Synthesis and Polymerization of Methyl 3-Methylcyclobutene-1-carboxylate

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ABSTRACT: A new cyclobutene monomer, methyl 3-methylcyclobutene-1-carboxylate (MMCB), has been synthesized and polymerized by radical and anionic initiators. The synthesis started from a [2 + 2] cycloaddition of *N*-(1-propenyl)piperidine to methyl acrylate, followed by methylation and treatment with base to yield the monomer. Free radical polymerization of MMCB led to low yields of low molecular weight polymers, probably due to chain transfer at the allylic hydrogen. However, *p*-methoxystyrene, styrene and methyl methacrylate gave high molecular weight copolymers with MMCB in high yields. Anionic homopolymerization with *tert*-butyllithium (*t*-BuLi), *t*-BuLi/bis(2,6-di-*tert*-butylphenoxy)ethylaluminum, lithium bis(trimethylsilyl)amide, and potassium bis(trimethylsilyl)amide in toluene at 0 and −78 °C proceeded smoothly and gave polymers in high yields. NMR and IR analyses of the polymers suggested that the polymerization proceeds via addition mechanism without ring-opening. Thermal properties of the polymers are also described briefly. In contrast to MMCB, methyl 3,3-dimethylcyclobutene-1-carboxylate MDCB did not polymerize due to excessive steric hindrance.

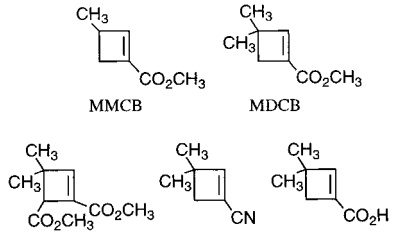
Introduction

Polymers containing 1,2- and 1,3-linked cyclobutane rings carrying a functional group are of interest for their good physical properties.[1−4] They can be considered for use in specialty high-tech applications. Wider use of such polymers has been limited because of difficulty in obtaining sufficient supplies of monomers by easy syntheses.

The main problem is the formation of a suitably functionalized cyclobutane. Among the common rings, the cyclobutane ring is the most difficult to form. However, Brannock et al.[5] reported very promising results from the [2 + 2]-cycloaddition reactions of enamines with electrophilic olefins. Cycloaddition of enamines possessing no β-hydrogen, such as *N*,*N*-dimethylisobutenylamine, to acrylonitrile, methyl acrylate, and diethyl fumarate led to an extensive series of functional *gem*-dimethylcyclobutanes. They were also able to obtain a second series of monomethyl cyclobutane derivatives from cycloaddition reactions with enamines that did possess a β-hydrogen, such as *N*,*N*-dimethylpropenylamine. Particularly interesting to us was the reported conversion of these cycloadducts to cyclobutenes by quaternization with methyl iodide, followed by treatment with base. Examples (Scheme 1) are methyl 3-methylcyclobutene-1-carboxylate (MMCB), methyl 3,3-dimethylcyclobutene-1-carboxylate (MDBC), dimethyl 4,4-dimethyl-1-cyclobutene-2,3-dicarboxylate, 3,3-dimethylcyclobutene-1-carbonitrile, and 3,3-dimethylcyclobutene-1-carboxylic acid.

We have been unable to find any reports of polymerization studies of these cyclobutenes. Among the potential cyclobutene monomers, we selected two monomers for further study, MMCB, with only one β-methyl group, and methyl 3,3-dimethyl-1-cyclobutenecarboxylate (MDCB). Steric repulsions between monomer and growing polymer chain might be substantial. The monomer carrying a single methyl group could react with growing radical or anion on the face away from the methyl substituent, but steric hindrance in MDCB might be too much. Accordingly, we set about establishing practical syntheses of these monomers within the framework of the reported synthesis[5] and studied their polymerizations using both radical and anionic initiation.

Scheme 1



Experimental Section

Measurements. NMR spectra were recorded on a Varian Gemini 200 or a Varian Unity Inova 500 spectrometer. The IR spectra were obtained on a Nicolet Impact 410 infrared spectrometer or a JASCO Herschel series FT/IR-410 spectrometer. Mass spectrometric low-resolution data (EI) were recorded on a HP 5988A GC/MS system. All high-resolution mass spectra including fast atom bombardment (FAB) with high- and low-resolution were taken on a JEOL HX 110A sector instrument. The elemental analyses were performed by Desert Analytics, Tucson, AZ. Molecular weight and molecular weight distribution were determined by size exclusion chromatography (SEC) using a JASCO 880-PU chromatograph equipped with Shodex SEC columns [KF-806L (30 cm × 0.8 cm) × 2] using chloroform as an eluent. The SEC chromatograms were calibrated against standard poly(methyl methacrylate) samples. Thermal analyses of the polymers were made on a SEIKO DSC 6200 and a SEIKO TG/DTA 6200.

Materials. Methyl acrylate were purified prior to use by filtering over a column with basic aluminum oxide. MMCB, styrene, *p*-methoxystyrene, isobutyl vinyl ether, methyl acrylate, *n*-butyl acrylate, and methyl methacrylate were purified

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prior to polymerization by distillation over calcium dihydride under reduced pressure and in a nitrogen or argon atmosphere. Toluene was purified in the usual manner, mixed with a small amount of butyllithium, and distilled under high vacuum. 2,6-Di-*tert*-butylphenol, obtained commercially (Tokyo Kasei Kogyo Co., Ltd.), was fractionally distilled, and used as a heptane solution. *tert*-Butyllithium (*t*-BuLi) in pentane (Aldrich Co., Ltd.) was used as a heptane solution. The concentration was determined by titration with butan-2-ol using *o*-phenanthroline as an indicator.[6] *tert*-Butylmagnesium bromide (*t*-BuMgBr) was prepared from magnesium turnings and *tert*-butyl bromide in diethyl ether.[7] The concentration of the *t*-BuMg group was determined by hydrolysis with excess 0.1 M HCl and back-titration with 0.1 M NaOH using phenolphthalein as an indicator. Lithium bis(trimethylsilyl)amide [$LiN(SiMe_3)_2$] as a hexanes solution and potassium bis(trimethylsilyl)amide [$KN(SiMe_3)_2$] as a toluene solution were purchased from Aldrich Co., Ltd. and used as received. $LiN(SiMe_3)_2$ concentration was determined by titration with butan-2-ol and that of $KN(SiMe_3)_2$ by acid−base titration. Bis(2,6-di-*tert*-butylphenoxy)ethylaluminum [$EtAl(ODBP)_2$] was prepared from 2,6-di-*tert*-butylphenol and triethylaluminum in heptane at 0 °C, according to the literature,[8] recrystallized from heptane, and used as a toluene solution.

