

The Curing Mechanism and Properties of Bismaleimide–Biscyanamide Resin

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SYNOPSIS

Thermoset networks consisting of *N,N*-bismaleimidediphenylmethane (BMI) and bis[4-(4-cyanamide-3-methylphenyl)]methane (BCMM) were investigated with the aim of correlating macroscopic behavior and structure as network composition was varied. The glass transition temperatures of these cured resins obtained from the dynamic mechanical data and thermal expansion data had a distinct minimum at the 50/50 molar ratio of BMI/BCMM. Also, at this molar ratio, the decomposition temperature at a 5% weight loss in helium atmosphere for cured resins was the lowest. These results provided a rough idea of the thermoset network structure.

INTRODUCTION

Bismaleimides yield cross-linked resins with excellent thermal stability and they have been used widely. However, the cured bismaleimide resins are extremely brittle because of the highly cross-linked structure. They have a high modulus of elasticity and a very low elongation at breaking. This disadvantage has been overcome by the modification with rubber^{1,2} or by chain-extended bismaleimide prepolymer molecules, which were prepared by the Michael addition reaction of bismaleimides with diamines^{3–8} or dithiols.^{9,10} But these modifications cause a reduction in thermal properties such as decomposition temperature and glass transition temperature because of their chain-extended structure.

In earlier papers,^{11,12} we reported on the formation of prepolymers by the Michael addition reaction of *N*-phenylmaleimide or bismaleimides with two aromatic cyanamides, *N,N*-biscyanamidediphenylmethane (BCDP) and bis[4-(4-cyanamide-3-methylphenyl)]methane (BCMM). We presumed that the chain-extended structure of these prepolymers (see Scheme 1) would make their handling easy, because they would have good solubility, whereas the active cyano groups would react and

the mechanical property of the cured resins would be compatible with their thermal stability because appropriate cross-linking density could be obtained. However, there have been no reports on the correlation between network structure and properties on the *N,N*-bismaleimidediphenylmethane (BMI)/BCMM resin systems.

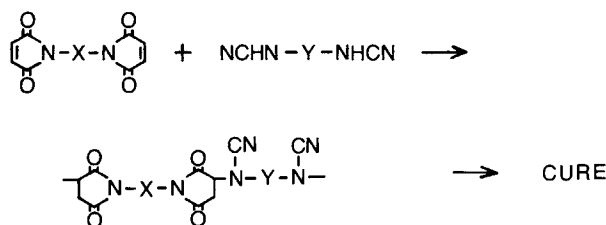
In this paper, we report on the modification of mixed systems consisting of BMI and BCMM, the thermal resistance of which is better than that of the BMI/BCDP system described previously.^{11,12} The viscoelastic, thermal, and dielectric properties of the modified resins were studied as a function of the amount of biscyanamide correlate macroscopic behavior and structure. Then, we proposed a network structure for the cured resin.

EXPERIMENTAL

Materials and Sample Preparation

The prepolymers were prepared from BMI (Mitsui Toatsu Chemicals) and BCMM (see Fig. 1) as described elsewhere^{11,12} at several molar ratios (Table I). Prepolymerization was done as follows: A 200 mL four-necked flask with a reflux condenser was charged with *N,N*-dimethylformamide (DMF, Wako Pure Chemical) and BMI. The amount of DMF was determined to get a 50 wt % prepolymer solution. This solution was heated at 120°C, using an oil bath

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Scheme 1

for 20 min with stirring. Then, BCMM solid was added to the flask and the solution were held at 120°C for 20 min with stirring.

The solution was cooled to room temperature and lightly coated on a polyester film. Then, DMF was removed by heating the polyester film in a thermostated oven at 150°C for 10 min and the prepolymer powder was obtained. Table I lists the thermal properties of the obtained prepolymers. Their gelation times (GTs) became shorter on increasing the fraction of BCMM. Then, when the fraction of BCMM was more than 0.6, molding was very difficult. Therefore, resins with the BCMM fraction less than 60% were examined.

The prepolymer powder was placed in a heated molding press with a 1 mm spacer and cured under a pressure of 40 kgf/cm². The molding temperature was 170°C for 5 min, and then it was raised to 220°C and held there for 2 h.

