Copolyimides Using 3-Phenyl Tricyclo[6,2,2,0^{2,7}]Dodeca-2,11-ENE-5,6,9,10-Tetracarboxylic Dianhydride as a Thermosetting Functional Group: Preparation, Characterization, and Thermal Curing Chemistry

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SYNOPSIS

Copolyimides were prepared by the reaction of 4,4'-oxydianiline (ODA) with two dianhydrides, namely, 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 3-phenyl tricyclo[6,2,2,0^{2,7}]dodeca-2,11-ene-5,6,9,10-tetracarboxylic dianhydride (PTDDA). ODA and BTDA first reacted in DMAc solvent, then following the addition of PTDDA, which was used as a thermosetting functional group in the polymer's backbone. Two homopolyimides prepared from the reaction of ODA with BTDA or PTDDA were also synthesized. The properties of homopolyimides such as solubility, thermal properties, and thermal curing mechanism were compared to those of copolyimides. The results showed that the tricyclic structure of the PTDDA unit underwent a reverse Diels–Alder reaction at near 300°C and it controlled the thermal behaviors of copolyimides.

INTRODUCTION

Polyimides[1-3] have been prepared conventionally by the condensation of a diamine with a dianhydride in amide solvents, such as NMP and DMAc. The intermediate, polyamic acid can be imidized by a thermal method[4] or a chemical method.[5,6] In general, the former usually gave a less soluble polyimide due to slight cross-linking in air.[7] However, 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) or pyromellitic dianhydride (PMDA) with 4,4'-oxydianiline (ODA) formed a polyimide that cannot dissolve in common organic solvents, imidized with either a thermal or chemical method. Copolymerization[7] should be useful to modify the solubility of these polymers.

In our laboratory, we prepared a dianhydride, 3-phenyl tricyclo[6,2,2,0^{2,7}]dodeca-2,11-ene-5,6,9,10-tetracarboxylic dianhydride (PTDDA),[8] which was formed by consecutive Diels–Alder addition reactions of the maleic anhydride molecule to 1,1-diphenyl ethylene as shown in Scheme (a). A similar synthetic method was reported in a patent,[9] in which alkyl-substituted styrene instead of 1,1-diphenyl ethylene was used.

In this study, we select our dianhydride as a comonomer during copolymerization due to its special thermosetting functionality. In addition to the characterizations of polymers concerned, their thermal curing chemistry was another important subject.

EXPERIMENTAL

Preparation of 3-Phenyl Tricyclo[6,2,2,0^{2,7}]dodeca-2,11-ene-5,6,9,10-tetracarboxylic Dianhydride (PTDDA)

To a 500 mL three-necked flask, equipped with a reflux condenser and a dropping funnel, 40 g (0.41 mol) of maleic anhydride, 30 mL toluene, and 0.34 g (0.0013 mol) N,N'-diphenyl-1,4-phenylene diamine were added with stirring. The flask was heated with a pan of silicone oil to dissolve the mixture by refluxing at 130°C. 1,1-Diphenyl ethylene, 36 g (0.2 mol), was then added dropwise from a funnel under nitrogen. After the completion of the addition, the reacting mixture was refluxed for an additional hour.
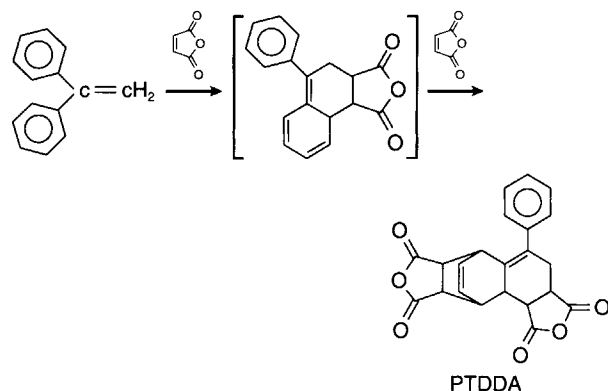
Scheme (a)

The dianhydride precipitated from the cooled solution was filtered off and dried at 200°C.

