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# Radical Polymerization of α-Methylenebenzocyclobutene, a Cyclic Analog of α-Methylstyrene

**Keisuke Chino, Toshikazu Takata,[†] and Takeshi Endo***

*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midoriku, Yokohama 226, Japan*

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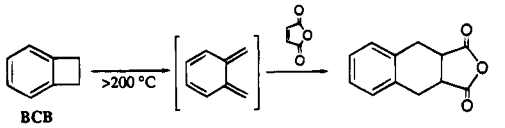
ABSTRACT: α-Methylenebenzocyclobutene (MB) was prepared by Wittig reaction of 1-(triphenylphosphonio)benzocyclobutene bromide with paraformaldehyde in 70% yield. Radical polymerization of MB afforded poly(α-methylenebenzocyclobutene) (PMB) in 66% yield ($\bar{M}_n = 20\,000$). MB, which can be regarded as a cyclic analog of α-methylstyrene, had a higher polymerizability than α-methylstyrene. The higher polymerizability of MB was confirmed by semiempirical molecular orbital calculation by comparison with that of α-methyleneindane. Radical copolymerizations of MB with styrene (St), methyl methacrylate (MMA), and maleic anhydride (MANH) gave corresponding copolymers quantitatively. Especially, the copolymerization with MANH afforded the corresponding alternating copolymer. *Q* and *e* values of MB were determined as 1.35 and −1.00, respectively, from the results of the copolymerizations with MMA. Thermal properties of the obtained PMB were examined, and the thermal decomposition of PMB was discussed.

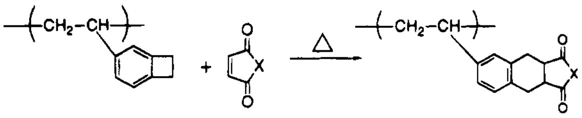
## Introduction

Benzocyclobutene (BCB) is a versatile synthetic intermediate and isomerizes by heating to *o*-quinodimethane (*o*-xylylene), which readily reacts with various dienophiles to yield the corresponding Diels–Alder adducts quantitatively (Scheme 1).[1–3] Diels–Alder polymerization of BCB has been reported.[4–8] Recently, we have demonstrated that the BCB moiety of poly(4-vinylbenzocyclobutene) in the side chain readily undergoes Diels–Alder reaction with dienophiles to quantitatively afford the corresponding adduct polymer over 200 °C (Scheme 2).[9] In the sense that various dienophiles can be introduced to polymer easily, polymers having such BCB function can be regarded as a useful reactive polymer. We have designed a novel BCB-containing polymer, poly(α-methylenebenzocyclobutene) (PMB), which can be obtained from α-methylenebenzocyclobutene (MB), a cyclic analog of α-methylstyrene. Since the isomerization temperature of 1,1-disubstituted benzocyclobutene seems to be lower than 200 °C, PMB having a 1,1-disubstituted benzocyclobutene moiety can be expected to undergo Diels–Alder reaction under a more mild condition. α-Substituted styrenes hardly undergo the radical homopolymerization due to the steric hindrance. However, some of their cyclized analogs have been reported to undergo radical polymerizations owing to their reduced steric hindrance by the cyclizations of the substituents. Ito and Ueda have reported that radical polymerizations of 3-methylenephthalide and 4-methylene-4*H*-1,3-benzodioxin-2-one proceed faster than that of α-acetoxystyrene.[10] Further, they have described that α-methyleneindane undergoes radical polymerization, although the polymerization rate is very low.[11] In this paper, we describe radical homo- and copolymerizations of MB, comparison of the polymerizability with those of α-methylstyrene and α-methyleneindane, and polymer reactions of PMB.

**Scheme 1**



**Scheme 2**



## Experimental Section

**Materials.** α,α′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Styrene (St), methyl methacrylate (MMA), and maleic anhydride (MANH) were purified according to conventional methods.

