

Monomer-Selective Living Copolymerization of *t*-Butyl Acrylate and Ethyl Methacrylate with *t*-Butyllithium / Bis(2,6-di-*t*-butylphenoxy)methylaluminum

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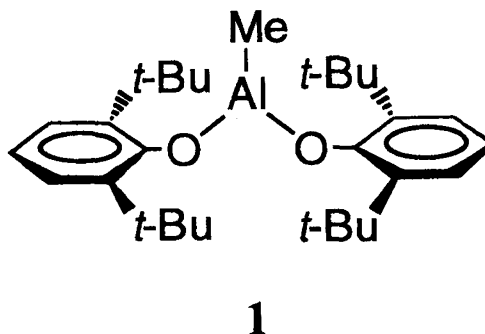
ABSTRACT: Anionic polymerizations of *t*-butyl acrylate (*t*-BuA) were carried out in toluene with a combination of *t*-butyllithium (*t*-BuLi) and bis(2,6-di-*t*-butylphenoxy)methylaluminum [MeAl(ODBP)₂] at low temperatures. The polymerization of *t*-BuA in the temperature range from -60°C to -20°C gave polymers with narrow molecular weight distribution (MWD). Anionic copolymerization of *t*-BuA and ethyl methacrylate (EMA) with *t*-BuLi/MeAl(ODBP)₂ in toluene at -60°C proceeded in a monomer-selective manner. The propagating anions react selectively with *t*-BuA which may be activated through the preferential coordination with MeAl(ODBP)₂. The copolymer showed a bimodal MWD, on-line SEC-NMR analysis of which revealed the formation of poly(*t*-BuA) as a lower molecular weight fraction and block-like copolymer as a higher molecular weight fraction. Increase in the polymerization temperature resulted in higher block efficiency, and the copolymers with narrow MWDs were formed at -40°C and -30°C . The ¹³C NMR spectra of the copolymers formed at and below -30°C indicated that the copolymers consisted of poly(*t*-BuA) block and poly(EMA) block. The copolymer formed at -20°C had narrow MWD and the random comonomer sequence.

KEY WORDS Monomer-Selective Copolymerization / *t*-Butyl Acrylate / Comonomer Sequence / Bis(2,6-di-*t*-butylphenoxy)methylaluminum / On-Line SEC-NMR /

Anionic polymerization of alkyl acrylates is often complicated by the occurrence of undesirable side reactions, involving nucleophilic attack of propagating species toward carbonyl carbons.^{1–3} Recently, it has been reported that several kinds of combined initiators comprising initiator components and stabilizers are effective to achieve living polymerization of acrylates.^{4–14} An early example of the combined initiators is a combination of *t*-butyllithium (*t*-BuLi) and lithium chloride (LiCl), which realized living polymerization of a bulky alkyl acrylate, *t*-butyl acrylate (*t*-BuA),^{4–6} in tetrahydrofuran (THF). More recently, a substantial improvement in the anionic polymerization of 2-ethylhexyl acrylate (2EtHA) and butyl acrylate has also been reported; the initiator used is alkyl α -lithioisobutyrate ligated with lithium *t*-butoxide.^{1,7–9} Furthermore, in addition to *t*-BuA and 2EtHA,^{10–13} some primary acrylates, such as methyl, ethyl, and butyl acrylates, have been polymerized by using diphenylmethylaluminum as an initiator, in the presence of chelating μ - σ type ligands, *i.e.*, polydentate lithium alkoxides, in toluene/THF mixtures at low temperatures.¹⁴ Thus, the living polymerization of acrylates has become possible by using additives which stabilize propagating species.

On the other hand, the living copolymerization of acrylates with methacrylates has been more difficult, because of the large difference in their reactivity in anionic polymerization.⁴ There have been a few successful examples, even though the copolymerization have been attempted by using the above-mentioned initiator systems.^{10,11,13} Bulky aluminum phenoxides have been used in living polymerization of methacrylate; high-speed living polymerization¹⁵ and screened living polymeriza-

tion,¹⁶ where the main roles of aluminum phenoxides are, respectively, the activation of monomer and the stabilization of propagation anion. We have reported that a combination of *t*-BuLi and bis(2,6-di-*t*-butylphenoxy)methylaluminum [MeAl(ODBP)₂, **1**] is an efficient initiating system for highly stereospecific living polymerization of methacrylates.^{17–25} We have also shown that the copolymerization of ethyl methacrylate (EMA) and trimethylsilyl methacrylate (TMSMA) with the same initiator system proceeded in a monomer-selective manner, since MeAl(ODBP)₂ selectively activates the less bulky monomer.^{19,25}