***N*-(1-Propenyl)piperidine (1).** The enamine was prepared by a condensation method described in the literature using anhydrous potassium carbonate.[9] The primary amination product (aminal) synthesized from 1 molar equiv of propionaldehyde (70 g, 1.20 mol) and 2 molar equiv of piperidine (204 g, 2.40 mol), was thermally decomposed by distillation. Very slow fractionation through a 12 cm Vigreux column under an argon atmosphere in vacuo provided 74% (111 g, 0.89 mol) of **1** as a colorless oil (bp 99−102 °C, 75 mmHg).[9,10] ^{1}H NMR ($CDCl_3$): δ 5.86−5.79 (m, ^3J = 13.8 Hz, ^4J = 1.4 Hz, 1 H, CH-(NR_2)), 4.38 (dq, ^3J = 6.4, 13.8 Hz, 1 H, C*H*(CH_3)), 2.75−2.70 (m, 4 H, α-ring-CH_2), 1.62 (dd, ^3J = 6.4 Hz, ^4J = 1.4 Hz, 3 H, CH_3), 1.65−1.41 (m, 5 H, β,γ-ring-CH_2). ^{13}C NMR: δ 141.6 (CH(NR_2)), 94.5 (C*H*(CH_3)), 50.2 (α-ring-CH_2), 25.7 (β-ring-CH_2), 24.7 (γ-ring-CH_2), 15.8 (CH_3). IR (neat): 3052, 3033 (=CH_2), 1694, 1660 (C=C) cm^{-1}. MS (EI): *m*/*z* (rel intensity) 125 (M^+, 42), 124 ($M^+ - H$, 33), 110 ($M^+ - CH_3$, 100), 96 (18), 82 (14), 68 (25), 55 (10), 41 (21). HRMS (EI): calcd for $C_8H_{15}N$ (M^+), 125.1204; found, 125.1202.

1-Methoxycarbonyl-3-methyl-2-(*N*-piperidinyl)cyclobutane (2). Similar to a procedure described in the literature,[5] enamine **1** (63 g, 0.50 mol) and methyl acrylate (43 g, 0.50 mol) in the presence of a trace of bis(3-*tert*-butyl-4-hydroxy-5-methylphenyl) sulfide as an inhibitor were combined under an argon atmosphere and stirred at ambient temperature. After 3 days, conversion of the starting materials to cyclobutane **2** was quantitative. Distillation through a 12 cm Vigreux column under reduced pressure (bp 92 °C, 1.0 mmHg) gave 88% (93 g, 0.44 mol) of cyclobutane **2** as a mixture of at least 2 isomers (lit.:[3] 67%). ^{1}H NMR ($CDCl_3$): δ 3.69, 3.67 (2 s, 3 H, OCH_3), 2.88−2.48 (m, 2 H, CH(NR_2), C*H*(CO_2CH_3)), 2.41−2.08 (m, 6 H, CH_2, α-ring-CH_2), 1.64−1.30 (m, 7 H, C*H*(CH_3), β,γ-ring-CH_2), 1.13, 1.05 (2 d, ^3J = 6.2 Hz, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): main isomer δ 174.8 (*C*O_2CH_3), 70.8 (CH-(NR_2)), 51.2 (CO_2CH_3), 50.7 (α-ring-CH_2), 39.8 (*C*H(CO_2CH_3), 31.7 (*C*H(CH_3)), 26.2 (CH_2), 25.2, 24.0 (β,γ-ring-CH_2), 20.7 (CH_3). IR (neat): 1732 (C=O) cm^{-1}. MS (FAB) *m*/*z* 212 (MH^+), 126 (MH^+(enamine)), 85. HRMS (FAB): calcd for $C_{12}H_{22}NO_2$ (MH^+): 212.1651; Found: 212.1650. Anal. Calcd. for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.00; N, 6.63. Found: C, 68.00; H, 10.15; N, 6.68.

N*-(1-Methoxycarbonyl-3-methyl-2-cyclobutyl)-*N*-methylpiperidinium iodide (3).** The quaternization of cyclobutane **2** (70 g, 0.33 mol) with methyl iodide (57 g, 0.40 mol) was carried out according to a method described in the literature.[11] After 4 days at ambient temperature, methiodide **3** solidified and was isolated in 86% yield (100 g, 0.28 mol) by filtration. Recrystallization from ethanol/petroleum ether (4:1) gave 68% of **3** (79 g, 0.22 mol) as slightly yellow crystals (mp 108 °C). ^{1}H NMR [dimethyl sulfoxide (DMSO)-d_6]: δ 4.12−4.03 (m, 1 H, C*H*($N^+(CH_3)R_2$)), 3.66 (s, 3 H, OCH_3), 3.62−3.55 (m, 1 H, C*H*(CO_2CH_3)), 3.37−3.14 (m, 4 H, α-ring-CH_2), 3.04 (s, 3 H, $N^+(CH_3)R_2$), 2.95−2.65 (m, 1 H, C*H*(CH_3)), 2.45−2.23 (m, 2 H, CH_2), 1.93−1.35 (br m, 6 H, β,γ-ring-CH_2), 1.16 (d, ^3J = 6.2 Hz, 3 H, CH(C*H*$_3$)). ^{13}C NMR (DMSO-d_6): δ 171.9 (*C*O_2-CH_3), 72.9 (*C*H($N^+(CH_3)R_2$)), 58.3, 58.1 (α-ring-CH_2), 52.0 (OCH_3), 43.4 (*C*H(CO_2CH_3)), 35.6 ($N^+(CH_3)R_2$), 27.7 (*C*H(CH_3)), 25.0 (CH_2), 20.2, 18.9 (β,γ-ring-CH_2), 19.7 (CH(C*H*$_3$)). IR (KBr) 1737 (C=O) cm^{-1}. MS (FAB): *m*/*z* 226 (MH^+(cation)), 185, 93, 75, 57. HRMS (FAB): calcd for $C_{13}H_{25}NO_2$ (MH^+(cation)), 226.1807; found, 226.1809. Anal. Calcd for $C_{13}H_{24}NO_2I$: C, 44.21; H, 6.85; N, 3.97. Found: C, 44.09; H, 6.90; N, 3.90. ***Note: Usually, crude cyclobutane **2** was used for the preparation of methiodide **3** without purification.

