

Preparation and Characterization of Aromatic Polyimides and Related Copolymers

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SYNOPSIS

Copolyimides containing BTDA-3DDS and BTDA-4ODA units have been synthesized by solution imidization methods. The copolyimides have high T_g 's (267–283°C) and high decomposition temperatures (540–575°C; nitrogen); both properties are dependent on composition. Those copolyimides with low concentrations of BTDA-4ODA are generally soluble in organic solvents, whereas those copolyimides with higher BTDA-4ODA content are only partially soluble or insoluble. However, all the copolyimides prepared can be compression molded. It has also been found that segmental motion above T_g is heavily suppressed in the BTDA-4ODA homopolymer relative to that in the BTDA-3DDS homopolymer. This reduction in molecular motion may severely hinder the solubility and fusibility of the BTDA-4ODA homopolymer. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Thermostable polyimides constitute a family of materials that have useful applications in both the electronic and aerospace industries because of good mechanical properties and performance at high temperatures. However, most of the polyimides synthesized by conventional two-step methods are infusible and insoluble, thereby making further processing difficult. Several approaches to improving the solubility of the polyimides have been reported. The introduction of a flexible linkage into the imide structural unit was an early idea, for it was believed at that time that rigidity was the cause of the poor solubility of the polyimides.^{1–7} Other approaches, such as attaching appropriate side groups onto the main chain, have recently been successful in improving their solubility.^{8–12} Many researchers found that solution (as distinct from thermal) imidization could improve the solubility of certain polyimides^{13–16} that were otherwise insoluble. Nevertheless, all these approaches have limitations. The ultimate solution of the problem

requires an understanding of the structure–property relation for polyimides. Relatively few studies have examined the structure–solubility and structure–processibility relations.

In this study, we synthesized a soluble aromatic polyimide by condensation of benzophenonetetracarboxylic acid dianhydride (BTDA) and 3,3'-diaminodiphenyl sulfone (3DDS) and an insoluble aromatic polyimide by condensation of BTDA and 4,4'-oxyphenyl diamine (4ODA). The solution imidization method was used to synthesize a copolymer series by systematically varying the ratios of the two diamine monomers (3DDS and 4ODA). The solubility and the processibility were evaluated as a function of this ratio. The segmental motion of the copolymers was investigated to study the structure–property relations.

EXPERIMENTAL

Materials

Benzophenonetetracarboxylic acid dianhydride (BTDA), 3,3'-diaminodiphenyl sulfone (3DDS), and 4,4'-oxyphenyl diamine (4-aminophenyl ether, 4ODA) were used as received (Chriskev Co. and Aldrich).

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N,N-Dimethylacetamide (DMAc) was purified by stirring with calcium hydride for 1 day and distilling in vacuum. *N*-Methylpyrrolidone (NMP), dichloroacetic acid (DCAA), cyclohexylpyrrolidinone (CHP), 2-methoxyethyl ether, diglyme/ethanone, and trichloroacetic acid (TCAA) were used without further purification.

Synthesis

(BTDA-3DDS) Polyimide

The synthesis essentially followed the technique reported by Summers.¹⁷ To a 250-mL flask were added 6 g (24.16 mmol) 3DDS and 7.798 g (24.200 mmol) BTDA. The system was purged, alternating nitrogen and vacuum, several times before fresh DMAc was added. Solid concentration was kept at about 15%. The mixture was stirred at room temperature under nitrogen for about 8 h to allow the viscosity to increase.

To a preheated sample (180°C, 25 mL) of CHP, the prepared polyamic acid was added through an addition funnel under nitrogen. The temperature was maintained at 175°C, and the reaction was allowed to continue for 20 h. At this temperature, water was effectively removed from the system by flowing nitrogen gas. The dark viscous solution was then poured into a large amount of a warm mixture (50/50 by volume) of diglyme/ethanone. Even though the yellowish polyimide precipitated immediately, the mixture was stirred for an additional 5 h. The polymer was then filtered and washed with large amounts of water, and dried at 200°C under vacuum for 5 days.