This paper reports the living polymerization of *t*-BuA with *t*-BuLi/MeAl(ODBP)₂ in toluene and the copolymerization with EMA. The copolymerization was found to proceed in a monomer-selective manner to afford a block-like copolymer. The copolymer obtained were minutely characterized by on-line SEC-NMR^{26–29} to elucidate molecular weight dependence of comonomer composition. The temperature dependence of monomer-

selectivity in the copolymerization was also studied and remarkable change of monomer-selectivity was found between the polymerization temperatures of -30°C and -20°C .

EXPERIMENTAL

Materials

t-BuA and EMA (Tokyo Chemical Industry Co., Ltd.) were purified by distillation, dried over calcium dihydride, and then vacuum-distilled just before use. Toluene and heptane were purified in the usual manner, mixed with a small amount of butyllithium, and distilled under high vacuum. Benzene was distilled and dried over sodium. *t*-BuLi in pentane (Aldrich Co., Ltd.) was used as a heptane solution by replacing the solvent under vacuum. The concentration was determined by titration with butan-2-ol using *o*-phenanthroline as an indicator.³⁰ MeAl(ODBP)₂ was prepared from 2,6-di-*t*-butylphenol and trimethylaluminum in toluene at room temperature,^{20,31} and recrystallized several times from heptane at -30°C .

Polymerization

All the polymerizations were carried out in glass ampoules filled with dried nitrogen passed through Molecular Sieves 4A cooled at -78°C . *t*-BuLi was added to MeAl(ODBP)₂ in toluene at the polymerization temperature at a molar ratio of [MeAl(ODBP)₂]/[*t*-BuLi] = 5. The polymerization reaction was initiated by adding the monomer or the mixture of monomers slowly to the initiator solution. The reaction was terminated by adding a small amount of methanol containing aqueous HCl at the polymerization temperature. The reaction mixture was concentrated to dryness under reduced pressure, and the residue was dissolved in benzene. Insoluble materials were removed by centrifugation, and the polymer was recovered from the solution by freeze-drying and dried under vacuum. Depending on necessity, 2,6-di-*t*-butylphenol resulting from the hydrolysis of MeAl(ODBP)₂ was removed by size exclusion chromatography (SEC) using a Shodex GPC column K-2003 (30 cm × 2.0 cm) with chloroform as an eluent.

Measurements

Molecular weights of the polymers and their distributions were determined by SEC using a JASCO TRI ROTAR-V chromatograph equipped with Shodex GPC columns KF-806L × 2 (8 mm i.d. × 300 mm) using THF as an eluent at 40°C . SEC chromatograms were calibrated against standard polystyrene samples.

¹H and ¹³C NMR spectra of the polymers were measured in chloroform-*d* at 55°C or in dimethyl sulfoxide-*d*₆/nitrobenzene-*d*₅ (3/1 vol/vol) at 100°C using a JEOL JNM AL400 spectrometer. Tacticities of the polymers were determined from ¹³C NMR spectra measured in chloroform-*d* at 100 MHz. Number-average molecular weight (\bar{M}_n) was also determined from the intensities of the ¹H NMR signal of *t*-butyl protons of the initiator fragment in the polymer chain-end, the methine proton signal due to *t*-BuA units and the proton signal of ester methylene group (OCH₂) due to EMA units.

On-line SEC-NMR measurement was performed on a

Table I. Polymerization of *t*-BuA with *t*-BuLi/MeAl(ODBP)₂ (1/5) in toluene at various temperatures^a

Run	Temp/ $^{\circ}\text{C}$	Time/h	Yield/%	\bar{M}_n (NMR)	$\frac{\bar{M}_w}{\bar{M}_n}$
1	-78	24	36.0	1500	1.12
2 ^b	-60	6	98.6	7200	2.00
3	-60	12	100.0	3800	1.26
4	-40	3	99.3	4700	1.21
5	-20	3	100.0	6900	1.22
6	0	3	91.2	6100	1.55

^a *t*-BuLi 0.2 mmol, MeAl(ODBP)₂ 1.0 mmol, *t*-BuA 5 mmol, toluene 10 mL. ^b Without MeAl(ODBP)₂.