Preparation of Polyimides

3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA; x mol fraction) was added to a stirred solution of 1 mol of 4,4'-oxydianiline (ODA) in dimethyl acetamide (DMAc, solids content 8–12% w/w) under N_2 at room temperature. The solution was stirred for 2 h; then, PTDDA (y mol fraction) was added. The reaction mixtures were stirred for another 24 h. After that, the solution was imidized by distilling water with toluene at 190°C and dehydration was continued for 8 h. The cooled solution was poured into a large excess of ethanol, and the precipitated polyimide was filtered, washed with acetone, and dried at 150°C under vacuum.

The Preparation of Model Bismaleimide and Cured Bismaleimide

To a 500 mL two-necked flask, ODA (0.1 mol) was dissolved in DMAc solvent. Maleic anhydride, 19.6 g (0.2 mol), was added with stirring at room temperature. After the mixture reacted for 3 h, chemical imidization was performed by the addition of acetic anhydride and CH_3COONa. The solution was heated to 70°C and dehydration was continued for 8 h at the same temperature. The cooled solution was precipitated by water, filtered, washed with acetone, and dried. The yellow bismaleimide was further cured at 340°C and analyzed by IR and ^{13}C-NMR instruments.

TG and DSC Thermography

A Dupont 2100 thermal analyzer having a TG 951 module and a DSC module was used to evaluate the thermal behavior of polyimides. The TG measurements were done in a N_2 atmosphere (flow rate: 50 cm^3/min) at a heating rate of 10°C/min. Isothermal TG studies of the polyimides at their maximum rate of decomposition were carried out in N_2. Before isothermal TG studies, the polyimides had been preheated to 240°C for 1 h to eliminate the absorbed water. DSC studies were carried out in N_2 gas at a heating rate of 20°C/min.

Instrumentation

Infrared and mass spectra were recorded with a Perkin-Elmer 842 and Joel D100 or JMS-HX110 spectrophotometers, respectively. Solid-state ^{13}C-NMR spectra were obtained from a Bruker MSL200 spectrometer. Viscosity measurements were carried out with a 0.5% (w/v) solution in DMAc at 30°C using an Ubbelhode suspended level viscometer.

RESULTS AND DISCUSSION

Preparation and Characterization of the Polyimides

The synthesis of polyimides are based on the reactions as shown in Scheme (b). BTDA and ODA first reacted in DMAc for 2 h, then following the addition of PTDDA, to complete copolymerization. The soluble polyamic acid solution with 8–12% solid concentration was then imidized by distilling water with toluene or thermal treatment. The polyimide chain in Scheme (b) was composed of two structural units, namely, BTDA/ODA and PTDDA/ODA.

Several things affected molecular weight, such as solvents, purity of the comonomers, temperature of the reaction, and steric structure of the monomer. All would give rise to the variation of molecular weight. Table I shows the inherent viscosities of polyamic acids. It was obvious that the molecular weight of polyimides decreased with PTDDA content. The low viscosity, as PTDDA was introduced, was attributed to the high steric structure[8] of PTDDA, which caused low polymerization.

The identification of polyamic acids and polyimides were characterized by IR spectra. The IR spectra of polyamic acids showed major absorption peaks at 1670, 1535, and 1720 cm^{-1}, assigned to the amide (I) band, amide (II) band, and carbonyl groups ($\backslash C = O$), respectively. As the degree of imidization increased, these absorption bands of polyamic acids gradually decreased or disappeared. Figure 1
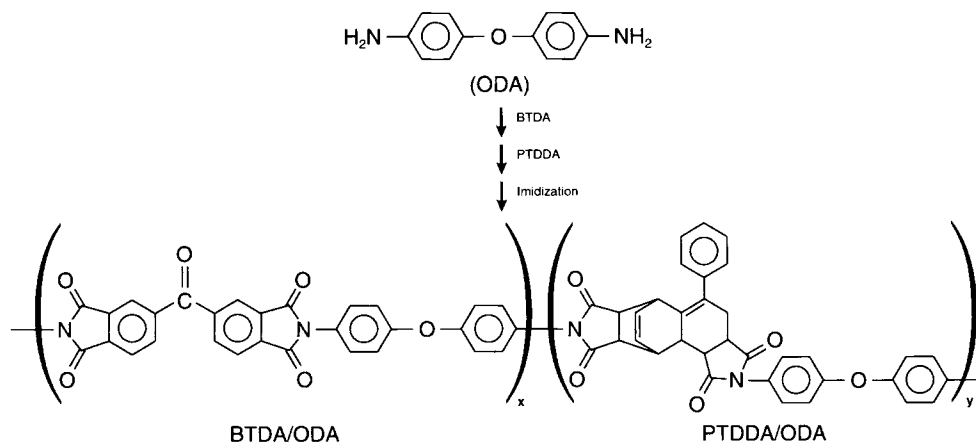
Scheme (b)