Methyl 3-Methylcyclobutene-1-carboxylate (MMCB). Under an argon atmosphere, a 60% dispersion of sodium hydride in mineral oil (11 g, 0.27 mol) was washed twice with low boiling petroleum ether (25 mL each) and suspended in dry tetrahydrofuran (THF) (350 mL). Methiodide **3** (79 g, 0.22 mol) was added through a powder funnel in one portion. The reaction starts immediately as witnessed by evolution of hydrogen gas and a moderate temperature increase. After the mixture was stirred at room temperature for 1.5 h, the yellow color had faded and no more gas evolved. The reaction mixture was centrifuged, the solution decanted, and the residues were washed three times with dry THF, each time followed by centrifuging and decanting. Subsequently, a trace of bis(3-*tert*-butyl-4-hydroxy-5-methylphenyl) sulfide (inhibitor) and some dry ice were added to the combined THF solutions, which were then poured onto brine containing a small amount of ice. After separation of the aqueous layer, the organic one was washed with brine, whereas piperidine was removed by extraction with 6 M HCl. After this was washed with water, the colorless organic layer was dried over $MgSO_4$, concentrated, and fractionated over a 6 cm Vigreux column under reduced pressure to give 71% (20 g, 0.16 mol) of cyclobutene MMCB as a colorless liquid (bp 70−71 °C, 15 mmHg). If inhibited with 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide, MMCB can be stored for several months at −50 °C without decomposition. ^{1}H NMR ($CDCl_3$): δ 6.81 (s, 1 H, =CH), 3.73 (s, 3 H, OCH_3), 2.92−2.75 (m, 2 H, C*H*(CH_3), C*H*H), 2.28−2.15 (m, 1 H, CH*H*), 1.19 (d, ^3J = 7.1 Hz, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 163.1 (*C*O_2CH_3), 151.5 (=CH), 136.5 (=*C*(CO_2CH_3)), 51.2 (OCH_3), 36.5 (CH_2), 34.9 (*C*H(CH_3)), 18.2 (CH_3). IR (neat): 3057 (C=C), 1726 (C=O), 1611, 1601 (C=C) cm^{-1}. MS (EI): *m*/*z* (rel intensity) 126 (M^+, 34), 111 (36), 95 (24), 67 (100). HRMS (EI): calcd for $C_7H_{10}O_2$, 126.0681; found, 126.0681.

Methyl 2-(dimethylamino)-3,3-dimethylcyclobutanecarboxylate.[5] A mixture of methyl acrylate (156 g, 1.82 mol), *N*,*N*-dimethylisobutylamine[12] (60 g, 0.61 mol), and acetonitrile (250 mL) was refluxed overnight. Solvent and unreacted starting materials were removed by rotary evaporation. Vacuum distillation gave 61 g (yield 54%) of 2-(dimethylamino)-3,3-dimethylcyclobutanecarboxylate, bp 60−65 °C at 2 mmHg. ^{1}H NMR($CDCl_3$): δ 3.60 (s, 3H), 2.74 (q, 1H, *J* = ∼9 Hz), 2.43 (d, 1H, *J* = 8.7 Hz), 2.02 (s, 6H), 1.69 (dd, 1H, *J* = 9.6. 10.5), 1.55 (dd, 1H, *J* = 9.6, 10.5), 1.07 (s, 3H), 1.05 (s, 3H) ppm. ^{13}C NMR-($CDCl_3$): δ 157.2, 72.3, 51.6, 43.1, 39.3, 35.4, 33.4, 29.8, 21.7 ppm.

***N*-(1-Methoxycarbonyl-3,3-dimethyl-2-cyclobutyl)-*N*,*N*,*N*-trimethylammonium Iodide.** Methyl iodide (63 g, 0.44 mol) was added to a solution of methyl 2-(dimethylamino)-3,3-dimethylcyclobutanecarboxylate (61 g, 0.33 mol in 300 mL of diethyl ether), and the mixture was stirred for 6 days. Then the mixture was filtered and dried in a vacuum to give 89 g (83%) of *N*-(1-methoxycarbonyl-3,3-dimethyl-2-cyclobutyl)-*N*,*N*,*N*-trimethylammonium iodide. ^{1}H NMR (DMSO-d_6): δ 4.00 (d, 1H, *J* = 10.4 Hz), 3.76 (q, 1H, *J* = 10 Hz), 3.64 (s, 3H), 3.09 (s, 9H), 1.91 (t, 1H, 10.2 Hz), 1.50 (t, 1H, *J* = 9.9 Hz), 1.36 (s, 3H), 1.24 (s, 3H) ppm. ^{13}C NMR (DMSO-d_6): δ 171.9, 74.0, 52.1, 51.7, 40.3, 36.2, 32.8, 29.4, 22.5 ppm.

Methyl 3,3-Dimethylcyclobutene-1-carboxylate (MDCB). Under an argon atmosphere, a 60% dispersion of sodium hydride in mineral oil (12 g, 0.30 mol) was washed twice with pentane (30 mL each) and suspended in dry THF (250 mL). *N*-(1-Methoxycarbonyl-3,3-dimethyl-2-cyclobutyl)-

N,N,N-trimethylammonium iodide (65.4 g, 0.20 mol) was added through a powder funnel in one portion. After the mixture was stirred overnight at room temperature, anhydrous ether (200 mL) was added. Then the reaction mixture was centrifuged and the solution decanted, and the residues were washed three times with anhydrous ether, each time followed by centrifugation and decantation. Subsequently, a pinch of bis(3-*tert*-butyl-4-hydroxy-5-methylphenyl) sulfide (inhibitor) and some dry ice were added to the combined organic solutions, which were poured onto a mixture of ice and brine. After separation of the aqueous layer, the organic layer was washed with brine, 5 M HCl and distilled water. The organic layer was dried over $MgSO_4$, concentrated, and vacuum distilled to give 18 g of cyclobutene. MDCB contained about 10% of a methanol adduct, methyl 3,3-dimethyl-2-methoxycyclobutane-1-carboxylate, which was confirmed by GC−MS, but was used as such for the polymerization studies. ^{1}H NMR($CDCl_3$): δ 6.78 (s, 1H), 3.67 (s, 3H), 2.38 (s, 2H), 1.17 (s, 6H) ppm. ^{13}C NMR($CDCl_3$): δ 163.5, 155.4, 134.2, 51.1, 42.5, 40.9, 25.3 ppm. MS (*m*/*z*): 141 (100%, $-CO_2$), 139, 125, 79, 53.

Radical Homopolymerization in Bulk. Freshly distilled MMCB (0.005 mol), and AIBN (2 mol %) were degassed by freeze−thawing and kept at 80 °C for 20 h. The clear, colorless product was highly viscous at 80 °C and a glass at room temperature. The reaction product was dissolved in a small amount of dichloromethane and the polymer precipitated into cold diethyl ether. The colorless polymer was washed repeatedly with diethyl ether followed by drying over P_2O_5 at 80 °C in vacuo. The poly(MMCB) is soluble in dichloromethane, chloroform, acetonitrile and acetone.

Radical Homopolymerization and Copolymerization in Solution. Solutions of freshly distilled MMCB (2.5 mmol) and AIBN (2 mol %) in *N,N*-dimethylformamide (DMF) or γ-butyrolactone (2.5 mL) were degassed by freeze−thawing. After 20 h at 80 °C, the reaction mixtures were poured into chilled diethyl ether. Isolation, purification, and drying of the polymers were carried out as described above.