BTDA-ODA Polyimide

The preparation of the BTDA-ODA polyamic acid was similar to that of the BTDA-3DDS polyamic acid. Solution imidization of the BTDA-4ODA polyamic acid resulted in an early precipitation of the BTDA-4ODA polyimide. The slurry solution was stirred at 175°C for 20 h. Polyimide was obtained by precipitation into a large amount of water, filtered, and dried at 200°C in a vacuum for 5 days.

Because the polyimide prepared in this way is insoluble, BTDA-4ODA polyimide was also prepared by the conventional two-step procedure so that films of this polyimide could be made. The conventionally prepared BTDA-4ODA polyamic acid was cast onto an aluminum disk. The resulting polyamic acid film was formed by drying the disk at room temperature

for 1 day and annealed at 150°C in a vacuum for 3 h and 220°C for 2 days to convert the polyamic acid into polyimide.

BTDA-3DDS/4ODA Copolymers

In a typical example, to a 250-mL flask were added 3 g (12.082 mmol) 3DDS, 2.4193 g (12.082 mmol) 4ODA, and 7.798 g (24.200 mmol) BTDA. The reaction system was then purged, alternating nitrogen and vacuum, several times before DMAc was added. The concentration was again held at about 15% solid. The reaction was allowed to continue for 5 h at room temperature under nitrogen. Polyamic acid copolymers with different mole ratios were synthesized in a similar way. Solution imidization was then employed to obtain the respective polyimides, as in the BTDA-3DDS polyimide synthesis. The copolyimide with 60% 4ODA content precipitated from the solution after the reaction. After imidization, the copolymers were poured into a large amount of diglyme/ethanone mixture (50/50 by volume), filtered, washed with water, and dried at 220°C in a vacuum for 5 days.

Copolymer Characterization

The intrinsic viscosities of the copolymers that were soluble in DMAc were measured in this solvent at 30°C. The intrinsic viscosity of copolymers that were not soluble in DMAc were measured in trichloroacetic acid at 65°C.

The glass transition temperatures and thermogravimetric analyses of the copolymers were determined with a Perkin-Elmer DSC-7 and a TGA module, using heating rates of 40°/min and 10°/min, respectively. Dynamic mechanical thermal analysis (DMTA) was performed using the Polymer Laboratory DMTA system and a heating rate of 3°/min at a frequency of 1 Hz. Samples for the DMTA were prepared by compression molding at 300–325°C, dependent on the T_g of the particular polymer or copolymer, in vacuum. For the infusible polyimide of (BTDA-4ODA), film was obtained through solid-state curing of the polyamic acid film.

RESULTS AND DISCUSSION

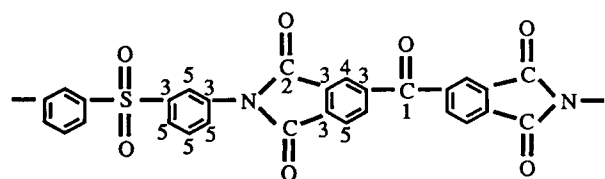
Structure and Properties

Solution imidization has been shown to improve the solubility of the polyimide products relative to that of polyimides made by thermal imidization.^{14–16} In

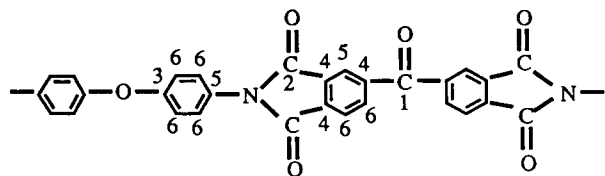
this study, we adopted the synthesis procedure of Summers^{16,17} for the imidization of polyamic acid. The CHP/NMP system has been shown to be a good medium for high-temperature removal of the water that is generated in the cyclization reaction. We used DMAc rather than NMP in the synthesis of the polyamic acids because of the high boiling point of NMP. The molecular structures of both BTDA-3DDS and BTDA-4ODA are shown in Scheme 1. In all cases, a yellowish powder was obtained and all the polyimides were amorphous, as determined by x-ray diffraction (not shown here).

