

Thermal Behavior and Reactivities of Prepolymers Prepared from Aromatic Biscyanamides and Bismaleimide

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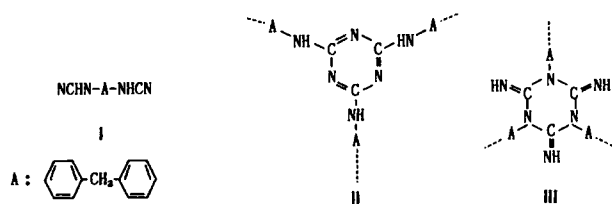
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SYNOPSIS

Novel polymers obtained by reaction of aromatic biscyanamide and bismaleimide compounds were investigated. By heating 4,4'-methylene bis(*o*-methylphenylcyanamide) (BMCA) with 4,4'-methylene bis(phenylmaleimide) (BMI) at 120°C in *N,N*-dimethylformamide (DMF), prepolymers were obtained by the conversion of cyanamide to cyanoguanidine and the addition of an imino group on the double bond of maleimide. The prepolymer showed suitable behavior for thermosetting resin used in molding, i.e., it melted temporarily and then polymerized in an isochronal heating process (5°C/min). On heating above 170°C, the prepolymer could polymerize with ring formation of melamine and isomelamine. The cured product had good heat-resistant properties.

INTRODUCTION

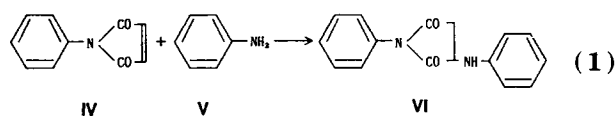
The ring formation of melamine (II) or isomelamine (III) by cycloaddition reaction of cyanamide (I) is well known.^{1,2}



Investigations of heat-resistant polymers obtained from various aromatic biscyanamides have been made by employing the above-mentioned reaction.³ In addition, the thermal behavior and reactivities of oligomers prepared from aromatic biscyanamide and aromatic diamine have also been reported.⁴

Another addition reaction, in this case of the double bonds of aromatic maleimide with aromatic diamine, is also known. For example, *N,N'*-diphenylaspartimide (VI) can be obtained by the reaction

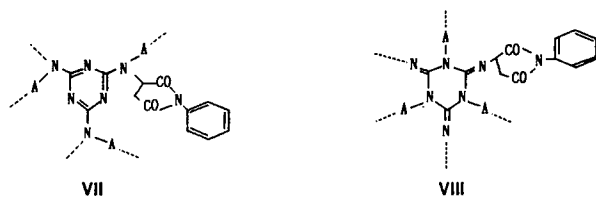
of *N*-phenylmaleimide (IV) with aniline (V) below 150°C⁵:



The addition-type polyimide obtained by such reactions has excellent thermal properties⁶ and has already been applied for multilayer printed wiring boards⁷⁻⁹ of large-scale computers and for Fiber Reinforced Plastic (FRP) of aerospace materials¹⁰:

But few studies concerning the reaction of aromatic biscyanamide with aromatic bismaleimide have been reported. The present work deals with novel heat-resistant polymers prepared by reacting aromatic biscyanamide with aromatic bismaleimide. In an earlier paper,¹¹ the reactions of 4,4'-methylene bis(phenylcyanamide) (BCA) and 4,4'-methylene bis(*o*-methylphenylcyanamide) (BMCA) with PM were investigated. The oligomers were obtained by heating BCA or BMCA with PM at 100°C in solution. In the process of oligomerization, both the conversion of cyanamide to cyanoguanidine and the addition of PM to biscyanamide or cyanoguanidine were confirmed. On heating at 170 or 220°C, the oligomers polymerized with the ring formation of melamine (VII) and isomelamine (VIII):

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In this paper, the thermal behavior and reactivities of prepolymers prepared by reacting BCA or BMCA with 4,4'-methylene bis(phenylmaleimide) (BMI) were studied.