shows the IR spectra of three polyimides. In the spectra of imides, the characteristic bands were at 1780, 1715, 1380, and 1240 cm^{-1}. The bands at 1780 and 1715 cm^{-1} are commonly attributed to the symmetric and asymmetric stretches of carbonyl groups of imide. The C — N band at 1380 cm^{-1} verified the formation of the imide structure. The band at 1240 cm^{-1} was the absorption of the C — O — C stretch. The spectrum of copolyimide in Figure 1(b) showed the absorption of alkane C — H stretching vibrations at 2750–2950 cm^{-1}, revealing the incorporation of PTDDA into copolyimide.

To comprehend the effect of PTDDA in copolyimides, solubility was tested. The solubilities of polyimides were tested at 5% solids (w/w) in NMP, DMAc, and DMF. Results were given in Table II. In this table, polyimide 1 from the homopolymerization of PTDDA with ODA could easily dissolve

in testing solvents. However, the copolyimides were not all soluble. A higher mol ratio of BTDA would increase the symmetry and regularity of the polymer's structure, which resulted in decreasing the solubility of polymer. As seen in Table II, copolyimide with the mol ratio of two dianhydrides (BTDA/PTDDA) at 0.5/0.5 was soluble in DMF, DMAc, and NMP solvents, but copolyimide 3 prepared by 0.7/0.3 mol ratio of two dianhydrides was only soluble in NMP solvent. Polyimides 4 and 5 were not soluble in the above solvents.

Table I The Properties of Polyimides

Polyimide	x^a	y^b	η_{inh}^c	Solubility^d		
				NMP	DMAc	DMF
1	0.0	1.0	0.31	s	s	s
2	0.5	0.5	0.47	s	s	s
3	0.7	0.3	0.49	s	p	p
4	0.8	0.2	0.62	i	i	i
5	1.0	0.0	0.89	i	i	i

^{a} The composition (%) of BTDA/ODA.
^{b} The composition (%) of PTDDA/ODA.
^{c} The inherent viscosities of polyimides 2–5 were determined in DMAc (0.5 w/v %) at 30°C; polyimide 1 was measured in NMP.
^{d} The solubility of polyimide obtained by the chemical method was tested in powder form at 5% solid content. s = soluble; p = partially soluble; i = insoluble.
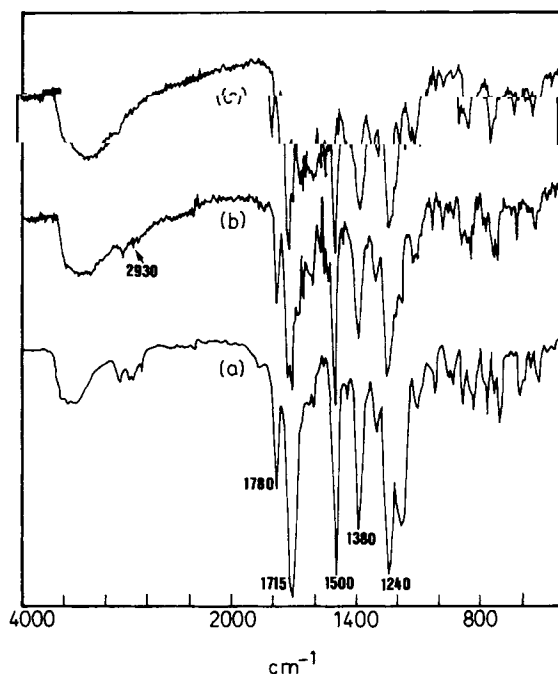

Figure 1 IR spectra of polyimides: (a) polyimide **1**; x = 0, y = 1; (b) polyimide **2**; x = y = 0.5; (c) polyimide **5**; x = 1, y = 0.

