherent viscosities of all polymers were measured using Cannon Fenske viscometers at a concentration of 0.5 g/dL in NMP at 30 °C. Differential scanning calorimeter (DSC) traces were measured on a Shimadzu DSC-60 under nitrogen at a heating rate of 10 °C/min and glass transition temperatures (T_g) were read at the onset of the heat capacity jump (Tig) from the second heating scan followed by JIS K-7121. Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50 in air or under nitrogen at a heating rate of 10 °C/min. ^{1}H NMR spectra were measured on a JEOL JNM-AL400 FT NMR in dimethyl sulfoxide-d_6 with tetramethylsilane (TMS) as an internal reference. IR spectra were measured on a JASCO IR Report-100 spectrophotometer.

Preparation of Polyimides

The preparation of polyimide and copolyimide was carried out by the method previously reported.[21–24] The imidization reaction of the poly(amic acids) was monitored by ^{1}H NMR technique[21–24] and the conversion from poly(amic acids) to polyimides were found to be 100%. Dianhydride compositions of obtained copolyimides were confirmed by ^{1}H NMR and detailed description are given in the next section and Figure 1. ^{1}H NMR spectra, IR Spectra and results of elemental analysis of representative copolyimides are as follows.

Cyclohexene-DA/BTDA/DDE (80/20/100 mol%) (Figure 1)

^{1}H NMR (DMSO-d_6): δ 1.40–1.50 (m, 1H, H$_C$), 1.95 (broad s, 3H, CH$_3$), 2.10–3.40 (unidentified overlapped peaks of H$_B$, H$_E$, H$_F$ and H$_G$, 5H), 3.50–3.62 (m, 2H, H$_A$), 5.54 (m, 1H, H$_D$), 7.10–7.60 (m, ArH of DDE), 8.15–8.30 (m, ArH of BTDA) ppm; IR (KBr): 1710 and 1770 (C=O), 1380 (C–N) cm^{-1}. *Anal.* Calcd for [$0.80 \times$ (C$_{25}$H$_{20}$O$_5$N$_2$)n + $0.20 \times$ (C$_{29}$H$_{18}$O$_8$N$_2$)n]: C, 70.39%; H, 4.35%; N, 6.38%. Found C, 69.72%; H, 4.39%; N, 6.45%.
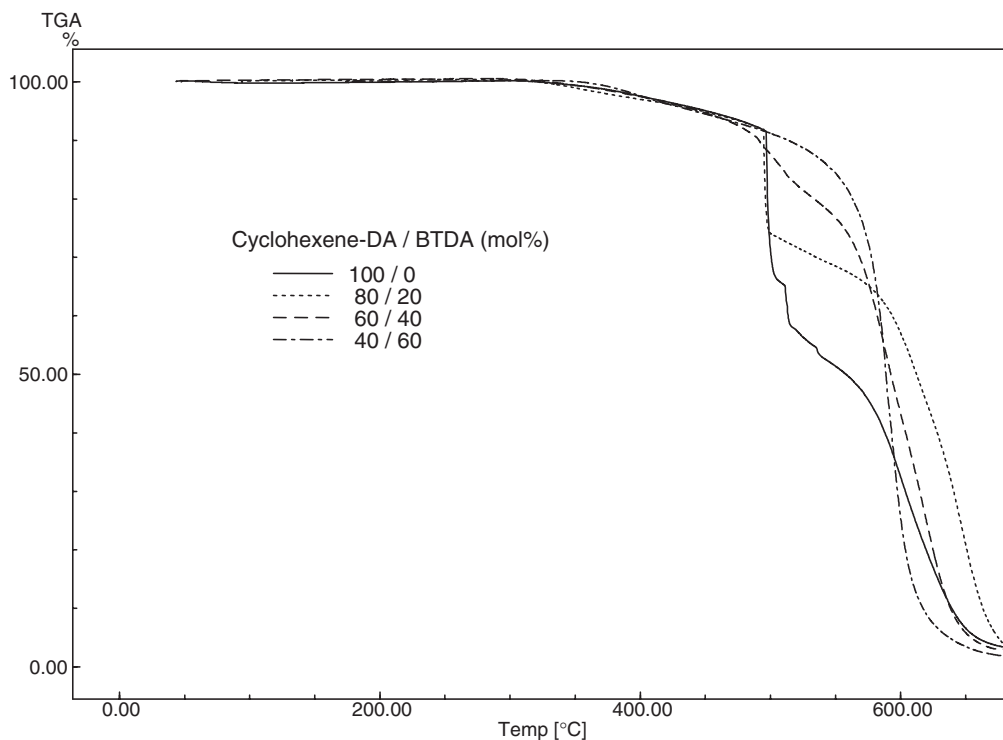
Figure 2. TGA curves of soluble polyimides and copolyimides based on cyclohexene-DA (cyclohexene-DA/BTDA/DDE) in air.