Measurements

Differential scanning calorimetry (DSC) was carried out using a Daini Seikoshya thermal analyzer (Model TAS-100) equipped with a DSC module

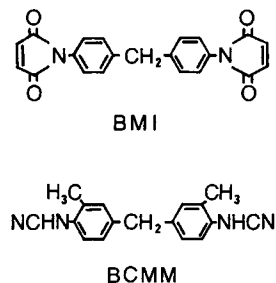


Figure 1 Structures of materials.

(Model 8240) at a heating rate of 10°C/min in air. The GTs were measured following procedure JIS-K5909, and activation energies were obtained from GTs at 170, 200, and 220°C. The densities of the cured products were evaluated using a bromoform (d : 2.9)-toluene (d : 0.86) mixture at 25°C. The density of the corresponding mixture was measured on an Anton Parr precision density meter (Model DMA-02C). Dynamic mechanical analysis (DMA) was done using an Iwamoto Seisakusho device (Model RPX-706) over a range from -180 to 400°C at a heating rate of 5°C/min and determined by means of an instrument employing forced longitudinal vibration at 10 Hz. The samples were rectangular strips, 40 × 4 × 1 mm in size. Thermal expansion measurements were conducted using a Shinku-Riko thermomechanical analyzer (Model TM3000) in air at a heating rate of 2°C/min. Dielectric constants were measured on a Hewlett Packard LF impedance analyzer (Model 4192A) following procedure JIS-C6481 at room temperature. Thermal gravimetric analysis (TGA) was done with a Shinku-Riko TGD (Model 7000RH) in air at a heating rate of 5°C/min.

Table I Thermal Properties of Prepolymers

Formulation	BCMM/BMI (molar ratio)	T_1^a (°C)	T_p^b (°C)	GT ^c (s)	E_a^d (kJ/mol)
1	0/100	183	222	160	91.5
2	20.1/79.9	133	210	108	72.6
3	25.0/75.0	133	209	76	66.2
4	30.0/70.0	146	204	40	67.0
5	40.0/60.0	124	190	32	66.0
6	50.0/50.0	145	180	—	—
7	60.0/40.0	127	177/215	—	—
8	100/0	153	202/225	—	—

^a Onset temperature for curing reaction.

^b Exothermal peak temperature.

^c Gelation time at 170°C.

^d Activation energy calculated from GT.

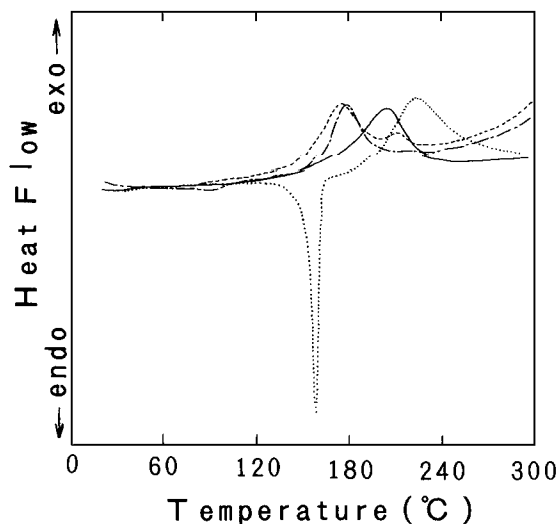


Figure 2 DSC scan of BMI/BCMM systems: (.....) formulation 1; (—) formulation 4; (-·-) formulation 6; (-----) formulation 7.

RESULTS AND DISCUSSION

Thermal Properties of Prepolymers

Preparations and properties of several cured bis-cyanamide resins were reported in our previous paper.¹³ Among them, molding with BCMM was the most difficult, because of its fast curing reaction. So properties of cured BCMM have not been investigated. On the other hand, the complete curing of BMI needs a long time and high temperature.¹⁴

However, the prepolymerization of BCMM with

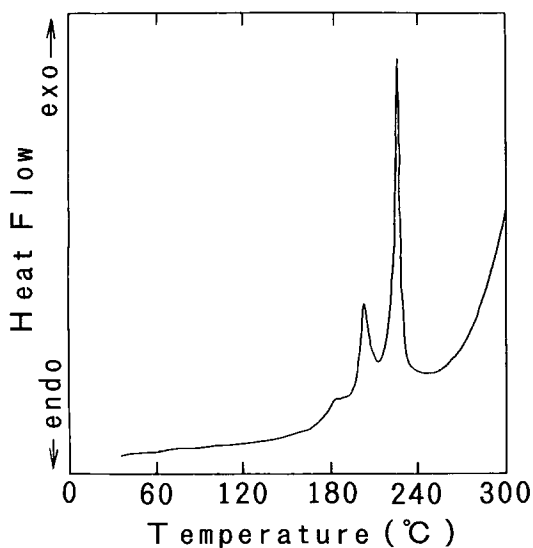


Figure 3 DSC scan of BCMM.