EXPERIMENTAL

Materials

BCA and BMCA were synthesized according to the same method described in the earlier paper.¹¹

BCA

A 1000 mL four-necked flask was charged with water (250 mL) and cyanogen bromide (BrCN, 94.4 g, 0.9 mol). After cooling to 0°C, *N,N*-dimethylacetamide (DMA, 120 mL) and sodium bicarbonate (NaHCO₃, 57 g, 0.7 mol) was added. A solution of 4,4'-methylene bis(aniline) (MBA, 59.4 g, 0.3 mol) in DMA (165 mL) was added dropwise into the flask over a period of 2 h at 0–10°C (under nitrogen atmosphere). After the addition was complete, the resulting mixture was mechanically stirred at 0–10°C for 2 h. After a small amount of insoluble matter

Table I Elemental Analysis of Biscyanamide Monomers (%)

Sample	C	H	N
BCA	71.95 (72.56)	4.83 (4.87)	22.67 (22.55)
BMCA	72.45 (73.89)	5.71 (5.84)	20.25 (20.28)

Theoretical values are given in parentheses.

was removed by filtration, the solution was added dropwise to cold water (3200 mL). The precipitate was collected and washed with water. After drying, 72.9 g of crude was obtained. This crude was dissolved in ethanol (200 mL), and the insoluble matter was removed by filtration. The filtrate was added dropwise into cold water (400 mL), and the precipitate was collected. BCA was obtained as white powder (65.6 g, 90%) by drying *in vacuo* (below 40°C) for 3 h.

BMCA

A 1000 mL four-necked flask was charged with water (220 mL) and cyanogen bromide (95.4 g, 0.9 mol). After cooling to 0°C, DMA (200 mL), and NaHCO₃ (51 g, 0.61 mol) was added. A solution of 4,4'-methylene bis(*o*-methylaniline) (82.2 g, 0.3 mol) in DMA (280 mL) was added dropwise into the flask over a period of 2 h at 0–10°C. The product precipitated readily during the reaction.

After the addition was complete, the resulting mixture was mechanically stirred at 0–10°C for 2 h and the reaction mixture was poured into cold water (3000 mL). The precipitate was collected and washed with water and methanol. BMCA was obtained as white powder (78.7 g, 95%) by drying *in vacuo* (below 40°C) for 3 h.

IR and NMR spectra of BCA and BMCA are shown in Figure 1. The results of the elemental analyses of BCA and BMCA are given in Table I, along with theoretical values. The observed values were in good agreement with the theoretical ones.

BMI

BMI (Mitsui Toatsu Chemical) was purified by recrystallization from methanol and dried at 60°C *in vacuo*.

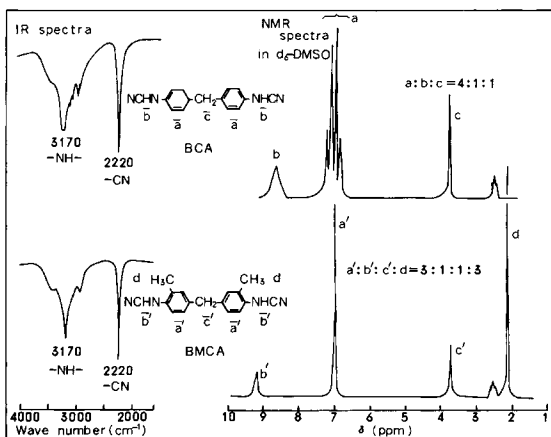


Figure 1 Characterization of 4,4'-Methylene bis(phenylcyanamide) (BCA) and 4,4'-Methylene bis(*o*-methylphenylcyanamide) (BMCA).

N,N-Dimethylformamide (DMF)

DMF (Wako Pure Chemical) was obtained commercially and used without further purification. The boiling range was 151–154°C.

Measurements

Infrared (IR) spectra were measured on a Hitachi 260-50 model infrared spectrometer by the KBr method.

Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were obtained using a Hitachi 250 model Fourier transform NMR spectrometer at 60 MHz in $\text{DMSO-}d_6$ solution. Chemical shifts (δ) were given in parts per million with tetramethylsilane as an internal standard.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a Shinkuriko TGD-3000 model thermal analyzer system. Measurements were made at a heating rate of 5°C/min in air with a flow rate of 100 mL/min.

Curability was measured on a Japan Synthetic Rubber JSR-type curelasmeter. The vibration angle was 0.5°. The curing rate was calculated from the slope at the 50% value in the curing curve, and the activation energy was obtained from the Arrhenius plot.

Glass transition temperature (T_g) of cured products was measured on a Shinku Riko TMA-1500 model thermal mechanical analyzer. The heating rate was 2°C/min. The sample was prepared by preheating prepolymer powder at 130°C for 15 min and then forming a disk of cured product using a mold heated at the desired temperature. The disk had a diameter of 10 mm and a thickness of about 2 mm.