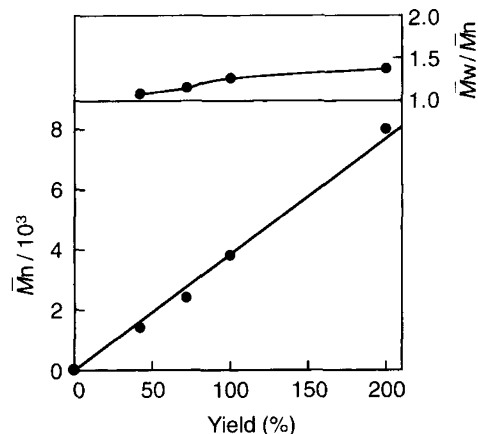


Figure 1. Relationships between \bar{M}_n (\bar{M}_w/\bar{M}_n) and yield in the polymerization of *t*-BuA with *t*-BuLi/MeAl(ODBP)₂ (1/5) in toluene at -60°C .

Varian Unity-INOVA 750 spectrometer using an ¹H inverse-geometry LC-NMR probe with pulsed field gradient coils.²⁶ A detection volume of the flow cell (2 mm i.d.) is approximately 60 μL . The sample inlet of the probe was connected to a JASCO PU-980 chromatograph equipped with a Shodex GPC column K-805L. Chloroform-*d* was used as an eluent and the flow rate was set to be 0.2 mL min⁻¹. The measurement temperature was 23°C and the sample amount injected was 0.6 mg in 50 μL each. A total of 28 spectra were collected every 36 s in an elution period from 39 to 56 min. With a 90° pulse (7.7 μs) and a pulse repetition time of 2.25 s, each spectrum was obtained by the accumulation of 8 scans, and stored into 32 K data points covering spectral width of 7490 Hz.

RESULTS AND DISCUSSION

Polymerization of *t*-BuA

The polymerizations of *t*-BuA were carried out with *t*-BuLi/MeAl(ODBP)₂ (Al/Li = 5) in toluene at various temperatures and the results are summarized in Table I. The polymerization at -78°C gave a polymer with narrow molecular weight distribution (MWD), but the monomer was not consumed quantitatively within 24 h (run 1). In the polymerization at -60°C , the polymer with narrow MWD was obtained quantitatively (run 3), while the polymerization without MeAl(ODBP)₂ gave a polymer with broad MWD (run 2). Even though the initiator efficiency of the polymerization with *t*-BuLi/MeAl-

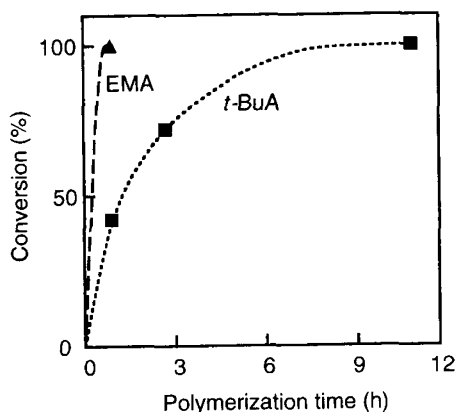


Figure 2. Time-conversion curves of the polymerizations of *t*-BuA and EMA with *t*-BuLi/MeAl(ODBP)₂ (1/5) at -60°C (monomer 5.0 mmol, *t*-BuLi 0.2 mmol, toluene 10 mL).

Table II. Copolymerization of *t*-BuA and EMA with *t*-BuLi/MeAl(ODBP)₂ (1/5) in toluene at -60°C ^a

Time/h	Yield/%	Conv./% ^b		\overline{M}_n (NMR)	\overline{M}_w \overline{M}_n
		<i>t</i> -BuA	EMA		
2	35.0	60.3	2.9	2600	1.13
6	52.0	93.2	3.3	3500	1.16
8	51.0	92.4	3.4	4300	1.19
9	70.0	94.3	42.1	5900	1.39
10	97.8	100	96.0	9300	1.84
12	99.0	100	98.4	8400	1.83

^a *t*-BuLi 0.2 mmol, MeAl(ODBP)₂ 1.0 mmol, *t*-BuA 5 mmol, EMA 5 mmol, toluene 10 mL. ^b Calculated from the total yields of copolymers and their compositions determined by ¹H NMR.