Figure 1 shows the solid-state high-resolution carbon-13 nuclear magnetic resonance (NMR) spectra of both homopolyimides and copolyimides. The chemical shift assignments are shown in Table I; the corresponding carbons are indicated in Scheme 1. Solution NMR spectra are not available because some of the copolyimides were not soluble in common solvents. The resonances were generally broad; and, because all the carbons are aromatic, many resonances overlapped one another. Information about the sequence distributions thus cannot be inferred from the spectra. However, the subunit sequence should be regarded as lying between alternating and random, because the oxyphenyl diamine (4ODA) is known to be more reactive than the diaminodiphenyl sulfone. It is likely that most of the 4ODA forms dimers and trimers with BTDA before reacting with DDS; the functional dimers or trimers then react further with the amine groups of the 3DDS to form high-molecular-weight copolymers.

The molecular weights (as inferred from the vis-



BTDA-3DDS



BTDA-4ODA

Scheme 1

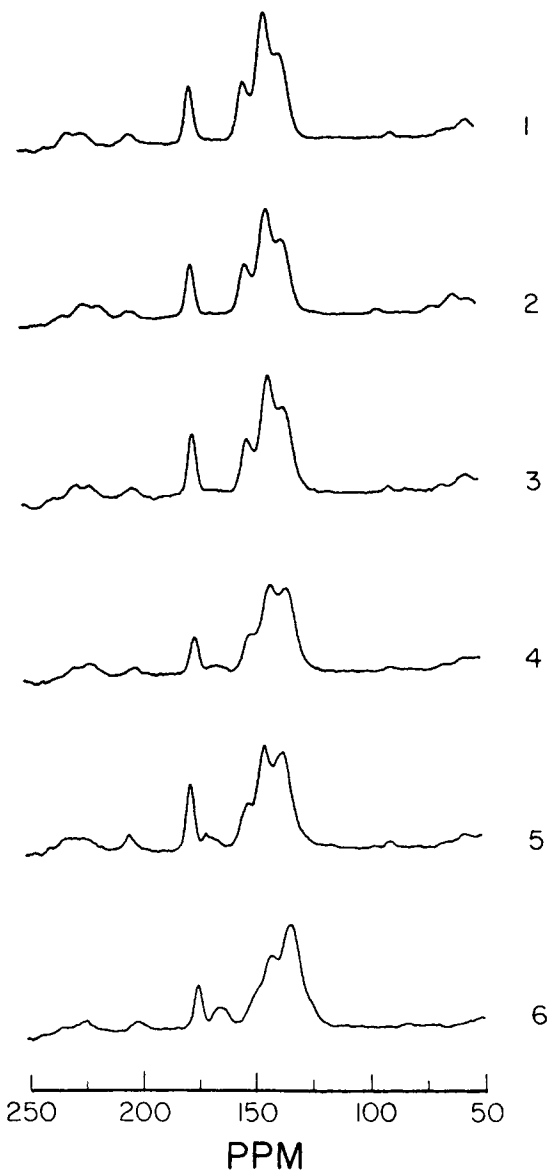


Figure 1 High-resolution carbon-13 NMR spectra of the homopolyimides and copolyimides. (1) BTDA-3DDS; (2) BTDA-3DDS/4ODA, 90/10; (3) BTDA-3DDS/4ODA, 80/20; (4) BTDA-3DDS/4ODA, 60/40; (5) BTDA-3DDS/4ODA, 40/60; (6) BTDA-4ODA.

cosities) of the copolyimides were generally higher at higher contents of the 4ODA unit. The polyamic acid solution of the BTDA-4ODA homopolymer had the highest viscosity in DMAc. Table II lists the viscosities of the homo- and copolyimides. The low viscosity of BTDA-4ODA homopolyimide (Table II) may be due to degradation during film formation in air. An increase of molecular weight during thermal imidization was not seen.

Table I Chemical Assignments of the ^{13}C NMR Spectra

BTDA-4ODA		BTDA-3DDS	
Chemical Shift (ppm)	Carbon Position ^a	Chemical Shift (ppm)	Carbon Position ^a
203	1	203	1
175	2	174	2
160	3	150	3
150	4	145	4
145	5	135	5
135	6		

^a See Scheme 1.