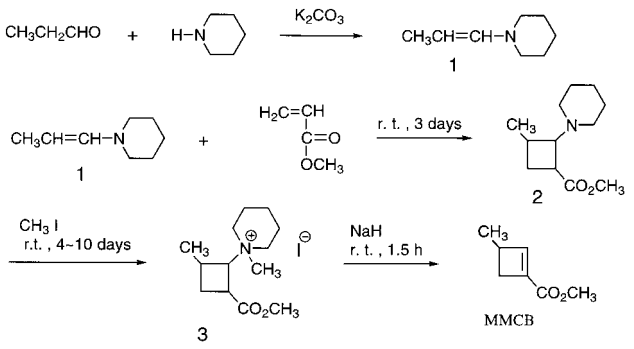
Polymerization in Aqueous Slurry. A mixture of freshly distilled MMCB (0.005 mol) in 3 mL of distilled water and aqueous solutions of $K_2S_2O_8$ (0.1 M) and $Na_2S_2O_4$ (0.05M) were degassed separately by freeze−thawing. Subsequently, $K_2S_2O_8$-(aq) (0.1 mL, 0.2 mol %) and $Na_2S_2O_4$(aq) (0.1 mL, 0.1 mol %) were added to the stirred monomer slurry using a syringe. After 1.5 h, another 0.1 mL of each solution was added. Polymerization started after about 10−20 min, and the reaction mixture was stirred at ambient temperature for additional 20 h. The slurry was filtered and washed with water, and the colorless polymer was treated twice with water in a blender and one time in methanol, followed each time by filtering and washing. The polymer was dried over P_2O_5 at 80−100 °C in vacuo to give the product in 56% yield.

Anionic Polymerization. All the anionic polymerizations were carried out in glass ampules, cooled at −78 °C and filled with dried nitrogen passed through molecular sieves 4A. The polymerization reaction was initiated by adding the monomer to the initiator solutions at the polymerization temperature and terminated by adding methanol containing a small amount of aqueous HCl.

Results and Discussion

Monomer Synthesis. The route shown in Scheme 2 illustrates the successful synthesis of methyl 3-methylcyclobutene-1-carboxylate MMCB, which was also utilized for methyl 3,3-dimethylcyclobutene-1-carboxylate MDCB. *N*-(1-Propenyl)piperidine (**1**), from the reaction of piperidine with propionaldehyde as reported by Brannock et al.,[5] was satisfactory as the enamine component. Cycloaddition of the enamine to methyl acrylate proceeded in high yield under moderate heating. Methyl iodide converted the cycloadducts to the quaternary ammonium salts. Precipitation of the salt from diethyl ether solution as it formed gave the pure salt as a mixture of isomers.

Scheme 2



Various methods to convert the salts to the cyclobutene monomers were examined. Brannock et al.[5] used potassium hydroxide for this elimination, which resulted also in saponification of the ester to the carboxylic acid. In our hands, sodium methoxide gave the monomer containing a substantial amount of methyl 2-methoxycyclobutane-1-carboxylate, possibly formed by Michael addition of the methoxide to the formed monomer. Sodium hydride, a nonnucleophilic non-hydroxylic base, in THF was used at several temperatures. At room temperature (28 °C), the best results were obtained, i.e., 71% yield of MMCB, without hydrolyzing the ester functionality. It is interesting that the reaction of an insoluble base with an insoluble salt proceeds so readily.

Radical Homopolymerization. The results of the free radical polymerization studies are summarized in Table 1. MMCB polymerized with AIBN initiation. However, neither the yields nor the molecular weights were high. The difficulty did not appear to be caused by impurities; rather we suspect that the tertiary allylic hydrogen acts as a chain transfer agent. In contrast to the homogeneous radical polymerizations, poly(MMCB) obtained with $K_2S_2O_8$ and $Na_2S_2O_4$ in a slurry polymerization in water, was not soluble in common organic solvents such as acetone, acetonitrile, chloroform, dichloromethane, DMF, DMSO, and THF. This is possibly due to cross-linking.

To ascertain if spontaneous polymerization or isomerization of the monomer occurs under the polymerization conditions, MMCB was separately heated neat at 80 °C for 20 h. No polymerization occurred, and the yellow liquid obtained consisted mainly of the thermally stable monomer (>95%, ^{1}H NMR, IR); i.e., no isomerization to 1,3-diene occurred.

The dimethyl-substituted monomer MDCB did not polymerize under free radical conditions. In an attempt to overcome the expected low ceiling temperature, we tried the homopolymerization at −50 °C using redox conditions. Although these conditions smoothly polymerized methyl acrylate, no polymerization of MDBC was observed. The difference in reactivity between MMCB and MDCB is ascribed to the additional methyl group at the 3-position of MDCB. Whereas MMCB has an exposed face without steric hindrance, in MDCB both faces of the cyclobutene ring are sterically hindered by the two methyl substituents.

Radical Copolymerization. Better results were obtained in copolymerization with electron-rich monomers. When *p*-methoxystyrene or styrene was copolymerized with MMCB, high molecular weight copolymers were obtained in high yields. Methyl methacrylate also copolymerized well with MMCB, but isobutyl vinyl ether gave only a low molecular weight product. The results

Table 1. Radical Polymerizations of MMCB with AIBN at 80 °C for 20 h[a]

run	solvent	initiator	monomer/initiator	yield/%	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]
1				0		
2		AIBN	50	20	7900	1.34
					58800 (shoulder)	2.31
3	DMF	AIBN	100	0		
4	H_2O	$K_2S_2O_8 + Na_2S_2O_4$	100	56		

[a] Monomer 2.5 mmol; solvent 2.5 mL. [b] Determined by SEC in $CHCl_3$, calibrated against PMMA standards.

Table 2. Radical Copolymerizations of MMCB and Several Comonomers with AIBN in Bulk at 80 °C for 20 h[a]

run	comonomer[b]	monomer/AIBN	isolated yield/%	MMCB compn/%[c]	M_w[d]
5	IBVE		0		
6	IBVE	25	67	96	4900
7	IBVE	50	56	87	<4000
8	pMeOSt		0		
9	pMeOSt	25	67	41	20100
10	pMeOSt	50	56	41	16200
11	St	100	47	40	12700
12	MMA	50	48	40	48000

[a] MCBM 2.5 mmol; comonomer 2.5 mmol. [b] Key: IBVE, isobutyl vinyl ether; pMeOSt, *p*-methoxystyrene; St, styrene; MMA, methyl methacrylate. [c] Based on elemental analysis. [d] Determined by SEC in CH_2Cl_2.

Table 3. Anionic Polymerizations of MMCB with Several Initiators in Toluene[a]

run	initiator	temp/°C	time/h	yield/%	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]
13	*t*-BuMgBr	0	24	trace		
14		−78	48	trace		
15	*t*-BuLi	0	24	85.2	(2100)[d]	(2.38)[d]
16		−78	48	12.5	(2270)[d]	(2.83)[c]
17	*t*-BuLi/[c]	0	24	55.3	4900	1.75
18	$EtAl(ODBP)_2$	−78	48	46.6	9000	1.26
19	$LiN(SiMe_3)_2$	0	24	65.9	(1280)[d]	(2.80)[d]
20		−78	48	74.9	(1280)[d]	(1.69)[d]
21	$KN(SiMe_3)_2$	0	24	95.5	4500	1.56
22		−78	48	93.5	6800	1.34

[a] Monomer 2 mmol; initiator 0.07 mmol; toluene 1 mL. [b] Determined by SEC in $CHCl_3$, calibrated against PMMA standards. [c] $EtAl(ODBP)_2$ 0.21 mmol. [d] Measured for $CHCl_3$-soluble fraction.

are summarized in Table 2. MMCB was also heated at 80 °C for 24 h with equimolar amounts of *p*-methoxystyrene, styrene, or isobutyl vinyl ether, but no spontaneous copolymerization was observed.