Table II   The Thermal Properties of Polyimides

Polyimide	$T_g{}^a$	$T_{d1}{}^b$	$T_1{}^c$	$T_2{}^c$	$T_3{}^c$	$I_{wl}{}^d$ (%)	$A_{wl}{}^e$ (%)
1	219	305	350	450	—	33.33	32.83
2	261	307	346	450	600	17.54	17.84
3	264	307	350	—	605	10.75	11.06
4	—	307	350	—	605	7.25	7.32
5	279	532	—	—	600	—	—

[a] T_g was determined by DSC with a heating rate at 20°C/min.

[b] T_{d1} refers to the initial decomposition temperature at the first stage by extrapolation from the TGA thermogram.

[c] $T_{1,2,3}$ represents the maximum rate of decomposition at each decomposition stage.

[d] I_{wl} denotes the ideally calculated weight loss percent 1,1-diphenyl ethylene (MW = 180).

[e] A_{wl} denotes the actual weight loss percent studied by isothermal TGA.

Thermal Properties of Polyimides

Glass transition temperature (T_g) and thermal stability were the major characteristics of polymers. The T_g value not only depends on the composition of the comonomer constituting the copolymer, but is also sensitive to the mode of arrangement of the comonomers. Figure 2 shows the DSC thermograms of three copolyimides and two homopolymers. T_g values of the two homopolymers could be clearly identified at 219 and 279°C (280°C)[7] for polyimide
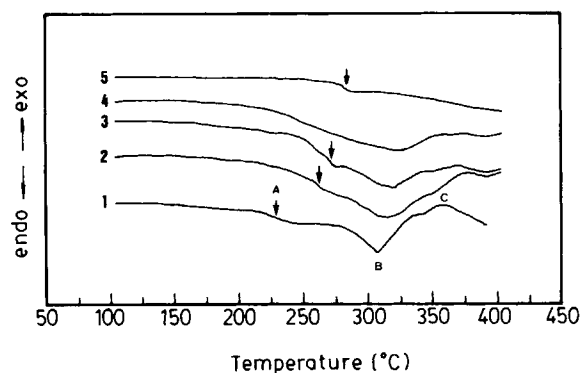

Figure 2   DSC thermograms of polyimides 1–5; (A) glass transition temperature; (B) endothermic peak; (C) exothermic peak.

1 and polyimide 5, respectively, while those of copolyimides 2 and 3 were observed at about 260°C. However, the transition region of copolyimide 4 was covered by an endothermic peak occurring at 270–325°C. All the T_g values are listed in Table II. The reason for the low T_g value of polyimide 1 might be attributed to the low packing of molecular chain from the high steric structure of PTDDA. X-ray diffraction in polyimide 1 verified that only a small degree of crystallinity[8] was observed. Since the T_g value of polyimide 1 was far lower than that of polyimide 5, we expected that the T_g of copolyimide

Bismaleimide
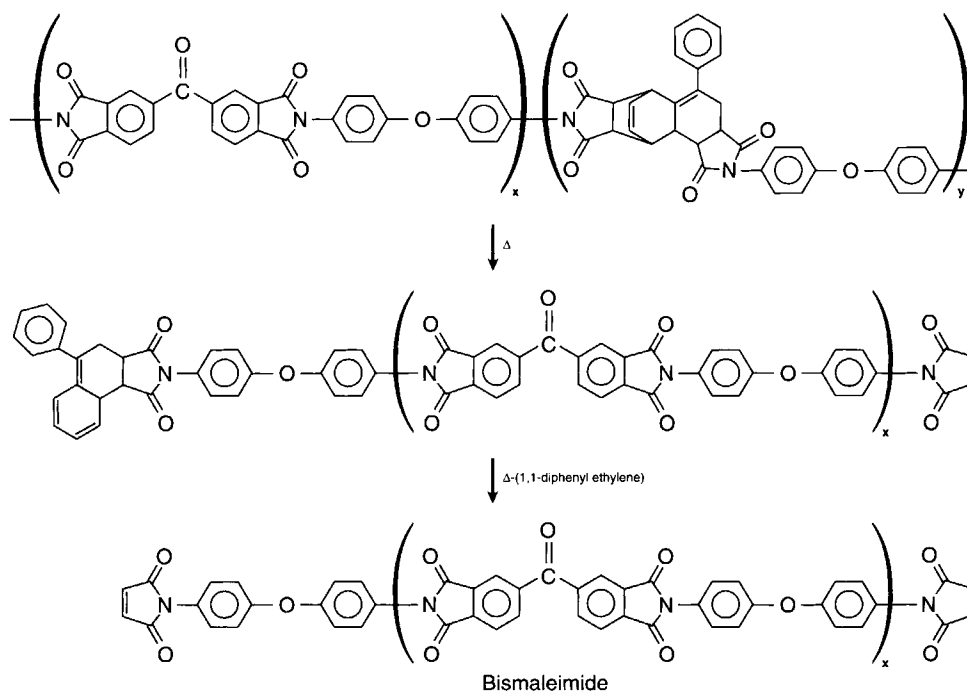
Scheme (c)