The BTDA-3DDS polyimide and the 90/10 BTDA-3DDS/4ODA copolyimide were soluble in DMAc when heated. However, BTDA-3DDS/4ODA copolyimides of 20–40% 4ODA content could only be swollen in boiling DMAc. A higher content of 4ODA in the copolyimide resulted in complete insolubility in DMAc, even though the copolymers were imidized in solution. Obviously, there is a transition of copolyimide solubility in DMAc at a composition of about 20–40% 4ODA. These results are summarized in Table III.

The fusibility of the copolymers is also shown in Table III. This property is defined in the table. The fusibility and the solubility of the series of copolymers both decreased as the 4ODA concentration increased, but their declines were not equivalent (i.e., solubility disappeared first), so certain fusible copolymers were regarded as insoluble. All the polyimides except the BTDA-4ODA homopolymer were fusible above their T_g under pressure. Transparent films were obtained in this way for the measurement of dynamic mechanical properties. After compression molding, the polymers became only partially soluble in DMAc but were still soluble in acid solvents.

Figure 2 shows the glass transition temperatures of six polyimides. The T_g increased as a function of 4ODA content. The glass transition temperatures of the homopolyimides were similar (i.e., 268° and 283°C for BTDA-3DDS and BTDA-4ODA, respectively) and agree with literature values. This similarity of the T_g 's suggests that the two macromolecular chains have similar flexibilities.

Cross-linking and rigidity of the polyimide chains are considered to be the two major factors causing the insolubility of the aromatic polyimides.^{18–22} Intermolecular instead of intramolecular cyclization

leads to the formation of a cross-linked network; and intermolecular imidization may occur in the solid-state reaction at high temperature.^{18–20} Imidization in solution, however, significantly reduces the possibility of such cross-linking. Rigidity of a polyimide severely hinders its molecular motion and affects the solubility properties.^{21,22} Rigidity of a polyimide is usually inferred from a high glass transition temperature. However, the results discussed above indicate that cross-linking and rigidity are not the probable cause of polyimide insolubility. The fact that the high-4ODA-containing copolyimides are insoluble in DMAc but soluble in stronger solvents such as dichloroacetic acid, which can form hydrogen bonds with the polymer, suggests that the high-4ODA-containing copolyimides have stronger intermolecular interactions. The glass transition temperatures of the copolyimides vary only slightly with composition, a result indicating similar flexibilities of the polymer chains (as shown in Fig. 2).

Figure 3 shows the dynamic mechanical response as a function of temperature for the polyimides. Figure 3(A) is the storage moduli of the homo- and copolyimides and Figure 3(B) is the loss tangents of the homo- and copolyimides. The α -transitions shown in Figure 3(B) were consistent with the T_g data obtained by differential scanning calorimetry (DSC). However, the intensity of the loss tangent of the α relaxation markedly decreased as the 4ODA content increased. This observation is in agreement with the trends in solubility and fusibility discussed above. The loss tangent is related to the energy absorption due to segmental motion of the molecular chain at a given frequency; the intensity of the loss tangent is also characteristic of the extent of the onset of segmental motion at the glass-rubber transition temperature. A relatively low segmental motion at higher temperatures leads to high bulk viscosity (other factors being equal) and therefore to

Table II Intrinsic Viscosity of Polyimides

BTDA-3DSS/4ODA Composition (mol %/mol %)	Viscosity (dL/g)
100/0	0.39 ^a
90/10	0.35 ^a
80/20	0.38 ^b
60/40	0.60 ^b
40/60	0.50 ^b
0/100	0.36 ^b

^a Measured at 30°C in *N,N*-dimethylacetamide.

^b Measured at 65°C in trichloroacetic acid.