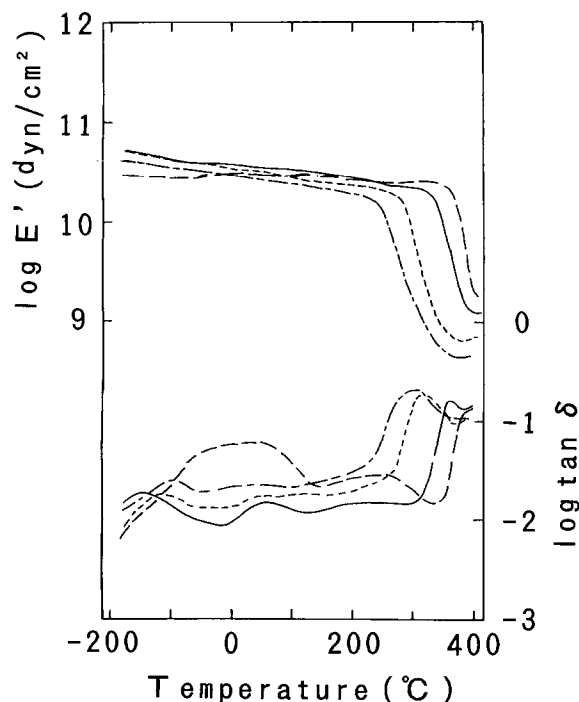


Figure 4 Dynamic mechanical spectra of cured BMI/BCMM systems: (---) formulation 2; (—) formulation 4; (-·-) formulation 6; (-----) formulation 7.

BMI has a good property for molding. Table I lists thermal properties of prepolymers and their DSC curves are shown in Figures 2 and 3. Their melting points disappeared on prepolymerization. In addition, the onset and peak temperatures for the curing reactions of these prepolymers shifted lower with increasing BCMM fraction. Prepolymer 7, in which the BCMM fraction was 0.6, shows two peak temperatures like those of BCMM, formulation 8.

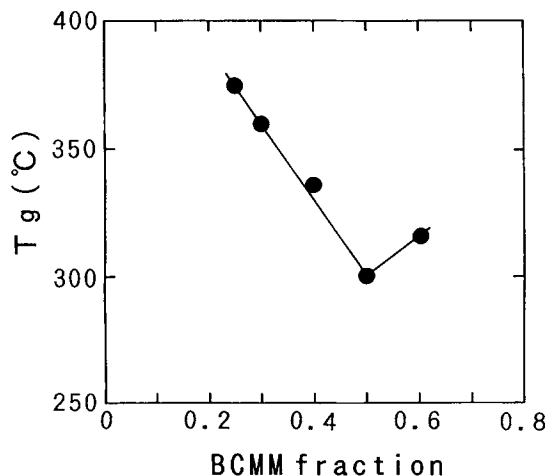


Figure 5 T_g from DMA vs. BCMM fraction.

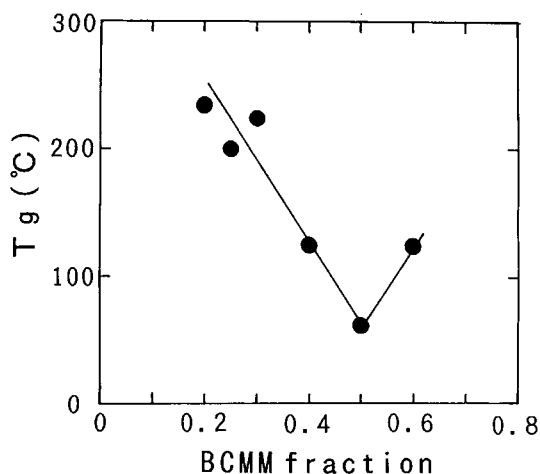


Figure 6 T_g from TMA vs. BCMM fraction.