*Tetralin-DA/BTDA/DDE (80/20/100 mol %) (Figure 2)*
^{1}H NMR (DMSO-d_6): δ 1.85–1.93 (m, 1H, H_E), 2.12–2.19 (m, 2H, H_F), 3.16–3.39 (m, 2H, H_B and H_C), 3.53 (m, 2H, H_A), 4.49 (d, 1H, H_D, J = 8.4 Hz), 7.10–7.70 (m, ArH of DDE), 7.80–7.85 (m, ArH of Tetralin-DA), 8.15–8.30 (m, ArH of BTDA) ppm; IR (KBr): 1720 and 1770 (C=O), 1380 (C–N) cm^{-1}. *Anal.* Calcd for [0.80 × (C$_{28}$H$_{20}$O$_5$N$_2$)n + 0.20 × (C$_{29}$H$_{18}$O$_8$N$_2$)n]: C, 72.25%; H, 4.05%; N, 5.98%. Found C, 71.55%; H, 4.21%; N, 6.27%.

RESULTS AND DISCUSSION

The synthetic route of the polyimides and copolyimides based on cyclohexene-DA or tetralin-DA/BTDA/DDE is illustrated in Scheme 1. Two step polymerization systems including poly(amic acids) synthesis and chemical imidization were performed. 4,4′-Diaminodiphenylether (DDE) and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) were used as a diamine monomer and a comonomer respectively. Poly(amic acids) and copoly(amic acids) were obtained by reacting the mixture of tetracarboxylic dianhydride with equimolar amounts of DDE at room temperature for 12 h under a nitrogen atmosphere. Polyimides and copolyimides were obtained by chemical imidization at 120 °C in the presence of pyridine as a base catalyst and acetic anhydride as a dehydrating reagent.