is in the range between the values of the parent homopolyimides and it is controlled by the chain segments of the BTDA/ODA structural unit [Scheme (b)], while the PTDDA monomer was added behind BTDA during copolymerization. Copolyimide having longer chain segments of the BTDA/ODA structural unit would show higher T_g values. Thus, the T_g order of polyimides is **5 > 4** (expected) **> 3 > 2 > 1.**

The endothermic peak in Figure 2 was interesting and further investigation was needed. We proposed that the endothermic peak was not a melting mode but a reverse Diels–Alder reaction occurring in the molecular chain. Several reports[10] showed that the reverse Diels–Alder degradation was an endothermic reaction. Wong and Ritchey[11] also showed the DSC thermogram of norborene end-capped prepolyimides and indicated that the endothermic peak occurring at 250–320°C was due to a reverse Diels–Alder reaction. Similar phenomenon was observed for our present polyimides **1–4.** The endothermic peak was in the range of 270–325°C. A possible thermal mechanism based on a reverse Diels–Alder reaction is shown in Scheme (c). In this scheme, polyimide lost 1,1-diphenyl ethylene and was decomposed to a bismaleimide that could undergo further polymerization by thermal curing. In the DSC thermogram (Fig. 2), the polymerization reaction of bismaleimide was also observed at over 325°C and polyimide **1** [x = 0 in Scheme (c)] showed an outstanding exothermic peak.

The thermal stabilities of copolyimides and homopolyimides were further evaluated by thermogravimetric analysis (TGA). Figure 3 shows the TGA thermograms of these polymers. Homopolymer of polyimide **5** decomposed at over 500°C, as re-
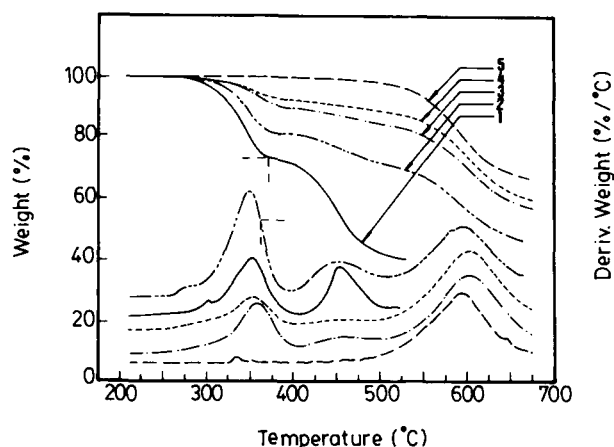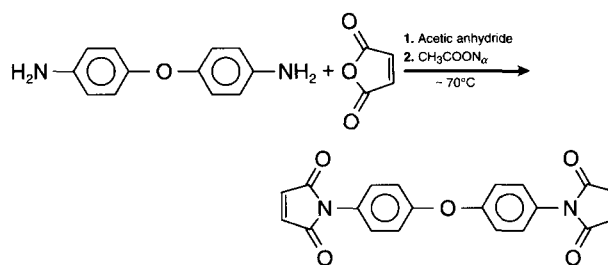

Scheme (d)

ported in the literature.[12] However, homopolymer of polyimide **1** decomposed in two stages, occurring at about 300 and 400°C, respectively. The first stage at 300°C was attributed to the decomposition of the tricyclic structural unit of the polymers. In this stage, a reverse Diels–Alder decomposition losing 1,1-diphenyl ethylene occurred as discussed for the DSC thermogram. Over 400°C, the thermal cured bismaleimide further decomposed.[13] In copolyimides, the thermal stabilities at the second stage obviously increase with increasing BTDA content. Table II shows the decomposition temperatures of the polyimides.