Although no initiators were added to the prepolymers, the GTs were shorter on increasing the BCMM fraction. When the BCMM fraction was more than 0.6, molding was very difficult because the GT of the prepolymer was so short. The activation energies obtained from the GT data decreased with increasing BCMM fraction.

Glass Transition Temperatures

The dynamic mechanical properties of cured resins prepared at different molar ratios of BCMM/BMI, ranging from 0/100 to 40/60, were examined. These results are shown in Figure 4. In samples that had a small amount of BMI, the storage modulus clearly decreased with temperature and there was one relaxation area, manifested by the corresponding loss peak. But as the amount of BMI component increased, the loss peak was broadened and became

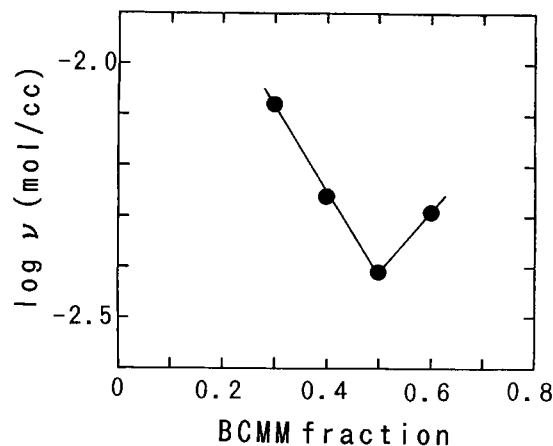


Figure 7 $\log \nu$ vs. BCMM fraction.

indistinct. Having one loss peak meant that BMI and BCMM reacted uniformly in these systems.

The glass transition temperatures (T_g 's) of cured resins, obtained from the loss peak of the dynamic mechanical data, are plotted as the molar ratios in Figure 5. The T_g decreased linearly with increasing BCMM fraction to 0.5, and after this, it increased. Results of the thermal expansion test showed a minimum T_g at this ratio also (Fig. 6). These results suggested that the cross-linking densities of the resins had a minimum at the ratio of 50/50 (BCMM/BMI).

Cross-linking Densities

The cross-linking densities can be obtained with the experimental equilibrium rubber modulus using the following equation¹⁵:

$$M_c = \phi \rho RT / G_e \quad (1)$$

Table II Properties of Cured Resins

Formulation	ρ (g/cc)	$\log \nu$ (mol/cc)	γ^a	ϵr at 1 kHz
1	1.53	—	0.191	3.14
2	1.40	(-2.08) ^b	0.198	3.48
3	1.45	(-2.14) ^b	0.200	3.65
4	1.44	-2.08	0.202	3.78
5	1.42	-2.26	0.205	3.96
6	1.38	-2.47	0.210	3.92
7	1.42	-2.29	0.215	4.04

^a The ratio of carbon atoms to heteroatoms calculated from ρ and constituent of each resin.

^b Estimated value from the relationship between $\log \nu$ and T_g as shown in Figure 11.

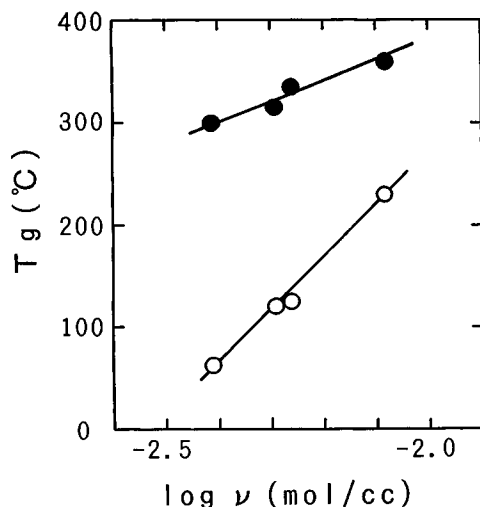


Figure 8 T_g vs. $\log \nu$: (●) T_g from DMA; (○) T_g from TMA.

where M_c is the average molecular weight between cross-links; ϕ , the front factor; ρ , the density at absolute temperature T ; R , the gas constant; and G_e , the equilibrium shear modulus. For rubber that experiences small strains, volume is constant during deformation and G_e may be replaced by $E_e/3$. In this work ϕ was assumed to be one.