**α-Methylenebenzocyclobutene (MB).**[15,16] To a solution of 35 g (78 mmol) of α-(triphenylphosphonio)benzocyclobutene bromide[14–16] prepared by triphenylphosphine and α-bromobenzocyclobutene,[12,13] in 200 mL of tetrahydrofuran, was added dropwise 62.5 mL of a 1.66 M (104 mmol) *n*-butyllithium–hexane solution, and the mixture was stirred for 20 min. A total of 15 g (0.5 mol) of paraformaldehyde was added to the mixture. The resulting mixture was refluxed for 3 h and then evaporated after cooling to room temperature. The residue was washed thoroughly with *n*-hexane. The *n*-hexane layer was evaporated, and α-methylenebenzocyclobutene (MB) (4.89 g, 54%) as colorless oil was obtained by distillation of the residue. Bp: 46 °C/8 mmHg (lit.[15] bp 45 °C/8 mmHg). IR (neat): 3067, 3020, 2951, 2922, 1678, 1658, 1593, 1448, 1421, 1327, 1282, 1167 cm$^{-1}$. $^1$H NMR (90 MHz, $CDCl_3$): $\delta$ 7.09 (s, 4H, aromatic), 5.25 (dd, $J = 1.9$ and 1.9 Hz, 1H, exomethylene), 4.86 (s, 1H, exomethylene), 3.52 (t, $J = 1.9$ Hz, 2H, cyclobutene $CH_2$). $^{13}$C NMR (22.5 MHz, $CDCl_3$): $\delta$ 145.3, 144.9, 128.9, 127.3, 122.5, 118.5, 103.0, 38.8, 29.7.

**Radical Polymerization of MB. Typical Procedure.** A mixture of MB (0.22 g, 1.92 mmol) and AIBN (9.5 mg, 0.058 mmol) was placed in an ampule, which was cooled, degassed, and sealed off *in vacuo*. After stirring at 60 °C for 24 h, the reaction mixture was poured into a large amount of methanol (200 mL). White precipitate obtained was separated by filtration, washed thoroughly with methanol, and dried under vacuum. Yield: 0.145 g (66%). IR (KBr): 3065, 3018, 2926, 1601, 1458, 1344, 1186, 1155 cm$^{-1}$. $^1$H NMR (90 MHz, $CDCl_3$): $\delta$ 7.5–6.0 (br s, 4H, aromatic), 2.2–3.6 (br s, 2H, benzyl), 2.2–0.5 (br s, 2H, main chain). $^{13}$C NMR (22.5 MHz, $CDCl_3$): $\delta$ 142.3, 141.8, 127.8–124.6, 123.2–118.6, 52.5, 44.0–41.9, 30.7.

**Radical Copolymerization of MB. Typical Procedure.** A mixture of MB (0.22 g, 1.92 mmol), St (0.20 g, 1.92 mmol),

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[†] JAIST (Japan Advanced Institute of Science and Technology), Tatsunokuchi, Ishikawa 923-12, Japan.

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and AIBN (19 mg, 0.12 mmol) was placed in an ampule, which was cooled, degassed, and sealed off *in vacuo*. After stirring at 60 °C for 24 h, the reaction mixture was poured into a large amount of methanol (200 mL). White precipitate formed was collected by filtration, washed thoroughly with methanol, and dried under vacuum. Yield of poly(MB-*co*-St): 0.38 g (90%). IR (KBr): 3061, 3026, 2920, 2847, 1601, 1493, 1454, 1184, 1070, 1028, 906, 750, 698, 542, 472 cm$^{-1}$. $^1$H NMR (90 MHz, $CDCl_3$): $\delta$ 7.1 (br d, aromatic), 4.2−3.3 (br s, benzyl), 3.3−0.6 (br d, main chain) (MB:St = 42:58).