(ODBP)₂ is less than unity, \overline{M}_n of the produced polymer increases linearly with the increasing yield of the polymer (Figure 1). When *t*-BuA was added to the polymerization mixture after completion of the polymerization, the polymerization proceeded further to give a polymer having the expected \overline{M}_n , keeping narrow MWD. Similar results were also obtained in the polymerizations at -40°C and -20°C . The polymerization at 0°C gave a polymer with broader MWD (run 6), suggesting the occurrence of side reactions. Thus the polymerization of *t*-BuA with *t*-BuLi/MeAl(ODBP)₂ is likely a living system at least at the temperature lower than -20°C .

Copolymerization of *t*-BuA and EMA at -60°C

As described in the introduction, the copolymerization of EMA, a primary methacrylate, and TMSMA, a tertiary methacrylate, with *t*-BuLi/MeAl(ODBP)₂ in toluene proceeds in a living and monomer-selective fashion.^{19,25} The order of the monomer consumption is consistent with the order of the rates of homopolymerizations of EMA and TMSMA (EMA > TMSMA). To examine whether monomer-selective copolymerization takes place for an acrylate-methacrylate pair with the aid of MeAl(ODBP)₂, the copolymerization of *t*-BuA, a tertiary acrylate, and EMA with *t*-BuLi/MeAl(ODBP)₂ was examined in toluene at -60°C . First, the homopolymerizations of *t*-BuA and EMA were carried out under the same conditions. Figure 2 shows the time-conversion plots for the each polymerization, which evidently indi-

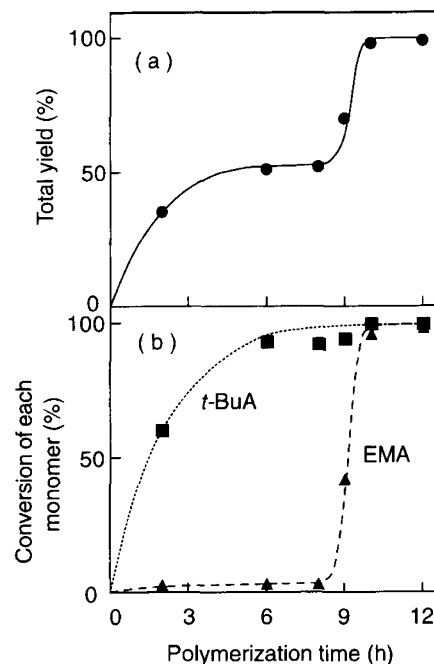


Figure 3. Time course of the copolymerization of *t*-BuA and EMA with *t*-BuLi/MeAl(ODBP)₂ (1/5) at -60°C (*t*-BuA 5.0 mmol, EMA 5.0 mmol, *t*-BuLi 0.2 mmol, toluene 10 mL).

cates that the polymerization of EMA proceeds much faster than that of *t*-BuA.

The copolymerization of *t*-BuA and EMA at an equal molar ratio with *t*-BuLi/MeAl(ODBP)₂ was carried out in toluene at -60°C (Table II). Figure 3a shows the time dependence of the polymer yield in the copolymerization, which indicates that the copolymerization apparently proceeded in two steps; the time-conversion curves of the respective monomers shown in Figure 3b reveal that *t*-BuA is polymerized preferentially, and, after almost all *t*-BuA is consumed, EMA starts to be polymerized much faster than *t*-BuA is polymerized in the first step. Thus, the copolymerization of *t*-BuA and EMA proceeds in a monomer selective manner but the order of monomer consumption is in the reverse order of the rates of homopolymerizations of the respective monomers.