Anionic Homopolymerization. Table 3 summarizes the results of the polymerizations of MMCB with several anionic initiators in toluene at 0 and −78 °C. Polymerization with *t*-BuMgBr, which is known to initiate living polymerization of methacrylates,[7] did not give polymers either at 0 or −78 °C. On the other hand, *t*-BuLi, a stronger base than *t*-BuMgBr, afforded polymers, and the yield at 0 °C was quite high. The products were only partially soluble in common organic solvents such as acetone, acetonitrile, chloroform, dichloromethane, DMF, DMSO, THF, and hexafluoropropan-2-ol (HFIP), and the molecular weight data were obtained only for chloroform-soluble fractions. The molecular weight distribution (MWD) of the soluble fraction was very broad. When *t*-BuLi was used in combination with bis(2,6-di-*tert*-butylphenoxy)ethylaluminum [$EtAl(ODBP)_2$], a bulky aluminum Lewis acid, the polymerization gave soluble polymers in moderate yields, whose MWDs were narrower than those of the polymers formed with *t*-BuLi. In particular, the polymer obtained at −78 °C showed fairly narrow MWD with an M_w/M_n value of 1.26. This effect of $EtAl(ODBP)_2$ on the anionic

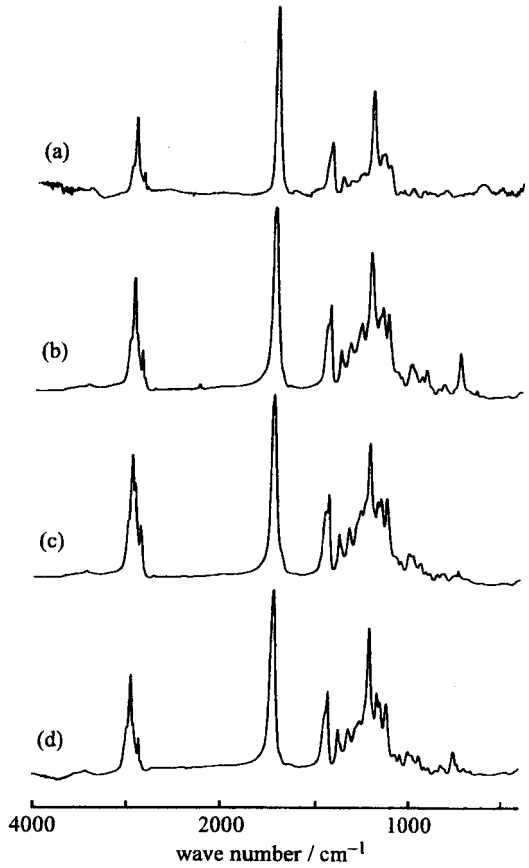


Figure 1. FT-IR spectra of poly(MMCB)s prepared with AIBN at 80 °C (a), $KN(SiMe_3)_2$ at 0 °C (b), *t*-BuLi at 0 °C ($CHCl_3$-soluble fraction) (c), and *t*-BuLi at 0 °C ($CHCl_3$-insoluble fraction) (d), measured by the KBr disk method.

polymerization has been well demonstrated in living polymerization of methacrylates and acrylates.[13−22] The present results provide an additional example of the utility of bulky aluminum compounds to control the anionic polymerization of carbonyl-containing polar monomers. Coordination of the bulky Lewis acid to the propagating anion may stabilize the anion and prevent it from unfavorable side reactions, and the Lewis acid coordination to the carbonyl group of MMCB may enhance its reactivity toward the nucleophilic propagating anion. In fact the polymer yield at −78 °C in this case is much higher than that with *t*-BuLi alone.

Lithium bis(trimethylsilyl)amide [$LiN(SiMe_3)_2$] and potassium bis(trimethylsilyl)amide [$KN(SiMe_3)_2$] are known as strong bases with low nucleophilicity. Nevertheless, the former has been used successfully for the polymerization of MMA, though the initiator efficiency was very low.[23] Since both the amides are supplied as solutions in nonpolar solvents, such as hexane and toluene, the polymerizations with these bases were examined in toluene under similar conditions as described above. The reactions proceeded smoothly and gave polymers in high yields at −78 and 0 °C. In

Table 4. Anionic Copolymerizations of MMCB and Acrylates in Toluene at −78 °C for 48 h[a]

run	initiator	comonomer[b]	yield/%	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	MMCB unit content/%[d]
23	*t*-BuLi	MA	50	9500	2.71	9
24		*n*-BuA	68	9800	3.49	11
25		MMA	72	(15400)[e]	(4.13)[e]	(60)[e]
26		MA	33	4400	2.82	9
27	*t*-BuLi/EtAl(ODBP)$_2$[f]	*n*-BuA	46	7200	3.33	13
28		MMA	10	16700	2.20	41
29		MMA[g]	64	5300	1.24	89

[a] MMCB 2 mmol; acrylate 2 mmol; *t*-BuLi 0.07 mmol; EtAl(ODBP)$_2$ 0.21 mmol; toluene 2 mL. [b] Key: MA, methyl acrylate; MMA, methyl methacrylate; *n*-BuA, *n*-butyl acrylate. [c] Determined by SEC in $CHCl_3$, calibrated against PMMA standards. [d] Determined by ^{1}H NMR. [e] Measured for $CHCl_3$-soluble fraction. [f] EtAl(ODBP)$_2$ 0.21 mmol. [g] *t*-BuLi 0.2 mmol; EtAl(ODBP)$_2$ 0.6 mmol.

particular, the polymerization with KN(SiMe$_3$)$_2$ gave polymers with fairly narrow MWD almost quantitatively even at −78 °C. In the polymerization with LiN(SiMe$_3$)$_2$, the reaction medium became heterogeneous as the reaction proceeded, and the polymer obtained was partly insoluble.

To examine the structural difference between the soluble and insoluble polymers, IR spectra of chloroform-soluble and -insoluble fractions of the polymer obtained with *t*-BuLi at 0 °C were measured as shown in Figure 1. The spectra of the polymers obtained with AIBN and KN(SiMe$_3$)$_2$,which are completely soluble, are also included. The IR spectra of these polymers were almost identical.

Anionic polymerization of the dimethyl derivative MDCB with the initiators listed in Table 3 did not give any polymeric products, similar to the radical polymerization case. Thus steric hindrance by the two methyl groups substantially suppresses the polymerization of MDCB in both free radical and anionic modes. Lack of ability to polymerize is not thought to be caused by the presence of ∼10% methoxy adduct, inasmuch as either are often used as solvents in anionic polymerizations.