**Radical Copolymerization of MB with Methyl Methacrylate (MMA). Determination of *Q*−*e* values.** A mixture of MB, MMA, and AIBN was placed in an ampule, which was cooled, degassed, and sealed off *in vacuo*. After stirring at 60 °C for 30 min, the reaction mixture was poured into a large amount of methanol (200 mL). White precipitate formed was collected by filtration, washed thoroughly with methanol, and dried *in vacuo* to afford poly(MB-*co*-MMA). The composition of the copolymer was determined by $^1$H-NMR spectroscopy. $r^1$ and $r_2$ were calculated from the feed ratio of MB and the composition of MB in copolymers on the basis of the nonlinear least-squares analysis method: $r_1 = 0.46$ and $r_2 = 0.32$. Alfrey−Price's $Q$−$e$ values of MB were calculated from the $r_1$ and $r_2$ values: $Q = 1.35$ and $e = -1.00$. IR (KBr): 2947, 1730, 1682, 1456, 1386, 1242, 1145, 1066, 989, 750, 715 cm$^{-1}$. $^1$H NMR (90 MHz, $CDCl_3$): $\delta$ 7.0−6.6 (br d, aromatic), 3.7−2.6 (br m, OMe), 2.6−0.4 (br m, main chain).

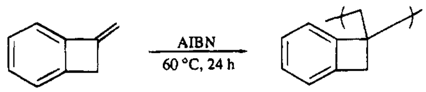
**Radical Copolymerization of MB with Maleic Anhydride (MANH). Determination of Copolymerization Parameters ($r_1$, $r_2$).** A mixture of MB, MANH, and AIBN was placed in an ampule, which was cooled, degassed, and sealed off *in vacuo*. After stirring at 60 °C for 15 min, the reaction mixture was poured into a large amount of methanol (300 mL). White precipitate formed was collected by filtration, washed thoroughly with methanol, and dried under vacuum to yield poly(MB-*co*-MANH). The composition of the copolymer was determined by elemental analysis. $r_1$ and $r_2$ were calculated from the feed ratio of MB and the composition of MB in copolymers on the basis of the nonlinear least-squares analysis method: $r_1 = 0.0025$ and $r_2 = 0.025$. IR (KBr): 3069, 2930, 1857, 1778, 1458, 1224, 1084, 986, 928, 754, 715, 608, 413 cm$^{-1}$. $^1$H NMR (90 MHz, $CDCl_3$): $\delta$ 7.2 (br s, aromatic), 4.3−3.3 (br s, benzyl), 3.3−0.5 (br m, main chain).

**Reaction of Poly(α-methylenebenzocyclobutene) (PMB) with Dienophile. Typical Procedure.** A mixture of PMB (0.12 g, 0.96 mmol, $\bar{M}_n = 7000$, $\bar{M}_w/\bar{M}_n = 3.51$), MANH (0.12 g, 1.22 mmol), and naphthalene (1.5 g) was placed in an ampule, which was cooled, degassed, and sealed off. After stirring at 230 °C for 3 h, the reaction mixture was poured into a large amount of *n*-hexane (300 mL) with vigorous stirring. White precipitate was collected by filtration, washed thoroughly with *n*-hexane, and dried under vacuum. Yield of PMB: 0.10 g (83%) ($\bar{M}_n = 1400$, $\bar{M}_w/\bar{M}_n = 1.40$). $^1$H NMR (90 MHz, $CDCl_3$): $\delta$ 7.2 (br s, 4H, aromatic), 3.3−0.5 (br s, 3H, main chain).

**Measurements.** GC analyses were performed on a Shimadzu GC8APF. IR spectra were recorded on a Jasco FT/IR-5300 spectrometer. $^1$H- and $^{13}$C-NMR spectra were recorded on JEOL PMX-60si, JNM EX-90, or JNM GX-500 spectrometers. Molecular weights were estimated by gel permeation chromatography (GPC) on a Tosoh HPLC CCPD equipped with three polystyrene gel columns (Tosoh TSK-GEL G5000Hxl, G4000Hxl, and G2500Hxl) at 35 °C, using THF as an eluent. Thermogravimetric analyses (TGA) were carried out with a Seiko TG/DTA200 at the heating rate of 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) analyses were made on a Seiko DSC220C at a heating rate of 10 °C/min.