Characterizations of Thermal Curing Chemistry

The thermal curing chemistry in Scheme (c) can be further characterized by isothermal TGA, IR, NMR, and mass spectra. Isothermal TGA studies operated at the maximum decomposition rate of the first stage (near 355°C) were tested to predict possible thermal curing mechanisms. Upon thermal curing, the actual weight loss (%) can be calculated by means of initial
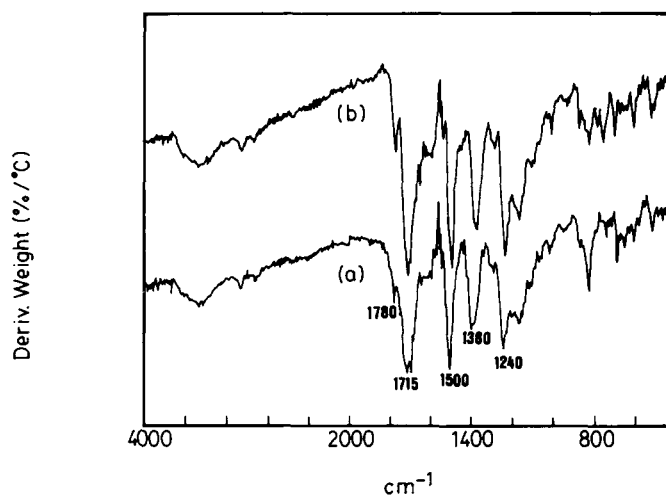

Figure 3 TGA thermograms of polyimides **1–5.**

Figure 4 IR spectra of (a) cured polyimide **1** and (b) cured bismaleimide.

weight and final equilibrium weight. The results are shown in Table II and polyimides **1–4** lost 32.83, 17.84, 11.06, and 7.32% by weight, respectively. We calculated the theoretical weight loss (%) of polyimides **1–4** and found that the loss of 1,1-diphenyl ethylene from polyimides **1–4** as shown in Scheme (c) were 33.33, 17.54, 10.75, and 7.25 wt %, which corresponded to the actual loss studied by isothermal TGA. This fact showed that Scheme (c) could be a major decomposition reaction, which produced 1,1-diphenyl ethylene and bismaleimide. Mass spectroscopy further verified the formation of 1,1-diphenyl ethylene (MW = 180). Samples were directly decomposed in a mass spectrometer, which was considered to be similar to the decomposition by TGA. We observed the formation of the m/e = 180 peak at a probe temperature near 300°C for polyimides **1–4** and confirmed the formation of 1,1-diphenyl ethylene. The solid-state cured bismaleimide residues from the decomposition of polyimides were further verified by IR and solid-state ^{13}C-NMR spectra. In this section, we introduce a bismaleimide model compound that was prepared as shown in Scheme (d) and that was cured at 340°C for comparison. Figure 4 shows the IR spectra of cured polyimide **1** and cured model bismaleimide. All spectra had imide characteristics at 1780 cm^{-1} ($\diagdown$C=O),

1715 cm^{-1} ($\diagdown$C=O), and 1380 cm^{-1} (C—N) and still presented C—O—C asymmetric stretching vibration at 1240 cm^{-1}. In comparison between the