Table III Solubility and Fusibility of Polyimides

Composition of BTDA-3DDS/4ODA (mol %/mol %)	Solubility ^{a,b}				Fusibility ^c
	DMAc	NMP	DCAA	TCAA	
100/0	s	s	s	s	+
90/10	s	s	s	s	+
80/20	p	p	s	s	+
60/40	p	p	s	s	+
40/60	I	I	s	s	+
0/100	I	I	s	s	-

^a DMAc, *N,N*-dimethylacetamide; NMP, *N*-methylpyrrolidone; DCAA, dichloroacetic acid; TCAA, trichloroacetic acid.

^b s, soluble; p, partially soluble; I, insoluble.

^c +, fusible; -, not fusible. Determined by testing for compression molding at about 50 degrees above the T_g . If transparent films were obtained, the copolymer was defined as fusible.

difficulties in processing; in this case, in the BTDA-4ODA polyimide the increase in the segmental motion was so small that the homopolymer could be expected to be insoluble and infusible. Consequently, we postulate that, as the concentration of the 4ODA units increased in this series of copolyimides, the subsequent decrease in segmental motion resulted in the observed decrease in the solubility and the processibility of the copolyimides. The specific structural factor hindering the motion of BTDA-4ODA polyimide is not clear, although it is probably related to the very strong intermolecular interaction or dipole coupling in the system.

Thermal Stability

Figure 4 shows the thermogravimetric analysis of the two homopolyimides and their copolyimides. The

thermal decomposition temperatures of the homopolyimides and their copolyimides were generally high, with the BTDA-4ODA polyimide decomposing at 575°C under nitrogen and the homopolyimide of BTDA-3DDS decomposing at 545°C. The decomposition temperatures of the copolyimides normally lay between those of the homopolyimides. However, the decomposition temperatures of the 10% and 20% copolymers were lower than those of the homopolyimides.

CONCLUSIONS

Aromatic homopolyimides and their copolyimides with high thermal stability were synthesized. The insolubility and the infusibility of the BTDA-4ODA polyimide were attributed to the relative immobility

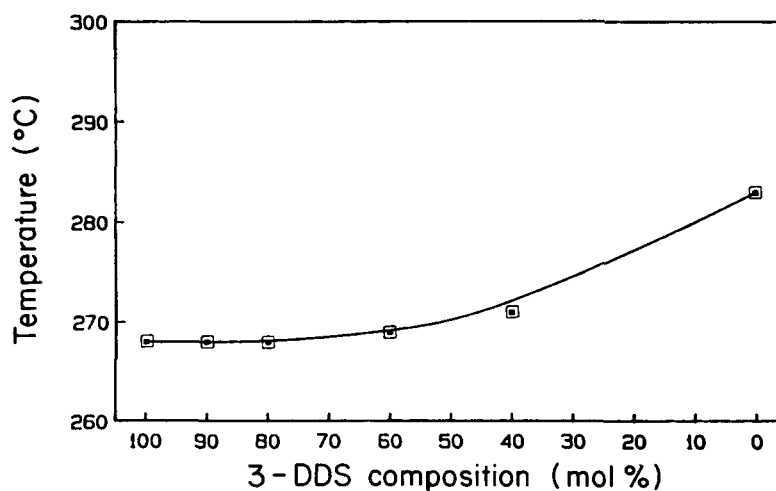


Figure 2 Glass transition temperatures of the copolyimides as a function of composition.