RESULTS AND DISCUSSION

Thermal Behaviors

The DTA curves of BCA, BMCA, and BMI are shown in Figure 2. In the case of BMI, the endothermic peak observed at 168°C is due to the fusion and the exothermic peak observed at 220°C is most likely due to the radical reaction between double bonds. On the other hand, in the case of BCA and BMCA, a sharp exothermic peak is observed for each at 153 and 228°C, respectively, but no endothermic peak. This is attributed to aromatic biscyanamides polymerization, by dimerization and trimerization, as soon as they melt.

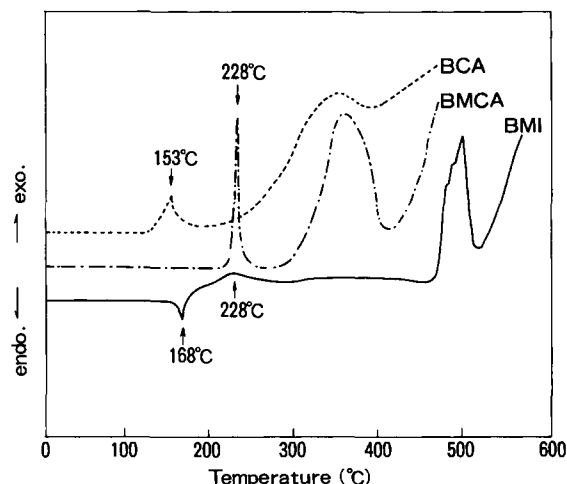


Figure 2 DTA thermograms of BCA, BMCA, and BMI.

Initial weight loss temperatures of the polymers that are obtained by heating the mixtures of BMI and biscyanamide, BCA or, BMCA are shown in Table II. The initial weight loss temperatures of polymers obtained from BMI and BCA are in the range of 240–326°C and much lower than that of BMI alone. This suggests that the polymerization of BCA is inhibited because melting of BMI does not occur near 153°C as shown in Figure 2.

On the other hand, the initial weight loss temperatures of polymers obtained from BMI and BMCA are from 363 to 410°C. The initial weight loss temperature of b-5, which is a mixture of BMCA (1 mol) and BMI (3 mol) is 20°C higher than that of BMCA alone: 390°C.

The DTA curves of the mixtures b-1 to b-5 are shown in Figure 3. Another exothermic peak appears at 194°C, besides the one at 228°C, on increasing the BMI content. In the case of b-4 obtained from BMCA (1 mol) and BMI (1 mol), a single exothermic peak is seen at 194°C, while an endothermic peak appears at 168°C. The exothermic peak at 194°C suggests that BMCA dissolves in the molten BMI at 168°C, resulting in lowering of the polymerization temperature of BMCA. In b-5 obtained from BMCA (1 mol) and BMI (3 mol), the exothermic peak shifts to 200°C and a broad exothermic peak is observed. Consequently, b-5 shows behavior in which it melts temporarily at 168°C and then polymerizes by an exothermic reaction in the range of about 170°C to 230°C. Further, for b-5, the temperature of the exothermic peak differs from the others, suggesting the participation of BMI in the reaction of BMCA.