**Molecular Orbital Calculation.** Molecular orbital calculations and full geometry optimization were made on an Apple Macintosh IICi using MOPAC version 6.02 (QCPE No. 455)[17,18] with the restricted Hartree−Fock (RHF) method and PM3 parameter.

**Scheme 3**



MB PMB

**Table 1. Homopolymerization of MB**[a]

| run | solvent | AIBN (mol %) | yield (%)[b] | $\bar{M}_n$[c] | $\bar{M}_w/\bar{M}_n$[c] |
|---|---|---|---|---|---|
| 1 | benzene (3 mol/L) | 2 | 31 | 6000 | 1.62 |
| 2 | none | 3 | 66 | 20000 | 4.75 |
| 3 | none | 20 | 70 | 7000 | 3.51 |

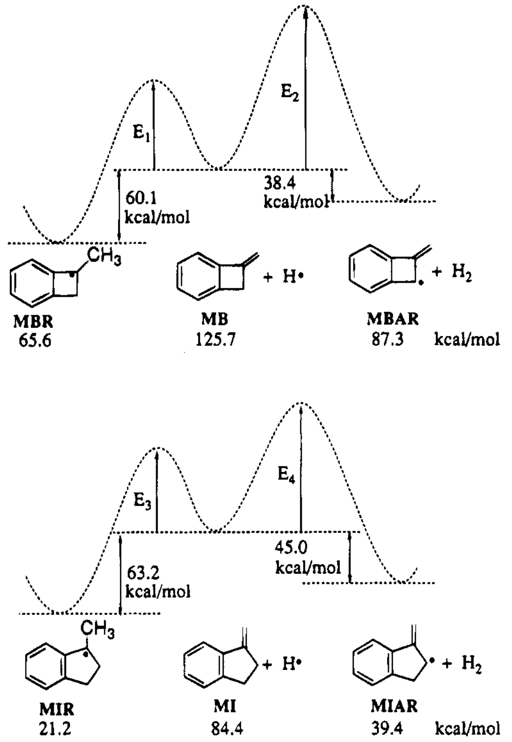
[a] 60 °C, 24 h. [b] MeOH-insoluble part. [c] Estimated by GPC (eluent, THF; based on PSt).

## Results and Discussion

MB[15,16] was synthesized by Wittig reaction of α-bromobenzocyclobutene, which was prepared by the reaction of benzocyclobutene and *N*-bromosuccinimide, with paraformaldehyde. Polymerization of MB was carried out at 60 °C for 24 h using AIBN as a radical initiator in benzene or in bulk (Scheme 3). The results are summarized in Table 1. The solution polymerization yielded the corresponding polymer, poly(α-methylenebenzocyclobutene) (PMB), as a white solid, although its yield and molecular weight were relatively low (run 1). The bulk polymerization gave higher molecular weight PMB in 66% yield. To obtain lower molecular weight PMB suitable for polymer reaction, the polymerization of MB was carried out in the presence of a large amount of initiator (20 mol %) and the polymer with $\bar{M}_n$ 7000 was collected in 70% yield. The structure of PMB was confirmed by IR, $^1$H-NMR, and $^{13}$C-NMR spectra. In the IR spectrum, the characteristic absorption at 1678 cm$^{-1}$ of the exomethylene group of MB completely disappeared after the polymerization. In accordance with the IR spectral change, an exomethylene signal at 3.5 ppm disappeared and instead a broad signal attributed to the main-chain protons at 2.2−0.5 ppm was confirmed in the $^1$H-NMR spectrum. In the $^{13}$C-NMR spectrum, an exomethylene carbon signal at 103 ppm disappeared, and all the carbon signals could be assigned for the PMB structure. These spectral data suggested the formation of PMB *via* vinyl polymerization.