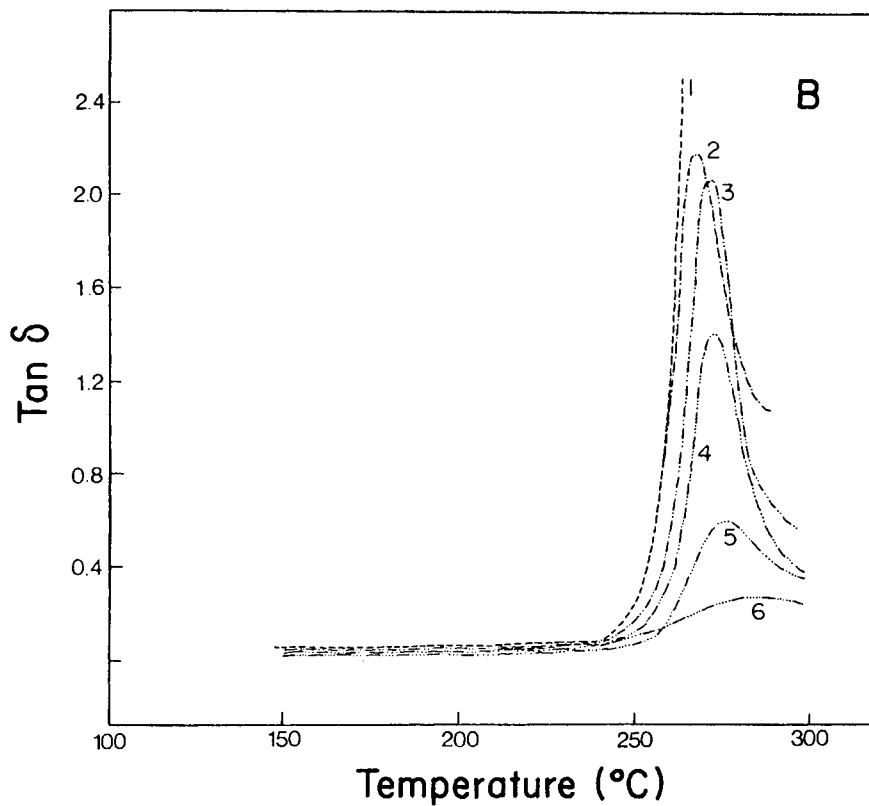
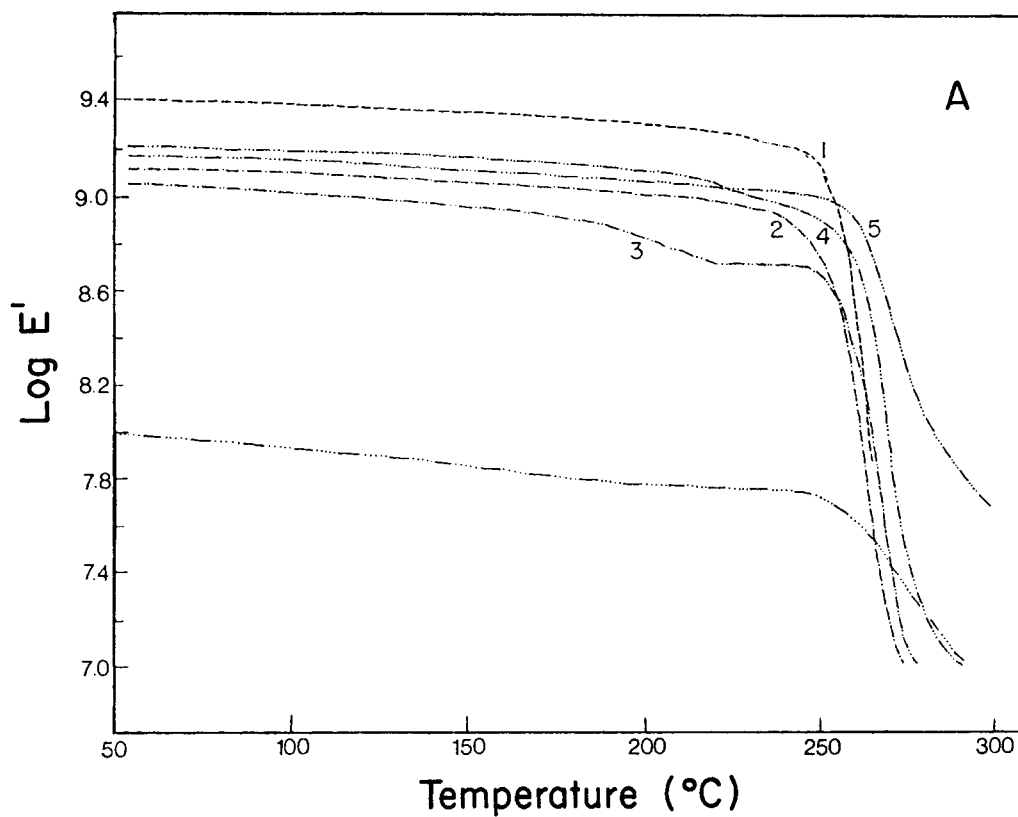