Anionic Copolymerization. Table 4 shows the results of copolymerizations of MMCB and several acrylates with *t*-BuLi or *t*-BuLi/EtAl(ODBP)$_2$ as initiators in toluene at −78 °C. In the case of copolymerizations with methyl or *n*-butyl acrylate, the copolymers formed with both initiators contained less than 10% of MMCB units. In contrast, copolymerization with MMA gave copolymers with higher MMCB contents. These results suggest that the reactivity of MMCB in anionic copolymerization is lower than acrylate but higher than methacrylate. The order of reactivity is not altered by the addition of EtAl(ODBP)$_2$. MMCB can be regarded as an α,*β*-disubstituted acrylate monomer. Methyl tiglate, a typical α,*β*-disubstituted acrylate, polymerized to a very small extent under the same conditions, probably due to steric hindrance.[24] The fact that MMCB exhibits even higher reactivity than MMA may be ascribed to enhanced reactivity of the C=C bond in the four-membered ring structure and smaller steric hindrance at the *β*-position where the substituent group is fixed within the ring structure.

NMR Spectra of Poly(MMCB). As described above, poly(MMCB)s were obtained under several different polymerization conditions. ^{1}H and ^{13}C NMR spectra of the polymers were studied in detail to examine to what extent the structural features of poly(MMCB)s are controlled in the polymerization reaction. Figure 2 shows ^{1}H NMR spectra of poly(MMCB)s obtained by radical and anionic polymerizations. As mentioned above, some of the polymers were partly insoluble, and the spectra were obtained only for the chloroform-soluble fractions. None of the polymers showed olefinic proton signals confirming that the polymerizations proceeded via addition mechanism. The signals were assigned as shown in the figure on the basis of chemical shift consideration, peak intensity, and COSY. The different spectral patterns observed in each signal

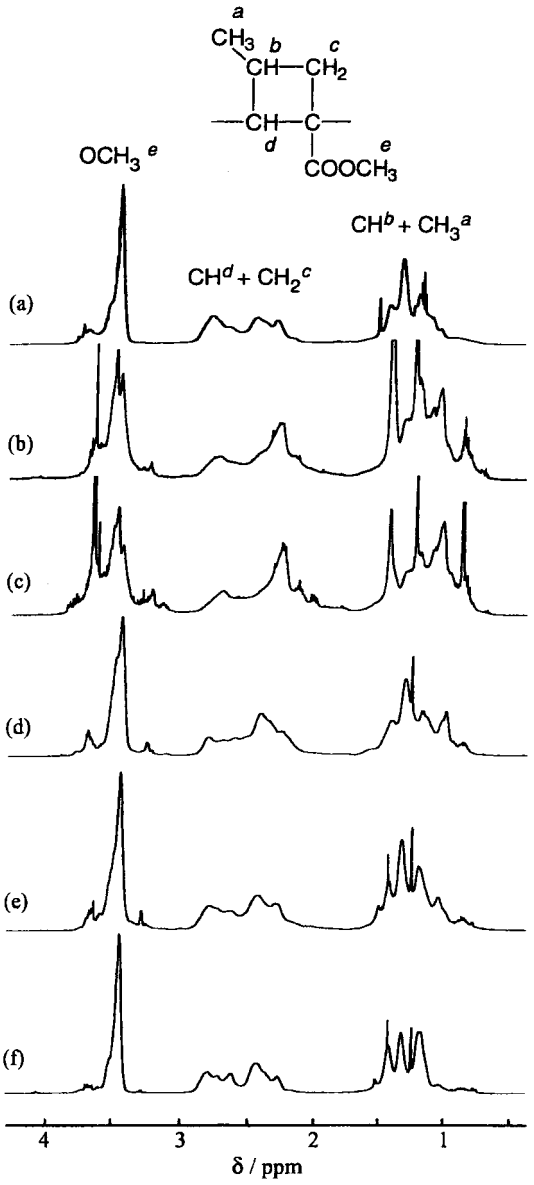


Figure 2. 500 MHz ^{1}H NMR spectra of poly(MMCB)s prepared with AIBN at 80 °C (a), *t*-BuLi at 0 °C (b), LiN(SiMe$_3$)$_2$ at 0 °C (c), KN(SiMe$_3$)$_2$ at 0 °C (d), *t*-BuLi/EtAl(ODBP)$_2$ at 0 °C (e), and *t*-BuLi/EtAl(ODBP)$_2$ at −78 °C (f), measured in $CDCl_3$ at 55 °C.

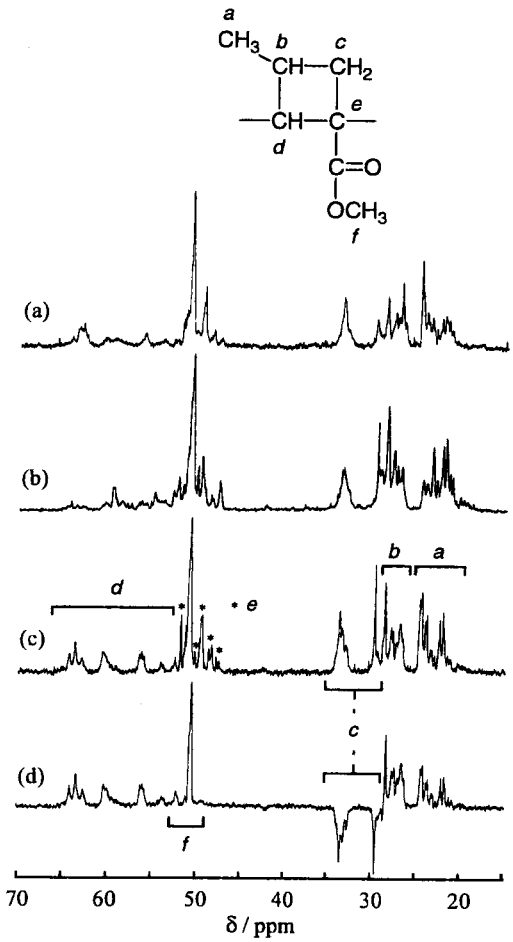


Figure 3. 125 MHz ^{13}C NMR spectra of poly(MMCB)s prepared with AIBN at 80 °C (a), $KN(SiMe_3)_2$ at 0 °C (b), and *t*-BuLi/EtAl(ODBP)$_2$ at −78 °C (c) and the DEPT-135 spectrum (d) of the mixture used in part c where CH_3 and CH carbons are detected upward and CH_2 carbons downward, measured in $CDCl_3$ at 55 °C.