Table II Initial Weight Loss Temperatures of Polymers

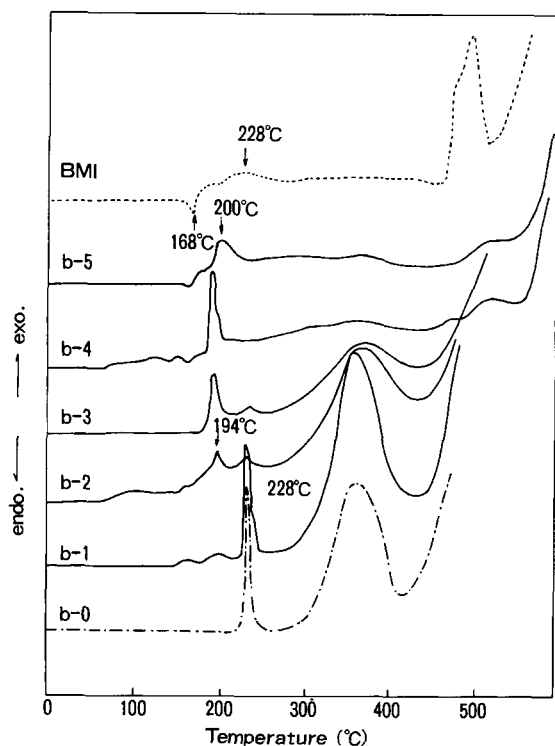
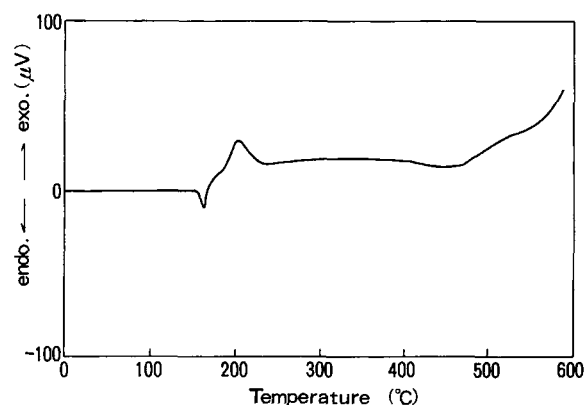
Sample	[BCA]/[BMI]	[BMCA]/[BMI] ^a	Initial Weight Loss Temperature (°C)
a-0	1/0		392
a-1	1/0.2		280
a-2	1/0.5		313
a-3	1/1		326
a-4	1/3		240
b-0		1/0	390
b-1		1/0.2	363
b-2		1/0.5	366
b-3		1/0.8	371
b-4		1/1	384
b-5		1/3	410
BMI			472

^a Temperature at 5% weight loss.

Prepolymerization by heating BCA or BMCA with BMI at 120°C in solution was attempted by considering the information obtained previously.¹¹ Compositions of 1 and 3 mol of BMI to 1 mol of BCA or BMCA were selected. Then, 120°C was chosen as the temperature necessary to dissolve BMCA

or BMI in DMF. When BMI (1 mol) to BCA (1 mol) or BMCA (1 mol) was used, a gel formed and the prepolymer could not be obtained. The DTA curve of the prepolymer prepared by reacting BMCA (1 mol) with BMI (3 mol) is shown in Figure 4. An endothermic peak appears at 168°C, and an exothermic one, at 200°C. The prepolymer shows the thermal behavior in which it melts temporarily at 168°C and then polymerizes in the range of about 170–230°C. Such behavior is well suited for thermosetting resin used in molding fabrication.

Next, the curability of the prepolymer was measured by a curelastermeter. The results are shown in Figure 5. The higher the reaction temperature is, the more rapid the curing rate is and the shorter the reaction time needed for final curing of the prepoly-

**Figure 3** DTA thermograms of mixtures.**Figure 4** DTA thermogram of prepolymer.

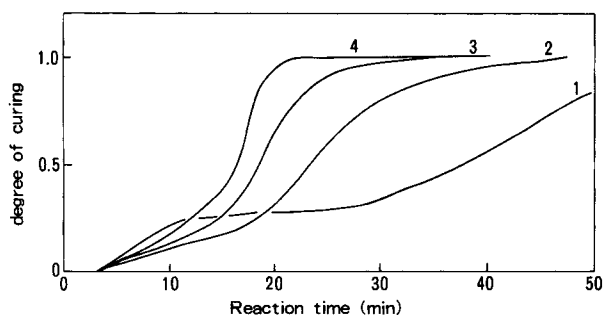


Figure 5 Curing curves of prepolymer at various temperatures; 1, 170°C; 2, 180°C; 3, 200°C; 4, 210°C.

mer. The curing process is completely finished in 40 minutes by heating above 200°C.

The Arrhenius plot that represents the relationship of the curing temperature and the curing rate is shown in Figure 6. The curing rate is obtained from the slope at the half-cured in Figure 5. As shown in Figure 6, the reaction with the activation energy, (E_a) of 18.5 kcal/mol proceeds at temperatures of 170–210°C.