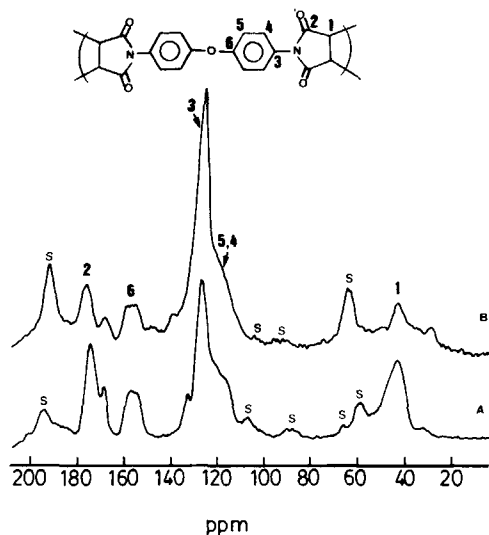two cured compounds, the IR spectra seemed to be similar. Solid-state ^{13}C-NMR spectra of cured polyimide **1** and cured model bismaleimide in Figure 5 further verified the similar results, having resonances at δ = 43.5, 127.5, 133.8, 157.9, 169.6, and 175.3 ppm. These results meant that the reverse Diels–Alder reaction actually occurred in our present investigations of polyimides **1–4**, which would show thermosetting behavior by producing bismaleimide.

CONCLUSION

PTDDA is a useful comonomer for copolymerization. It can change the properties of polymer, such as solubility and thermal behaviors. The latter was rather special since PTDDA offered a thermosetting functional group that was different from the end-capped nadimide prepolymers[14,15] and bismaleimides.[16,17]

The thermal curing chemistry of copolyimides was studied by TGA and DSC thermograms. Although the polymers decomposed only at 300°C, it was also the beginning of another reaction (cross-linking). We proposed that the reverse Diels–Alder reaction controlled the curing chemistry and produced bismaleimides and 1,1-diphenyl ethylene. Spectroscopy such as mass spectra, IR spectra, and solid-state ^{13}C-NMR spectra were used to confirm above results; that is, copolymers having long BTDA/ODA segments thermally reduced to the long chain of bismaleimides and showed superior thermal stability at the second stage of decomposition. The long chain of bismaleimide will have preferable toughness and will decrease the cross-linking density of materials upon thermal curing.

Figure 5 Solid-state ^{13}C-NMR spectra of (A) cured model bismaleimide and (B) cured polyimide **1**. S denotes side band.

REFERENCES

1. J. R. Evans, R. A. Orwoll, and S. S. Tang, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 971 (1985).
2. N. Kardush and M. P. Stevens, *J. Polym. Sci. A-1*, **10**, 1093 (1972).
3. W. A. Feld, B. Ramalingam, and F. W. Harris, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 319 (1983).
4. P. R. Young, J. R. J. Davis, A. C. Chang, and J. N. Richardson, *J. Polym. Sci. Polym. Chem.*, **28**, 3107 (1990).

5. A. N. Krasovskii, N. P. Antonov, M. M. Koton, K. K. Kalnin'sh, and V. V. Kudryartsev, *Polym. Sci. U.S.S.R.*, **21**, 1038 (1977).

6. F. W. Harris and Steve L.-C. Hsu, *High Perform. Polym.*, **1**, 3 (1989).

7. F. W. Harries and R. B. Seymour, *Structure-Solubility Relationships in Polymers*, Wiley, New York, 1977.

8. C. Y. Su and Y. D. Lee, *J. Polym. Sci. Polym. Chem.*, **28**, 3347 (1990).

9. K. Kunimasa and S. Yasuhisa, Jpn. Pat. 633-37118 (1989).

10. W. E. Franklin, C. H. Mack, and S. P. Rowland, *J. Polym. Sci. A-1*, **7**, 1169 (1969).

11. A. C. Wong and W. M. Ritchey, *Macromolecules*, **14**, 825 (1981).

12. C. E. Sroog, *J. Polym. Sci. Macromo. Rev.*, **11**, 161 (1976).

13. I. K. Varma and R. Tiwari, *J. Thermal Anal.*, **32**, 1023 (1987).

14. A. K. St. Clair and T. L. St. Clair, *Polym. Eng. Sci.*, **16**, 314 (1976).

15. D. A. Scola and M. P. Stevens, *J. Appl. Polym. Sci.*, **23**, 231 (1981).

16. K. N. Ninan, R. George, K. Krishnan, and K. V. C. Rao, *J. Appl. Polym. Sci.*, **37**, 127 (1989).

17. K. N. Ninan, K. Krishnan, and J. Mathew, *J. Appl. Polym. Sci.*, **32**, 6033 (1986).