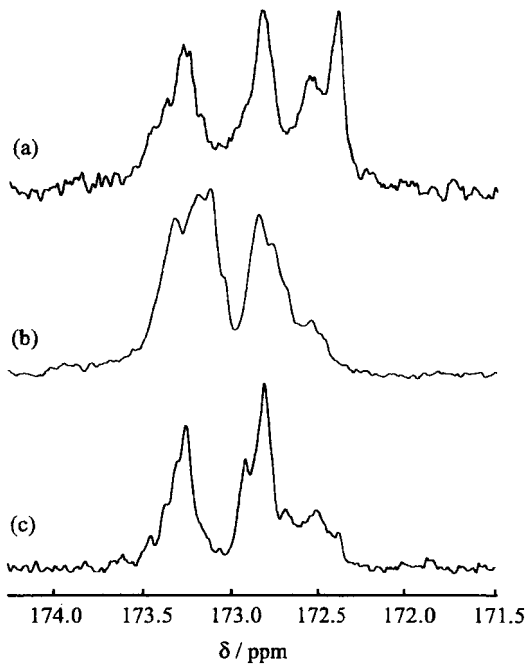
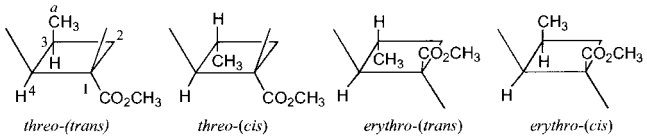


Figure 4. Carbonyl carbon resonances in 125 MHz ^{13}C NMR spectra of poly(MMCB)s prepared with AIBN at 80 °C (a), $KN(SiMe_3)_2$ at 0 °C (b), and *t*-BuLi/EtAl(ODBP)$_2$ at −78 °C (c), measured in $CDCl_3$ at 55 °C.

Scheme 3. Four Possible Stereoisomeric Monomer Units[a]



[a] The stereochemical configuration in the main chain is described by erythro/threo notation, and (trans) and (cis) denote the geometrical arrangement of the 3-methyl group relative to the ester group.

region reflect the difference in the stereochemical structures, such as cis−trans isomerism within the cyclobutane ring unit and/or tacticity along the main chain. Among them, the methoxy proton signals at 3.4−3.6 ppm, which are free from spin−spin coupling complexity, showed splittings reflecting such stereochemical structures. Though the assignments are not made, the polymer obtained with *t*-BuLi/EtAl(ODBP)$_2$ at −78 °C showed the simplest signal pattern and probably has the most regular structure.

Figure 3 shows the partial ^{13}C NMR spectra of poly(MMCB)s prepared with AIBN at 80 °C, with $KN(SiMe_3)_2$ at 0 °C and with *t*-BuLi/EtAl(ODBP)$_2$ at −78 °C, together with the DEPT-135 spectrum of the latter polymer. From the DEPT spectrum, the CH (*b*) and quaternary carbon (*e*) signals were assigned as indicated in the figure. Except for the simple OCH_3 signal at 51 ppm, all other carbon signals show complicated splitting. Expanded carbonyl carbon spectra are shown in Figure 4. The spectra seem to consist of three or four peak groups. Since the monomer unit contains two sites of stereoisomerism in the main chain and one at the 3-position in the cyclobutane ring, the latter is derived from the racemic nature of the starting MMCB. Since NMR is only sensitive to the relative configuration of these three sites of stereoisomerism, four kinds of stereoisomeric monomer units are possible, as shown in Scheme 3. According to the IUPAC nomenclature,[25] the main-chain stereoisomerism is denoted as *erythro* and *threo*. To describe the relative configurations at the 3-position, the cis and trans notation is employed in Scheme 3 for clarity, that is, cis (and trans) means that 3-methyl group [CH_3 (*a*)] is cis (trans) relative to the ester group in the same cyclobutane ring. Thus the four isomers are named erythro-(cis), erythro-(trans), threo-(cis) and threo-(trans). Though the assignments for these four possible structures are not made, it is evident that the polymer formed with *t*-BuLi/EtAl(ODBP)$_2$ is much simpler than that obtained radically. Further splittings observed in each peak group should reflect the stereochemical sequences along the main chain.

Figure 5 displays the expanded spectra of CH_3 (*a*) carbon at 3-position in the shift range of 20−25 ppm, which in principle should split into eight peaks. A diad sequence consists of six sites of stereoisomerism and 32 relative configurations are possible. However, since the chemical shift of CH_3 (*a*) is expected to be most sensitive to relative configurations of the carbonyl groups in the same monomer unit and the nearest neighboring unit, the diad tacticity of two ester groups is to be taken into consideration. The eight possible diads are illustrated in Scheme 4, in which the relative configuration of the other unit attached at the C (*e*) side is neglected. Though the assignments of the eight peaks are not completed, the spectra clearly indicate the difference in the stereo-

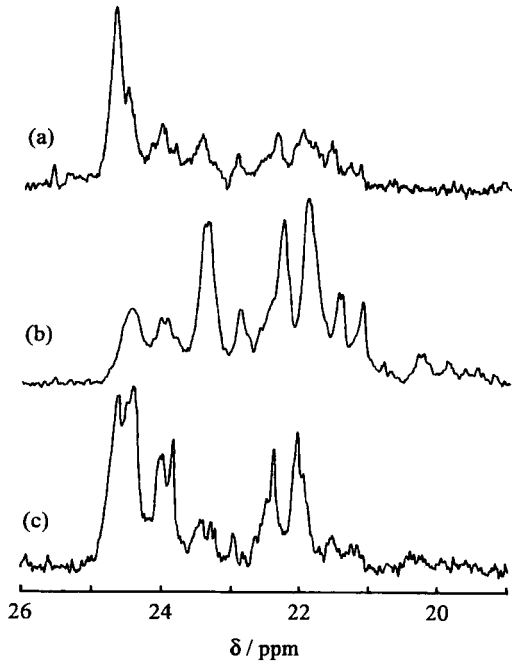
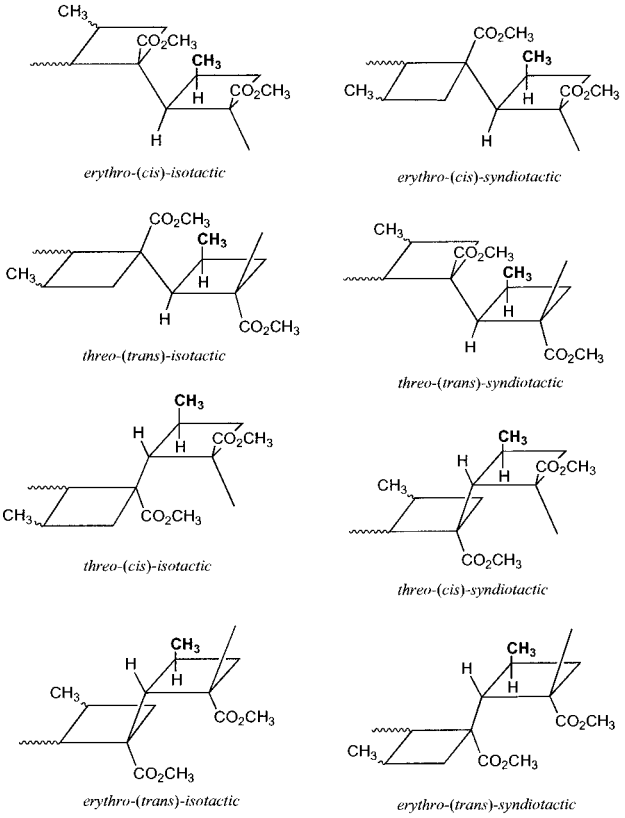


Figure 5. Methyl carbon resonances in 125 MHz ^{13}C NMR spectra of poly(MMCB)s prepared with AIBN at 80 °C (a), $KN(SiMe_3)_2$ at 0 °C (b), and *t*-BuLi/$EtAl(ODBP)_2$ at −78 °C (c), measured in $CDCl_3$ at 55 °C.