The experimental results of copolymerization based on cyclohexene-DA/BTDA/DDE and tetralin-DA/BTDA/DDE are summarized in Table I. Cyclohexene-DA/DDE homopolyimide and cyclohexene-DA/BTDA/DDE copolyimides containing 40 mol % cyclohexene-DA or more were soluble in NMP, while copolyimides containing 20 mol % or less cyclohexene-DA were insoluble in NMP because of the increment of aromatic components in the polymer backbone. Tetralin-DA/DDE homopolyimide and tetralin-DA/BTDA/DDE copolyimides containing 60 mol % tetralin-DA or more were soluble in NMP, while copolyimides containing 40 mol % or less tetralin-DA were insoluble in NMP because of the increment of aromatic components in the polymer backbone. In the case of soluble polyimides, clear polyimide solutions were eventually obtained. In other cases, clear poly(amic acid) solutions were obtained as well, however, gelation or precipitation happened in the course of imidization. Dianhydride compositions in the final copolymers can be measured from ^{1}H NMR measurement (Table I). In the case of cyclohexene-DA/BTDA/DDE copolymers, the dianhydride compositions were firstly tried to calculate by the intensity ratio of aromatic protons and H_D in Figure 1. However, observed compositions of cyclohexene-DA segments (34 mol %, 41 mol %, 71 mol %, respectively) were somewhat less than initial monomer compositions of cyclohexene-DA (40 mol %, 60 mol %, 80 mol %, respectively). It was reported that 3,4-positioned cyclic double bond in cyclohexene-DA was rearranged and
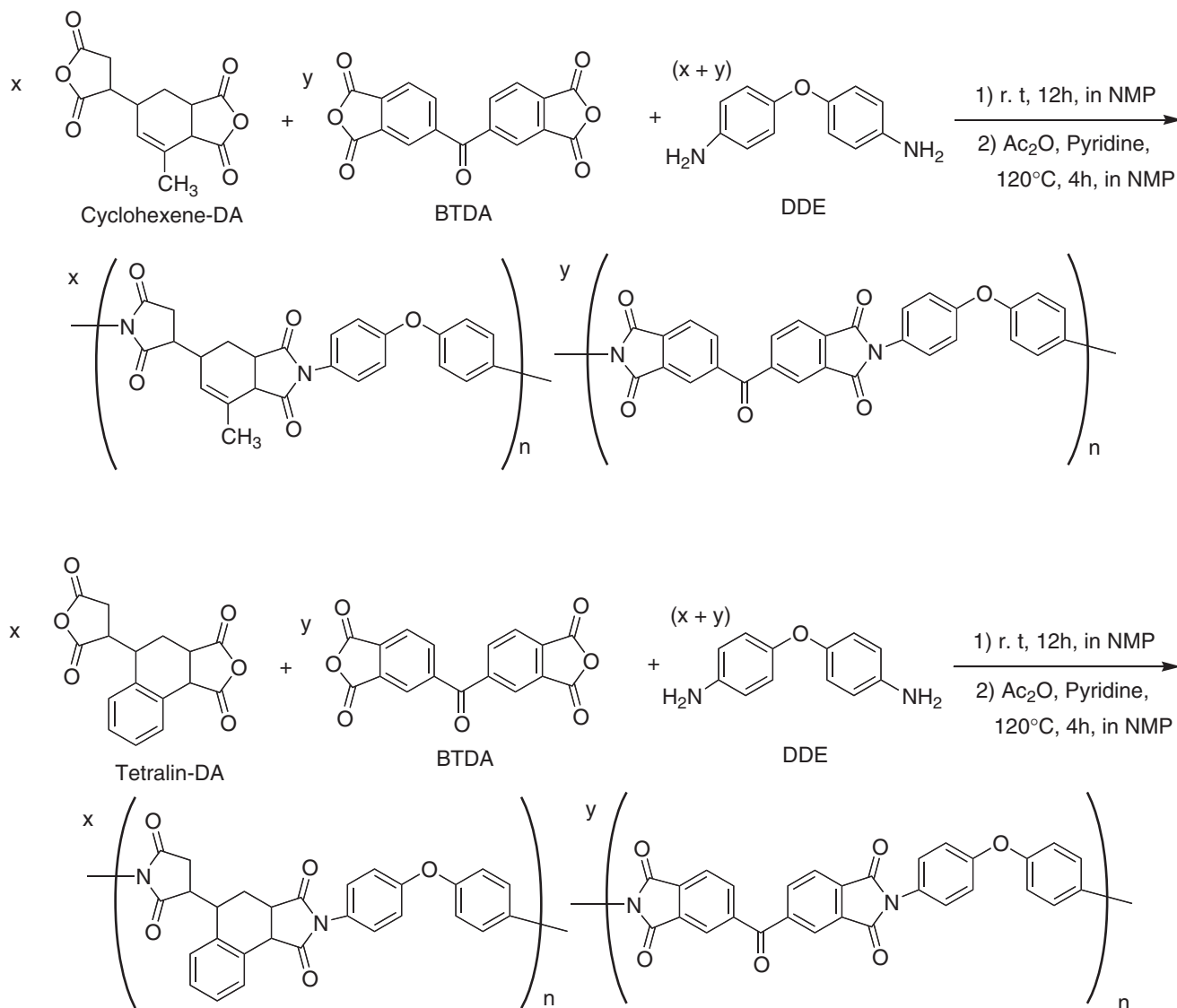
Scheme 1. Synthesis of polyimides and copolyimides based on cyclohexene-DA and tetralin-DA.

the intensity of double bond proton signal (H_D) was decreased.[27] It is speculated that above rearrangement was somewhat proceeded in these imidization systems. Thus, the dianhydride compositions were measured by the intensity ratio of aromatic protons based on BTDA and those of DDE, and observed values are in a fair agreement with the initial monomer compositions (Table I). In the case of tetralin-DA/BTDA/DDE copolyimides, the dianhydride compositions were measured by the intensity ratio of all aromatic protons and H_D in Figure 2, and observed values are in a fair agreement with the initial monomer compositions (Table I). It was observed that cyclohexene-DA was more effective than tetralin-DA for the enhancement of solubility. It can be assumed that aromatic structure in tetralin-DA slightly disturb the enhancement of solubility. The previous paper reported that TCA-AH/BTDA/DDE copolyimides containing 35 mol% or more were soluble in NMP. It can be con-

cluded that the effect of cyclohexene-DA for the enhancement of solubility is almost same as TCA-AH.

Inherent viscosities (η_{inh}) decreased by the incorporation of alicyclic tetracarboxylic dianhydride. This is probably due to the lower reactivity of these monomers compared to aromatic tetracarboxylic dianhydride such as BTDA. However obtained soluble copolyimides showed enough inherent viscosities for forming tough films.