MB can be regarded as a cyclic analog of α-methylstyrene. The radical polymerizability of MB seems to be fairly higher than that of α-methylstyrene. This can be explained by the cyclized planar substituent of the double bond of MB, by which the steric hindrance in the transition state of the propagation should be largely reduced in comparison with the case of α-methylstyrene ($T_c$ = 7 °C). By the reduced steric hindrance, the ceiling temperature of MB would be elevated and MB could polymerize under the conditions (60 °C). Similarly, α-methylene-*N*-methylpyrrolidone[19] and *N*-phenyl-α-methylene-*β*-lactam[20] undergo radical homopolymerization, whereas their acyclic analogs, N,N-disubstituted methacrylamides, do not polymerize.[21] Further, the yield of PMB was higher than that of poly(α-methyleneindane).[11] Ueda *et al.* have explained that the low yield of poly(α-methyleneindane) from α-methyleneindane (MI) is attributed to the allylic degradative chain transfer.[11] Then, we examined the semiempirical molecular orbital calculation[17,18] of the corresponding model allyl radical of MB (MBAR) as well as that of α-methyleneindane (MIAR) for comparison. Actually, the reactivity should be discussed by each activation

**Scheme 4. Proposed Energy Diagram of the Addition of Hydrogen Radical to MB or MI**

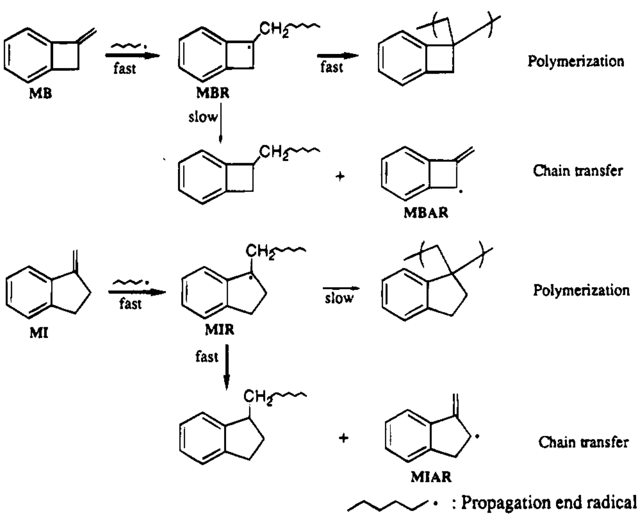


energy, but calculation of the activation energy is difficult for some reason (hardware and software). Since activation energy is presumed to be generally proportional to the difference in enthalpy between the starting material and product, it would be acceptable to discuss the reaction pathways and possibilities on the basis of the enthalpy difference in this case. The results based on heats of formation (kcal/mol) of the hydrogen radical and MB or MI are summarized in Scheme 4. MBR and MIR are the model radicals of the normal propagation ends for the vinyl polymerization, while MBAR and MIAR are the model allyl radicals formed *via* allylic hydrogen abstraction from MB and MI with the propagation radicals. Hydrogen radical means a model propagation end radical. As shown in Scheme 4, formation of allylic radicals (MBAR or MIAR) is easier in the MI system than in the MB system (6.6 kcal/mol), in comparison with that of benzyl radicals (MBR or MIR). That is to say, $E_1$ would be nearly equal to $E_3$, while $E_2$ would be larger than $E_4$. It indicates that the MI undergoes allylic degradative chain-transfer reaction more easily than MB. Consequently, MB undergoes polymerization without chain-transfer reaction, while MI undergoes chain-transfer reaction (Scheme 5).

Radical copolymerization of MB with St, MMA, and MANH was examined using 3 mol % of AIBN at 60 °C for 24 h, and the corresponding copolymers were obtained as shown in Table 2. In copolymerization with MANH in bulk, the obtained polymer was insoluble in any solvents because of increasing molecular weight. Using benzene as a solvent (0.1 mol/L), the obtained polymer can be soluble in most solvents. Glass transition temperatures ($T_g$) of the obtained polymers were around 100 °C. The $T_g$ of the copolymer with MMA cannot be decided for some reason.