NMR Study of Monomer Coordination with MeAl(ODBP)₂

In order to examine the possibility of the preferential activation of *t*-BuA due to the coordination with MeAl(ODBP)₂, the ¹³C NMR spectra of an equimolar mixture of *t*-BuA and EMA was measured in toluene-*d*₈ at -60°C in the presence or absence of MeAl(ODBP)₂. As shown in Figure 4, the signals of carbonyl carbons of the monomers shifted to lower magnetic field upon the addition of MeAl(ODBP)₂, indicating the presence of the coordination between each monomer and MeAl(ODBP)₂. The signals of β -methylene carbons of the monomers shifted to lower magnetic field in the presence of MeAl(ODBP)₂, suggesting the decrease of electron density at the β -methylene carbon through the coordination of MeAl(ODBP)₂ to the carbonyl group (Table III). This suggests that the coordination of MeAl(ODBP)₂ gives rise to the activation of the monomers toward nucleophilic attack of the propagating anions.¹⁵ The mixtures of the monomers

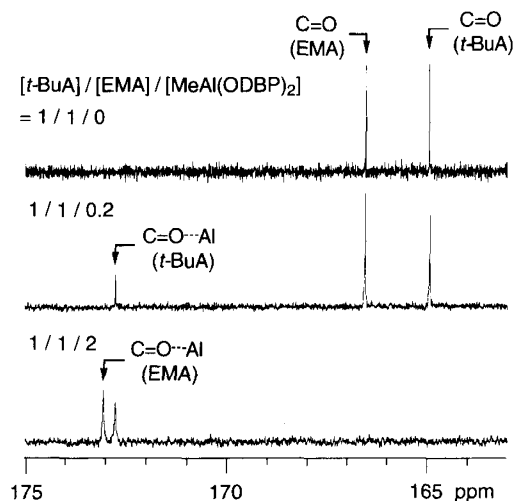


Figure 4. ^{13}C NMR spectra of carbonyl carbons of *t*-BuA and EMA in the presence or absence of MeAl(ODBP)_2 in toluene- d_6 at -60°C .

Table III. Chemical shifts in ppm of β -methylene carbons of *t*-BuA and EMA in the presence or absence of MeAl(ODBP)_2 in toluene- d_6 at -60°C

[<i>t</i> -BuA]/[EMA]/[MeAl(ODBP)_2]	<i>t</i> -BuA	EMA
1/1/0	129.7	125.1
1/1/2	137.8	137.2
	$\Delta\delta$	
	8.1	12.1

and MeAl(ODBP)_2 were examined at different molar ratios. At the feed molar ratio of *t*-BuA/EMA/ MeAl(ODBP)_2 of 1/1/0.2 which corresponds to the copolymerization condition (cf. Table II), *t*-BuA showed the carbonyl carbon signal (172.8 ppm) due to the coordinated species in addition to that of "free" *t*-BuA (164.9 ppm), while EMA showed a single peak due to "free" EMA (166.6 ppm). The results indicate that MeAl(ODBP)_2 coordinates preferentially with *t*-BuA over EMA. Though the former has a bulky *t*-butyl ester group, the substituent directly attached to the carbonyl carbons, vinyl or isopropenyl groups, seems more significant in steric effect upon the coordination. In the copolymerization of *t*-BuA and EMA, the propagating species stabilized through the coordination by MeAl(ODBP)_2 should react preferentially with the activated monomer (*t*-BuA) coordinated with MeAl(ODBP)_2 . Therefore, in the early stage of the copolymerization, almost all MeAl(ODBP)_2 coordinate to *t*-BuA and the activated *t*-BuA is polymerized preferentially. The selective monomer-coordination is one of the reasons that the copolymerization of *t*-BuA and EMA with $t\text{-BuLi/MeAl(ODBP)}_2$ (Al/Li=5) proceeds in a monomer-selective manner.

Chain-End Analysis

In order to obtain information on monomer selection in the initiation process, the structure near the initiating chain-end of the copolymer was studied by ^1H NMR spectroscopy. The spectrum of the copolymer obtained at -60°C for 12 h (Figure 5) showed signals due to the two kinds of *t*-butyl groups at the initiating chain-ends;

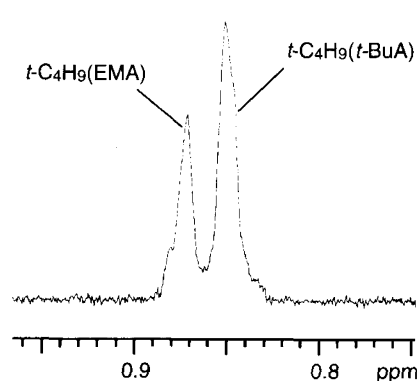


Figure 5. ^1H NMR spectrum of *t*-butyl group at the initiating chain-end of the copolymer of *t*-BuA and EMA prepared with $t\text{-BuLi/MeAl(ODBP)}_2$ (1/5) in toluene at -60°C for 12 h (*t*-BuA 5.0 mmol, EMA 5.0 mmol, *t*-BuLi 0.2 mmol, toluene 10 mL).