DSC and TGA were used to evaluate the thermal properties of obtained soluble polyimides and copolyimides (Table I). T_g of polyimides and copolyimides based on cyclohexene-DA were in the range of 275–282 °C, while those based on tetralin-DA were in the range of 312–314 °C, and about were 30 °C higher than those based on cyclohexene-DA. As T_g of these polyimides are probably due to the alicyclic dianhydride segments, this rise of T_g in polyimide and copolyimides based on tetralin-DA are most prob-

Table I. Polyimides and copolyimides based on alicyclic-DA/BTDA/DDE

Dianhydride[a]		Polyamic acid		Polyimide						
Alicyclic-DA	BTDA	η_{inh}[b]	Solubility in NMP	η_{inh}[b]	Dianhydride composition[c]		T_g[f]	10% Weight loss temperature[g]		
					Alicyclic-DA	BTDA		in Air	in N$_2$	
mol %		dL g^{-1}		dL g^{-1}	mol %		°C	°C	°C	
Cyclohexene-DA										
0	100	1.22	insoluble							
20	80	0.88	insoluble							
40	60	0.86	soluble	0.51	43[d] (34)[e]	57[d] (66)[e]	not observed	512	507	
60	40	0.81	soluble	0.50	55[d] (41)[e]	45[d] (59)[e]	275	495	465	
80	20	0.79	soluble	0.55	78[d] (71)[e]	22[d] (29)[e]	282	490	457	
100	0	0.70	soluble	0.53			278	495	451	
Tetralin-DA										
0	100	1.22	insoluble							
20	80	1.14	insoluble							
40	60	0.92	insoluble							
60	40	0.83	soluble	0.57	60[e]	40[e]	314	448	480	
80	20	0.80	soluble	0.58	80[e]	20[e]	313	438	462	
100	0	0.60	soluble	0.58			312	426	449	

[a]Equimolar amount of BTDA was used to the total amount of diamine. [b]Measured at 0.5 g dL^{-1} in NMP at 30 °C. [c]Calculated from ^{1}H NMR measurement. [d]Calculated from the intensity ratio of aromatic protons based on BTDA and those of DDE. [e]Calculated from the intensity ratio of all aromatic protons and H$_D$ in Figure 2. [f]Measured by DSC at a heating rate of 10 °C/min in N$_2$ on second heating. [g]Measured by TGA at a heating rate of 10 °C/min.
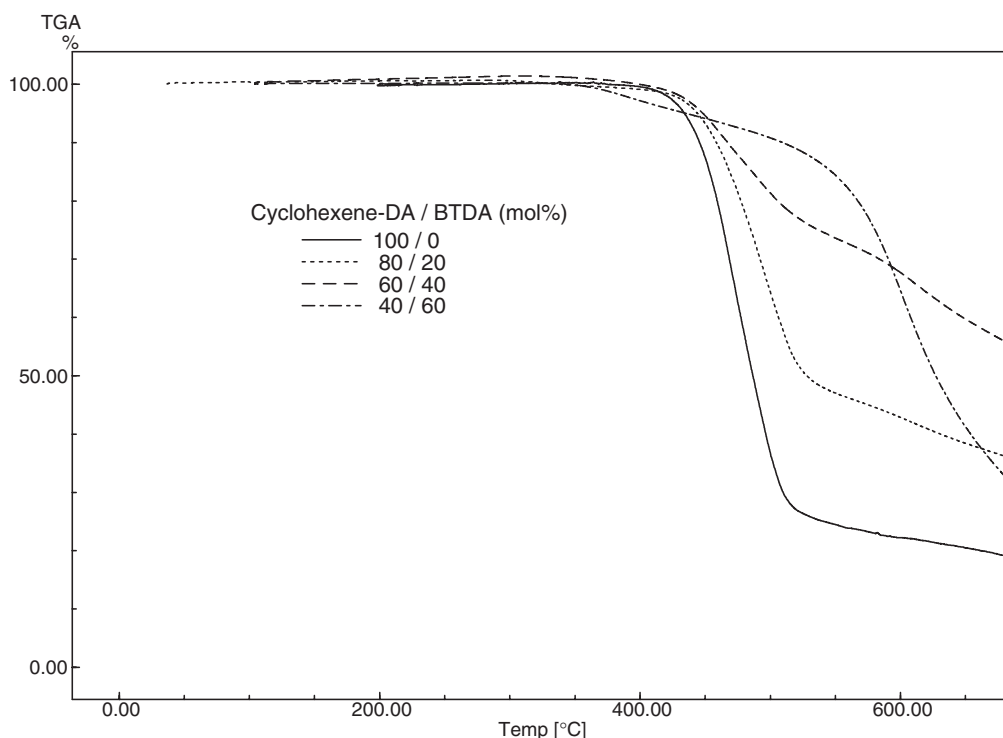