To evaluate $Q-e$ values of MB, the copolymerizations of MB with MMA were carried out at 60 °C for 30 min in the presence of AIBN (3 mol %). The conversion of the monomers was kept below 5%, and the compositions of the obtained copolymers were determined by the $^1$H-NMR spectra. The feed ratio–copolymer composition curve is shown in Figure 1.

**Scheme 5. Proposal Reaction Mechanism**



Copolymerization parameters, $r_1$ and $r_2$, were calculated on the basis of the nonlinear least-squares analysis method: $r_1 = 0.46$ and $r_2 = 0.32$. Since $r_1r_2$ (0.147) is too small, it is suggested that the obtained copolymer has some alternating character, in accordance with the curve shape (Figure 1). Alfrey–Price's $Q-e$ values of MB were calculated from the $r_1$ and $r_2$ values as $Q = 1.35$ and $e = -1.00$, respectively. Since the $Q$ value of α-methylstyrene is 0.98, the terminal end radical of MB is more resonance-stabilized than that of α-methylstyrene, probably due to the planar system of MB. MB appears to be more electron-deficient than α-methylstyrene, judging from their $e$ values [MB (−1.00) and α-methylstyrene (−1.27)].

Since MANH is a more electron-deficient monomer than MMA, MB is expected to undergo radical copolymerization with MANH to give the corresponding alternating copolymer. The feed ratio–copolymer composition curve is shown in Figure 2. The $r_1$ and $r_2$ values of the copolymerization were calculated as 0.0025 and 0.025, respectively, and the $r_1r_2$ value ($6.25 \times 10^{-5}$) clearly indicated the alternating copolymerization of MB with MANH as understood from Figure 2. This copolymerization behavior of MB is similar to those of styrene and α-methylstyrene.[22,23]

TGA analysis of PMB (Figure 3) suggested that the decomposition started from ca. 230 °C. The DSC curve (Figure 3) showed two endothermic transitions: the first transition is around 150 °C and the second transition around 215 °C. These two transitions are explained later in the thermal reaction of PMB in the presence of dienophile.

Reaction of PMB ($\bar{M}_n = 7000$, $\bar{M}_w/\bar{M}_n = 3.51$) with MANH was examined at temperatures ranging from 130 to 230 °C. However, no Diels–Alder adduct was observed, but only a decrease of the molecular weight of PMB was observed at any temperature tested (Scheme 6). Similar phenomena were also observed in the reaction of poly(MB-*co*-St) with MANH. To clarify the thermal decomposition mechanism, PMB alone was heated with or without solvent [1,2,3,4-tetrahydronaphthalene (THN)]. The results are shown in Table 3. The degree of decomposition of PMB clearly depended on the reaction temperature. MB as an elimination product was not observed. In the $^1$H-NMR spectrum of the

**Table 2. Copolymerization of MB**[a]

| run | comonomer | solvent | yield (%)[b] | MB unit (%)[c] | $\bar{M}_n$[d] | $\bar{M}_w/\bar{M}_n$[d] | $T_g$ (°C)[e] |
|---|---|---|---|---|---|---|---|
| 1 | St | none | 90 | 42 | 6 000 | 1.89 | 110 |
| 2 | MMA | none | 95 | 50 | 20 000 | 2.75 | [g] |
| 3 | MANH | benzene[f] | 60 | 54 | 10 000 | 2.40 | 122 |

[a] MB: comonomer (molar ratio) = 1:1; AIBN, 3 mol %, 60 °C, 24 h. [b] MeOH-insoluble part. [c] Determined by $^1$H NMR. [d] Estimated by GPC (eluent, THF; based on PSt). [e] Determined by DSC. [f] 0.1 mol/L. [g] An indistinct $T_g$ point was observed at 81 °C.