t-butyl group attached to the first *t*-BuA unit [$t\text{-C}_4\text{H}_9\text{-}(t\text{-BuA})$] at 0.85 ppm and that to the first EMA unit [$t\text{-C}_4\text{H}_9\text{(EMA)}$] at 0.88 ppm (in dimethyl sulfoxide- d_6 /nitrobenzene- d_5 = 3/1). The intensity ratio of $t\text{-C}_4\text{H}_9\text{-}(t\text{-BuA})$ and $t\text{-C}_4\text{H}_9\text{(EMA)}$ signals was found to be 58/42, which corresponds to the relative reactivity of *t*-BuA and EMA against *t*-BuLi in the initiation reaction. The result means that the addition of *t*-BuLi to *t*-BuA and EMA is almost non-selective even though there exists the activated *t*-BuA. This suggests that the stabilization of acrylate and methacrylate anions by MeAl(ODBP)_2 is inevitable for the monomer-selective propagation in this copolymerization, and *t*-BuLi is too reactive to differentiate the activated and non-activated monomers.

On-Line SEC-NMR Analysis

The SEC chromatogram of the final product formed in the copolymerization of *t*-BuA and EMA with $t\text{-BuLi/MeAl(ODBP)}_2$ in toluene at -60°C for 12 h is bimodal. Thus, molecular-weight dependence of the compositions of the copolymer as well as those obtained at 6 h and 9 h were studied by the on-line SEC-NMR²⁶⁻²⁹ system consisted of a 750 MHz ^1H NMR spectrometer as a detector. The copolymer composition of each elution fraction can be calculated from signal intensities of the respective monomer units by measuring NMR spectrum continuously against elution time. Figure 6 shows the ^1H NMR-detected SEC curves of the products obtained at -60°C . The SEC chromatograms corresponding to *t*-BuA and EMA units can be obtained from the intensities of the signals at 1.26 ppm [$\text{OC}(\text{CH}_3)_3$] and 4.04 ppm (OCH_2), respectively. Relative intensities of the chromatograms were normalized to represent the molar ratios of *t*-BuA and EMA units. Thus, the copolymer composition can be directly determined from the elution curves at any specified region in the chromatograms. As shown in Figure 6a, the SEC curve of the product obtained at 6 h, when the polymerization of *t*-BuA proceeds preferentially, is unimodal. As the polymerization of EMA takes place, the SEC curve shows a shoulder at higher molecular weight side (Figure 6b). The final product obtained at 12 h in 100% conversion shows a bimodal SEC curve (Figure 6c), in which the lower molecular weight peak

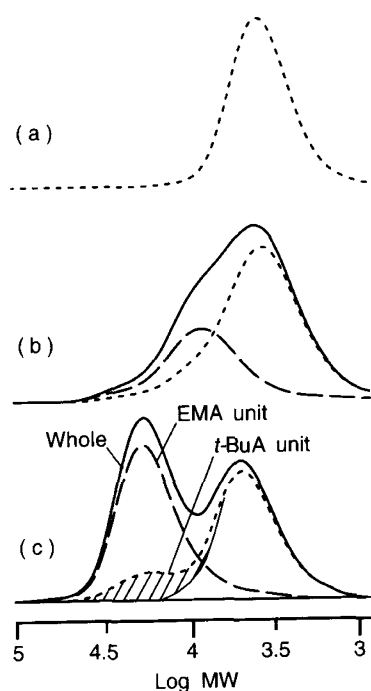


Figure 6. On-line SEC-NMR analysis of the copolymers of *t*-BuA and EMA prepared with *t*-BuLi/MeAl(ODBP)₂ (1/5) in toluene at -60°C for (a) 6 h, (b) 9 h, and (c) 12 h (*t*-BuA 5 mmol, EMA 5 mmol, *t*-BuLi 0.2 mmol, toluene 10 mL). Dotted line (----); *t*-BuA unit, broken line (---); EMA unit, solid line(—); whole unit.