Figure 3. TGA curves of representative soluble polyimides and copolyimides based on cyclohexene-DA (cyclohexene-DA/BTDA/DDE) under nitrogen.

ably due to a rigid benzene ring in tetralin-DA moiety. The thermal stability of these copolyimides was evaluated by 10% weight-loss temperatures ($T_{d_{10}}$) in TGA measurements (Table I, Figures 2–5). The $T_{d_{10}}$ of co-

polyimides were sufficiently high and in the range of 426–512 °C in air and 449–507 °C under nitrogen (Table I). As the incorporation of BTDA resulted in a reduction of aliphatic components of the polyimides,

Table II. Solubility behavior of polyimides and copolyimides based on alicyclic-DA/BTDA/DDE in various solvents

Alicyclic-DA	BTDA	Solubility[b]							
mol %		NMP	DMF	DMAc	DMSO	DMI	m-Cresol	THF	CH$_2$Cl$_2$
Cyclohexene-DA									
40	60	S(h)	I	I	S(h)	S(h)	I	I	I
60	40	S(h)	S(h)	S(h)	S(h)	S(h)	I	I	I
80	20	S	S	S	S(h)	S(h)	I	I	I
100	0	S	S	S	S	S	S(h)	I	S
Tetraline-DA									
60	40	S(h)	S(h)	S(h)	S(h)	I	I	I	I
80	20	S(h)	S(h)	S(h)	S(h)	S(h)	I	I	I
100	0	S	S	S	S	S	S	I	I

[a] An eqimolar amount of DDE was used with respect to the total amount of tetracarboxylic dianhydride. [b] S, soluble; S(h), soluble after heating; I, insoluble.

$T_{d_{10}}$ of copolyimides tended to increase by the increment of the BTDA component. These polyimides obtained from our study show similar thermal stability compared with soluble polyimides and copolyimides based on TCA-AH/BTDA/DDE showing $T_{d_{10}}$ as 422–482 °C in air and 457–519 °C under nitrogen, while these show about 100 °C lower thermal stability compared with aromatic soluble polyimides using fluorine containing monomers such as 4,4′-hexafluoroisopropilidenedi(phtalic anhydride) (6FDA).[21] The representative TGA profiles were shown in Figures 2 and 3. The steep weight-loss in air was observed at around 500 °C in cyclohexene-DA/BTDA homopolyimides (Figure 2), and this value (about 60% weight-loss) almost corresponds to the weight content (61 wt %) of cyclohexene-DA segments in the polymers. Furthermore, the degree of weight-loss was decreased with the decrease of cyclohexene-DA contents (Figure 2). Thus, it can be speculated that cyclohexene-DA segments in polymer backbones were decomposed at about 500 °C. Similar phenomenons were observed in all polyimides and copolyimides both in air and under nitrogen. Although alicyclic moieties are tend to easily decompose compared with aromatic segments, these can still hold in polymer backbones up to about 500 °C. The $T_{d_{10}}$ of polyimides under nitrogen are generally higher than in air, however, the $T_{d_{10}}$ of polyimides based on cyclohexene-DA show opposite tendency (Table I, Figures 2 and 3). According to previous papers,[29,30] the weight increase of polymer such as polyethylene is more than the weight decrease due to volatilization of degraded materials in the earlier stage of thermal oxidation, because terminal vinyl groups in polyethylene absorb oxygen by thermal oxidation. It is speculated that the radical addition of oxygen to the allyl positions in cyclohexene-DA moieties occurs at the initial stage of degradation and $T_{d_{10}}$ in air is apparently higher than that under nitrogen.

The solubility of the obtained polyimides was determined in eight common solvents at 5 wt % concentration (Table II). The polyimides based on these alicyclic dianhydrides showed good solubility in polar solvent such as NMP, DMSO, DMI and m-cresol. It is particularly interesting that cyclohexene-DA/DDE polyimide was soluble in less polar solvent, dichloromethane. Most of copyimides based on BTDA as comonomer were less soluble than homopolyimides, but eventually soluble after heating.

In conclusion, it was confirmed that soluble polyimides based on cyclohexene-DA and tetralin-DA were easily obtained and showed the good solubility and thermal stability. As both cyclohexene-DA and tetralin-DA are commercially available, these fundamental experimental results are useful for industrial application such as polyimide alignment films for liquid crystal displays (LCDs).

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