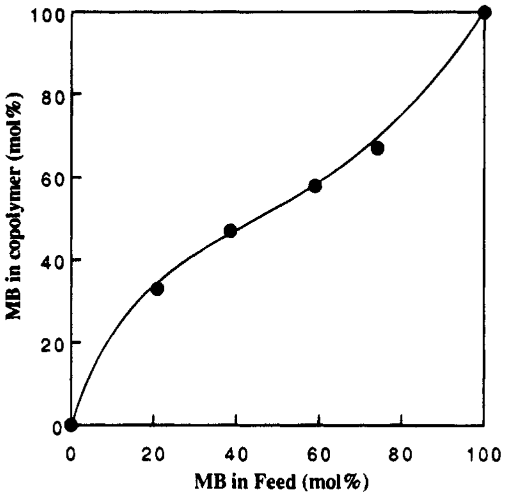


**Figure 1.** Feed ratio–copolymer composition curve of the copolymerization of MB with MMA.

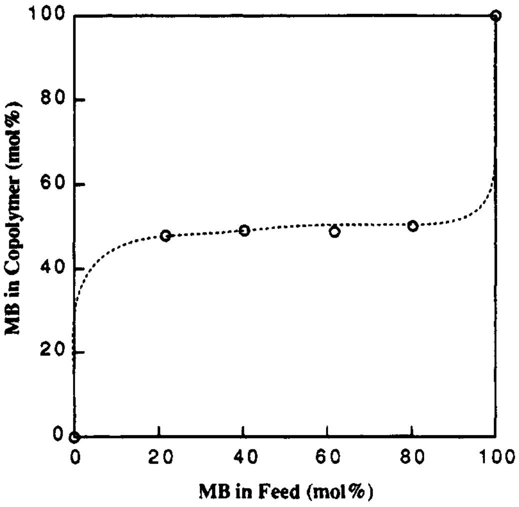


**Figure 2.** Feed ratio–copolymer composition curve of the copolymerization MB with MANH.

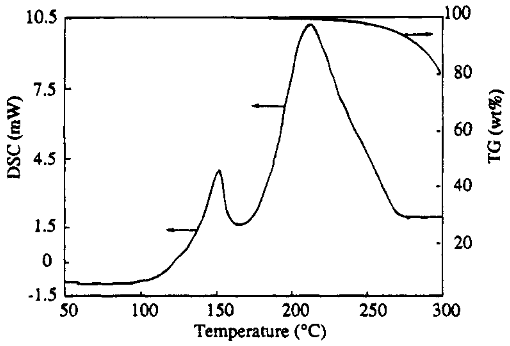


**Figure 3.** DSC curve of PMB (under $N_2$; heating rate, 10 °C/min).

product obtained by the reaction at a temperature over 160 °C for 24 h, signals due to the methylene protons of the cyclobutene ring completely disappeared. So, it can be speculated that the cleavage of the main chain of PMB occurs even below 160 °C and the cleavage of cyclobutene proceeds above 160 °C as suggested by the $^1$H-NMR spectrum. The second transition in the DSC curve (Figure 3) may be attributed mainly to the cleavage and successive reaction of the cyclobutene ring. However, the detailed decomposition mechanism of PMB is somewhat unclear at the present time.

### Scheme 6

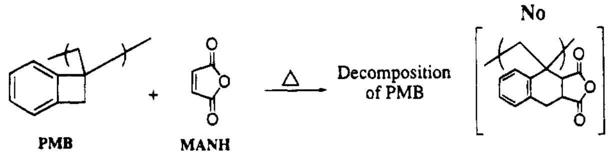


**Table 3. Thermal Decomposition of PMB**[a]

| run | solvent | temp (°C) | $\bar{M}_n$[c] | $\bar{M}_w/\bar{M}_n$[c] |
|---|---|---|---|---|
| 1 | none | 150 | 2000 | 2.15 |
| 2 | none | 230 | 640 | 1.94 |
| 3 | THN[b] | 150 | 3500 | 1.64 |
| 4 | THN[b] | 230 | 1100 | 1.60 |

[a] 24 h. Starting PMB: $\bar{M}_n$ = 7000, $\bar{M}_w/\bar{M}_n$ = 2.7. [b] 1,2,3,4-Tetrahydronaphthalene. [c] Estimated by GPC (eluent, THF; based on PSt).

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