Thus, eq. (1) may be written

$$\nu = \rho/M_c = E_e/3RT \quad (2)$$

where ν is the cross-linking density. The modulus at $T_g + 40^\circ\text{C}$ obtained from DMA data was selected as the E_e .¹⁶ Cross-linking densities obtained by the above relationship are listed in Table II.

The relationship between cross-linking densities and the BCMM fraction is shown in Figure 7. The cross-linking densities were lowest at the ratio 50/50 of BCMM/BMI, similar to the result for T_g 's. Also, T_g varies linearly with logarithmic cross-linking density, as shown in Figure 8.

Thermal Stability

Table III lists thermal resistance data of the BMI/BCMM systems. BMI and BCMM are both good heat-resistance resins. However, the decomposition temperatures at a 5% weight loss of mixed cured resins revealed a distinct minimum at 0.5 for the BCMM fraction (Fig. 9), as did T_g and cross-linking density data. This thermal resistance behavior was unexpected. We could attribute the drop of thermal

stability to the reduction of cross-linking density of cured resin, as shown in Figure 10.

Dielectric Property

Dielectric property is described by dielectric constant (ϵ^*):

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (4)$$

Here ϵ' is the dielectric constant; and ϵ'' , the loss factor. When materials have many dipole groups in a unit volume, their dielectric constants are generally high. Dielectric property of cured resin was obtained by measuring the capacitance of each cured resin from 10 Hz to 1 MHz. No relaxation with frequency was observed at room temperature. Figure 11 shows the dielectric constant, ϵ' , at 1 kHz. The larger the BCMM ratio, the higher was the dielectric constant of cured resin. This result suggested that dipole groups included in the cured resin varied with increasing BCMM fraction. These results are shown in Table II.

Network Structure

We do not have any direct structural information for these resins. We presumed a structure from the above-mentioned observed properties of the cured resins.

Figure 12 shows dielectric constants of cured resins as a function of the ratio of carbon atoms to the

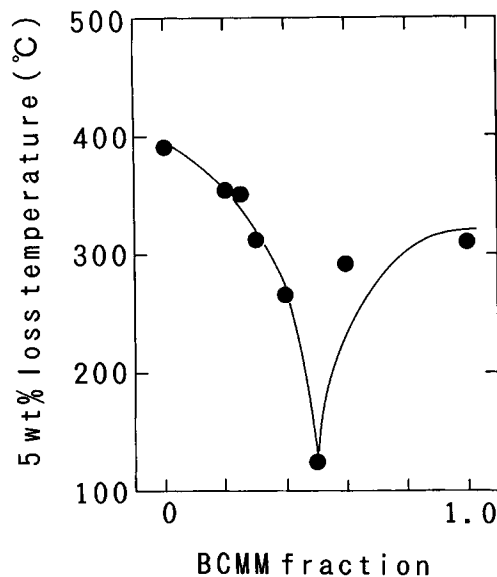


Figure 9 5 wt % loss temperature of cured resin vs. BCMM fraction.

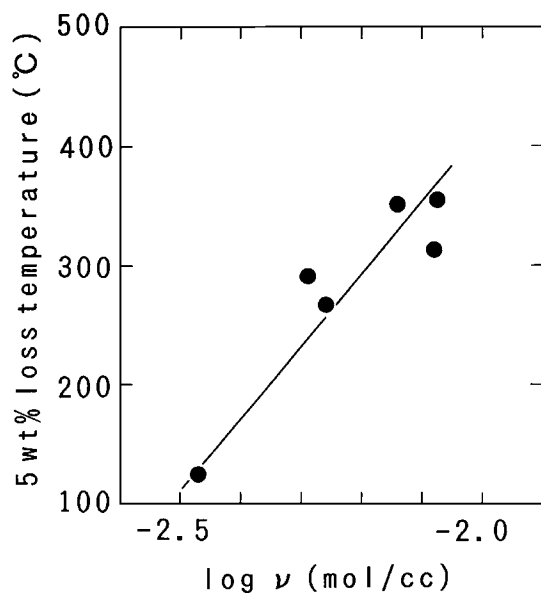


Figure 10 5 wt % loss temperature of cured resin vs. $\log \nu$.

sum of nitrogen and oxygen atoms included in unit volume of cured resins, γ , calculated from density data and formulation. Table III lists these values. This γ value means concentration of the dipole groups, for example, C=N and C=O groups. Dielectric constants varied linearly with γ values, ranging from 0.191 to 0.205. This suggested that the number of dipole groups contained in the cured resin increased linearly with increasing BCMM ratio. However, the dielectric constant varied more slowly when the N + O/C value was more than 0.210, i.e., the amount of BCMM fraction was more than 0.5.