Scheme 4. Eight Possible Stereoisomeric Diads[a]



[a] The terms "*isotactic*" and "*syndiotactic*" denote the relative configurations of two C-1 carbons bearing ester groups. See also Scheme 3.

chemical structure between the polymers obtained by radical and anionic processes. It should be mentioned that the monomer itself is a racemic mixture, and thus the presence of 3-methyl group may cause further complications in stereochemical features of this polymer.

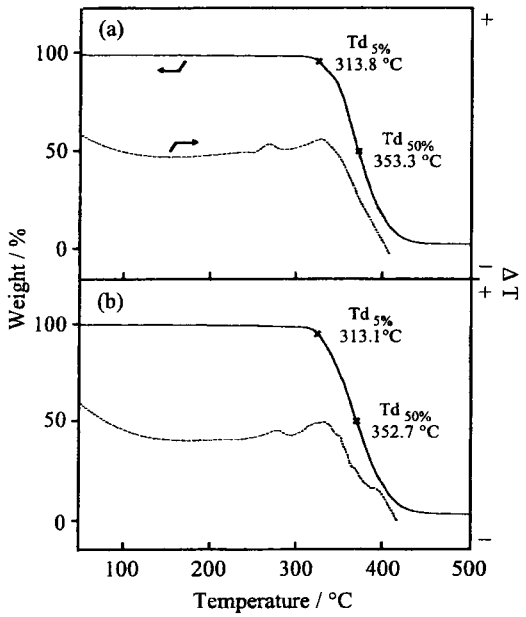


Figure 6. TGA (solid line) and DTA (dotted line) curves of poly(MMCB)s prepared with AIBN at 80 °C (a) and *t*-BuLi/$EtAl(ODBP)_2$ at −78 °C (b), measured at a heating rate at 20 °C/min under nitrogen.

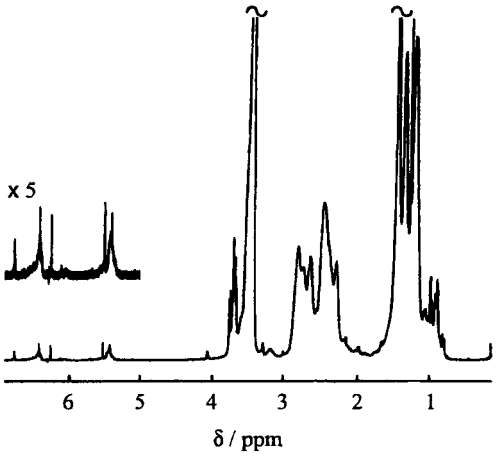


Figure 7. 500 MHz ^1H NMR spectrum of thermally treated poly(MMCB) (Table 3, run 18) at 280 °C, measured in $CDCl_3$ at 55 °C.

Thermal Properties. DSC measurements were carried out for several polymers obtained by different methods. In the temperature range from −50 to +150 °C, the homopolymers did not show a clear glass transition, or a melting endotherm. The copolymer with MMA (cf. Table 2) showed a T_g at 138 °C, which is higher than that of PMMA. These results suggest that inclusion of MMCB units contributes to an increase in the rigidity of the polymer chain.

Thermal gravimetric analysis (TGA) of the poly(MMCB)s revealed that it starts to decompose at about 300 °C and almost completely degrades at about 400 °C as shown in Figure 6. There was no substantial difference between radical and anionic poly(MMCB). Some thermal changes were observed in differential thermal analysis (DTA) measurement in the temperature range from 200 to 280 °C, at which the weight loss was negligibly small. When the polymer was recovered after heating to 280 °C, the ^1H NMR spectrum of the product showed olefinic proton signals at 5.4−5.5 and 6.4−6.5 ppm (Figure 7). These should be related to the

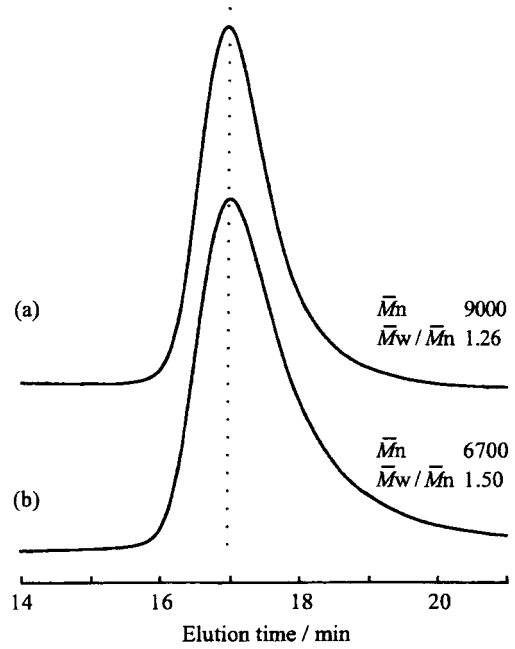
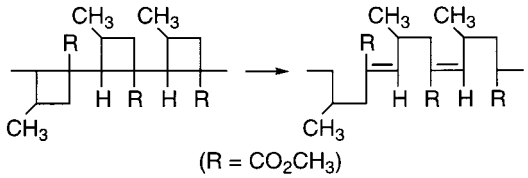


Figure 8. SEC curves of poly(MMCB) prepared with *t*-BuLi/EtAl(ODBP)$_2$ at −78 °C (a) and thermally treated at 280 °C (b) (1.0 wt % loss), calibrated against PMMA standards.

Scheme 5



ring opening of the cyclobutane units and the formation of C═C bonds between successive monomer units as shown in Scheme 5. The polymer thus formed contains units hypothetically derived from 2-methoxycarbonyl-penta-1,3-diene through 1,4-addition polymerization. Though the synthesis of this compound was recently reported,[26] there has been no report of its polymerization, and thus the thermal treatment described above might provide an alternative route to the diene polymer with functional carboxylate group. The SEC curve of the heated polymer showed tailing toward the low-molecular-weight side (Figure 8), showing that the thermal reaction is accompanied by main-chain scission to some extent but the scission did not cause degradation by unzipping to cause substantial weight loss. Further investigation is needed to clarify this phenomenon. We are currently investigating the polymerization of methyl cyclobutene-1-carboxylate, a simple analogue of MMCB, the polymer of which is expected to be better suited for a detailed investigation both of the stereochemical structure and the isomerization reaction.

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