Thermal properties and TG curves of the polymer (B-5) prepared by heating above-mentioned prepolymer at 220°C for 120 min are shown in Table III and Figure 7 with that of aminobismaleimide polymer (PAM) prepared by reacting BMI (3 mol) with DMA (1 mol). This aminobismaleimide polymer is treated at 170°C for 60 min and then at 220°C for 120 min. The T_g of polymer (B-5) is 290°C, which

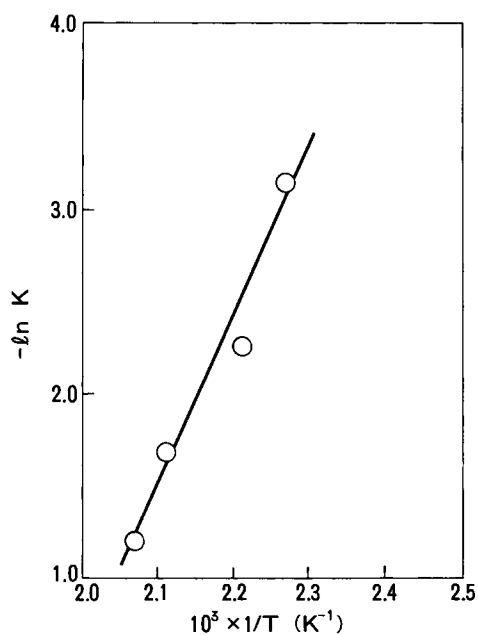


Figure 6 Arrhenius plots of curing reaction.

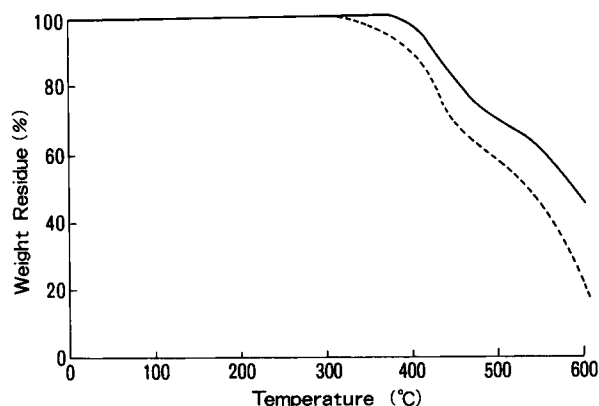


Figure 7 Thermogravimetric analysis of polymers: (—) B-5; (----) PAM.

is 90°C higher than that of PAM when cured under the same heating conditions. Further, B-5 has an initial weight loss temperature of 410°C, 30% weight loss temperature of 500°C, and char yield of 45% at 600°C.

Consequently, polymer (B-5) obtained from this investigation has a heat resistance superior to that of aminobismaleimide polymer, which has been widely recognized as a good heat-resistant polymer.

Reaction of Prepolymer

The IR spectra of the prepolymer that was obtained by reacting biscyanamide (1 mol) with bismaleimide (3 mol) are shown in Figures 8 and 9.

An absorption peak attributed to succinimide (C—N—C) (Ref. 12) appears at 1180 cm^{-1} . This is

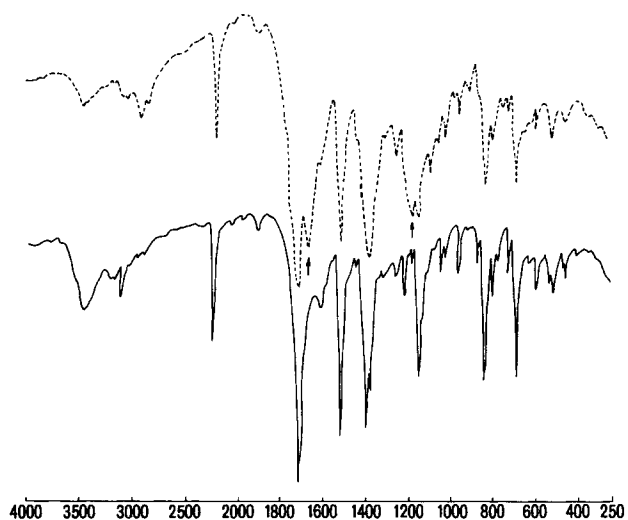
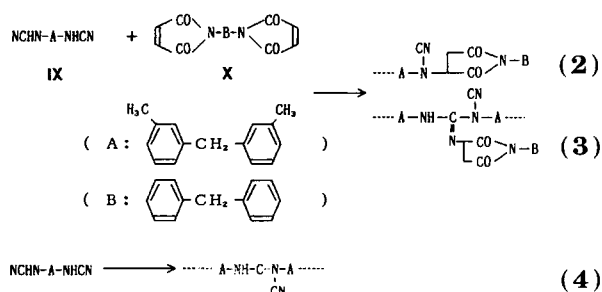


Figure 8 IR spectra of mixture a-4 and its prepolymer; (—) mixture, (----) prepolymer.