Figure 3 Dynamic mechanical thermal analyses of the homo- and copolyimides. (A) Storage moduli of homo- and copolyimides. E' is in pascals. (B) Loss tangents of homo- and copolyimides. (1) BTDA-3DDS; (2) BTDA-3DDS/4ODA, 90/10; (3) BTDA-3DDS/4ODA, 80/20; (4) BTDA-3DDS/4ODA, 60/40; (5) BTDA-3DDS/4ODA, 40/60; (6) BTDA-4ODA.

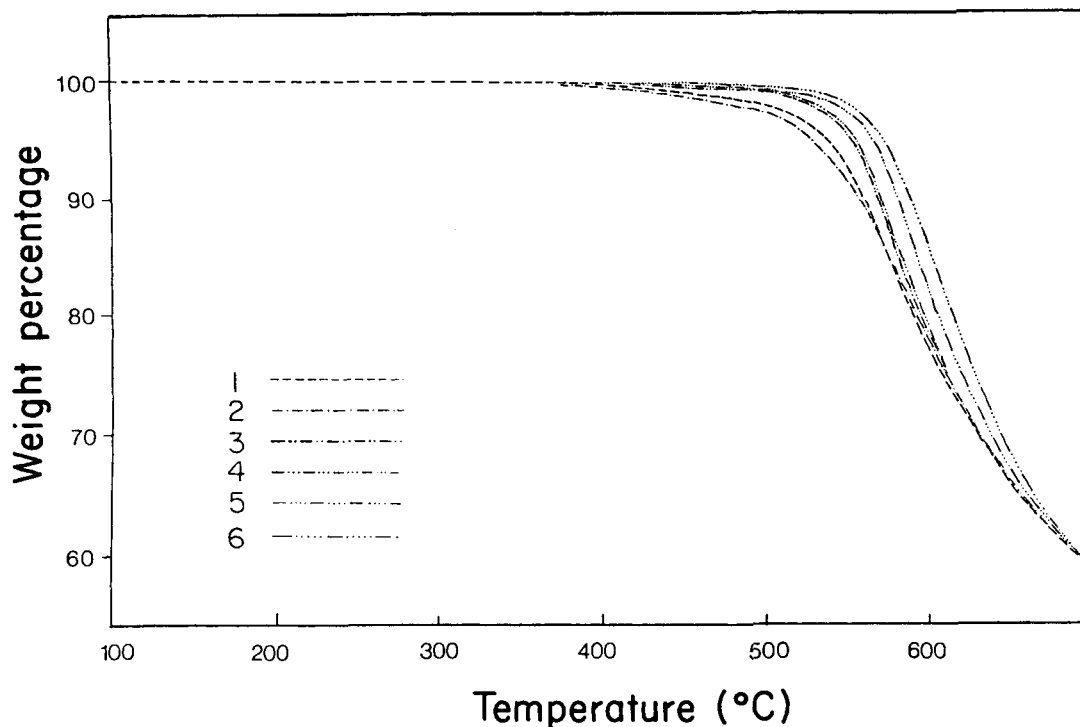


Figure 4 TGA of the homo- and copolyimides. (1) BTDA-3DDS; (2) BTDA-3DDS/4ODA, 90/10; (3) BTDA-3DDS/4ODA, 80/20; (4) BTDA-3DDS/4ODA, 60/40; (5) BTDA-3DDS/4ODA, 40/60; (6) BTDA-4ODA.

of the segments at high temperature, which was probably a result of the very strong intermolecular interaction of BTDA-4ODA segments. The solubility of this homopolymer could be improved by copolymerizing with a polyimide having very mobile segments, such as the BTDA-3DDS moiety. The copolymer retained the excellent solvent resistance of the BTDA-4ODA polyimide while showing a significant improvement in processibility. The thermal stability of the copolyimide was dependent on the structure of both components and on the copolymer composition.

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