Cyclotrimerization forms a melamine or iso-mel-

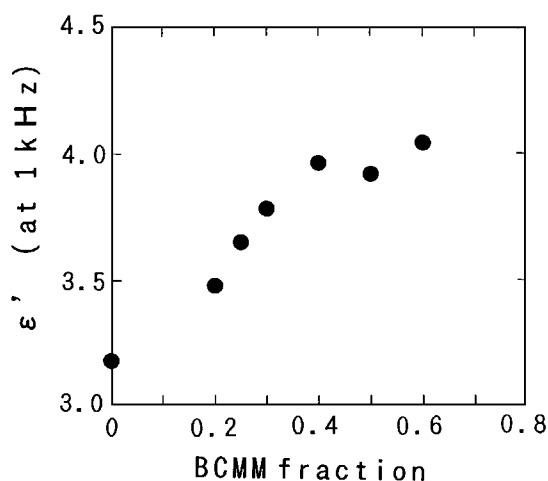


Figure 11 ϵ' vs. BCMM fraction.

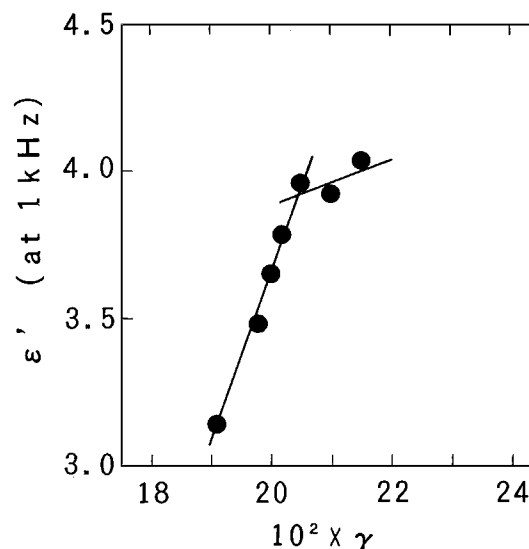


Figure 12 ϵ' vs. the ratio of carbon atoms to heteroatoms.

amine ring that has a small dipole moment. So we thought that cyclotrimerization of the biscyanamide alone occurred when the BCMM fraction was more than 0.5. When it was less than that, cyclotrimerization did not occur at all or only very little. This assumption may explain the reason why the cross-linking density of this system had a distinct minimum at 50/50 of BCMM/BMI.

Although the mechanism of the cross-linking reaction and structure were not completely explained, we were able to obtain structural information for a series of resins based on BMI and BCMM. Final clarification of their structure awaits further investigation.

CONCLUSION

We obtained some structural information for a series of resins based on *N,N*-bismaleimidediphenylmethane (BMI) and bis[4-(4-cyanamide-3-methylphenyl)]methane (BCMM) as follows: The glass transition temperatures of cured resins obtained from dynamic mechanical and thermal mechanical analyses had a distinct minimum when the BCMM fraction was 0.5. In addition, the decomposition temperature at a 5% weight loss had a minimum at this molar fraction, and the increasing rate of dielectric constants also changed here.

Judging from the above macroscopic properties of the cured resins, we presumed the following curing reaction mechanism:

1. When the BCMM fraction ranged from 0.2 to 0.5, the linear extension reaction by BMI

Table III Thermal Properties of Cured Resins

Formulation	T_5^a (°C)	T_{50}^b (°C)
1	392	571
2	355	516
3	351	617
4	313	642
5	267	534
6	125	598
7	292	535
8	311	565

^a 5% weight loss temperature in helium.

^b 50% weight loss temperature in helium.

and BCMM, which was a Michael addition reaction, occurred more than did the self-condensation reaction.

- When the BCMM fraction was more than 0.5, the cyclotrimerization reaction occurred besides the linear extension reaction.

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