Table III Thermal Properties of Polymers

Polymer	T_g (°C)	TG Results		
		Initial Weight Loss (°C)	30% Weight Loss (°C)	Char Yield at 500°C (%)
B-5	290	410	500	45
PAM	200	374	442	18

the same as for reactions of biscyanamide and *N*-phenylmaleimide that were reported in the earlier paper.¹¹ This supposes that the reaction (2, 3) of the imino group of BCA or BMCA (IX) with the double bond of BMI (X) occurs when heated at 120°C for 20 min:



An absorption peak due to guanidine appears at 1660 cm^{-1} ; therefore, it is clear that cyanoguanidine is formed (4), the same as in the previous case.¹¹

The increased absorbance at 1180 and 1660 cm^{-1} in the a-4 spectrum is more than that in the b-5 spectrum. Therefore, it can be assumed that the po-

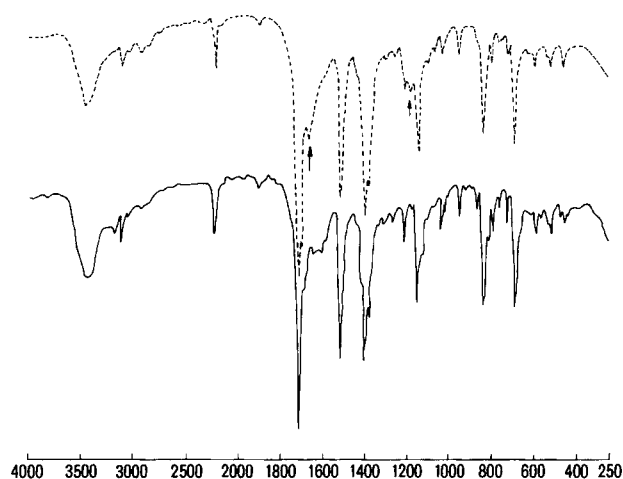
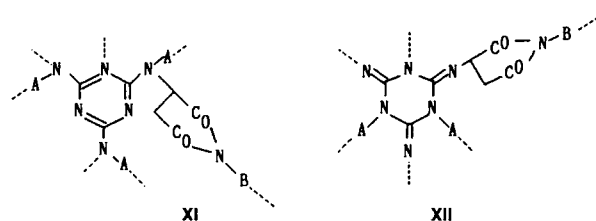


Figure 9 IR spectra of mixture b-5 and its prepolymer; (—) mixture, (----) prepolymer.

lymerization reaction proceeds by the formation of succinimide and cyanoguanidine.

The spectra of the polymers obtained by heating prepolymer of b-5 at 170°C for 60 min and at 220°C for 120 min are shown in Figure 10. After heating at 170°C, the absorption peak of cyanoguanidine at 1660 cm^{-1} disappears and new peaks at 1590 and 1620 cm^{-1} appear. These are assigned to melamine (XI) and isomelamine (XII), respectively:



This suggests that trimerization occurs, forming three-dimensional polymers under the above curing conditions. After heating at 170°C, the absorption of the cyano group still appears, but after heating at 220°C, it almost disappears. So it is suggested

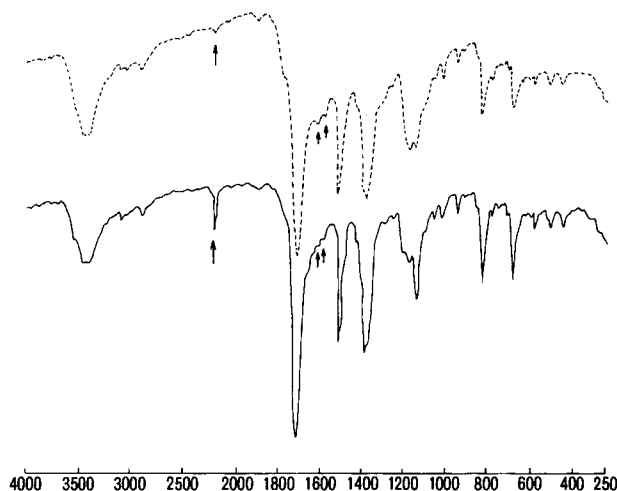


Figure 10 IR spectra of polymers; curing condition: (—) 170°C, (----) 220°C.

that all the cyano groups are consumed in the trimerization.

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