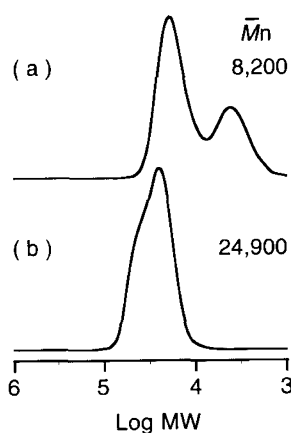


Figure 7. Change of SEC curve of the copolymers of *t*-BuA and EMA prepared with *t*-BuLi/MeAl(ODBP)₂ (1/5) at -60°C (a) before and (b) after the addition of second feed of *t*-BuA (*t*-BuLi 0.2 mmol, toluene 10 mL, *t*-BuA 5 mmol and EMA 5 mmol for the first feed, *t*-BuA 21 mmol for the second feed).

consists of *t*-BuA units almost exclusively, suggesting a large part of poly(*t*-BuA) anions formed in the first stage of the copolymerization failed to propagate further. The higher molecular weight peak is mainly consisted of EMA units with a small amount of *t*-BuA units. The existence of *t*-BuA units in the high molecular weight fraction is a strong evidence that the fraction is a block copolymer comprising a relatively short poly(*t*-BuA) block and a long poly(EMA) block.

Since the polymerization of *t*-BuA under the same conditions is proved living, the cause of the low molecular weight fraction is not likely a termination reaction. To confirm this, *t*-BuA was added to the copolymerization

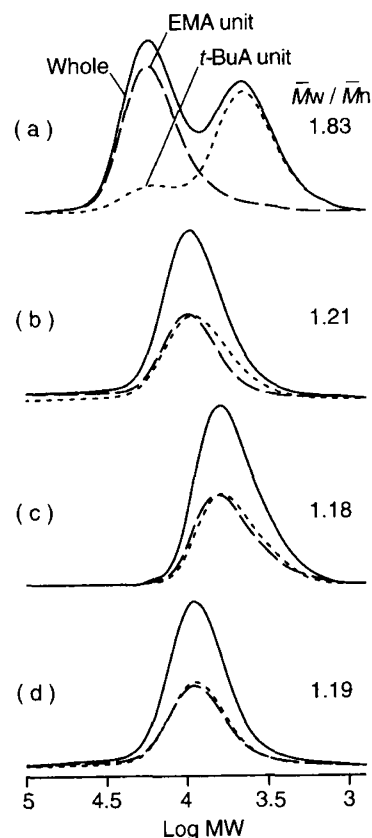


Figure 8. On-line SEC-NMR analysis of the copolymers of *t*-BuA and EMA prepared with *t*-BuLi/MeAl(ODBP)₂ (1/5) at (a) -60°C , (b) -40°C , (c) -30°C , and (d) -20°C (*t*-BuA 5 mmol, EMA 5 mmol, *t*-BuLi 0.2 mmol, toluene 10 mL). Dotted line (----); *t*-BuA unit, broken line (---); EMA unit, solid line(—); whole unit.

mixture after completion of the reaction. As shown in Figure 7, the peak at the lower molecular weight side disappeared as expected, indicating that the poly(*t*-BuA) anions were living. Thus, the formation of the lower molecular weight fraction is due not to termination reactions but to a sluggish crossover reaction from the poly(*t*-BuA) anions to EMA; that is, the cross propagation is relatively slow as compared with the much faster homopolymerization of EMA as seen in Figure 2. In conjunction with the time-conversion data shown in Figure 3, the SEC-NMR data reveal that the poly(*t*-BuA) anions formed in the first stage of copolymerization partly grow into the higher molecular weight products by adding EMA in the later stage of the copolymerization. In the SEC curve detected for *t*-BuA units in the final product (Figure 6c), the peak area of the higher molecular weight side amounts to ca. 20% of the total area, suggesting that 20% of the poly(*t*-BuA) anions grow to the block copolymer, as far as the reactivity of the poly(*t*-BuA) anions does not depend on their molecular weights.

Temperature Dependence of Copolymerization of *t*-BuA and EMA

Figure 8 shows the on-line SEC-NMR data of the products prepared at various temperatures. As described above, the ¹H NMR detected SEC curve of the product

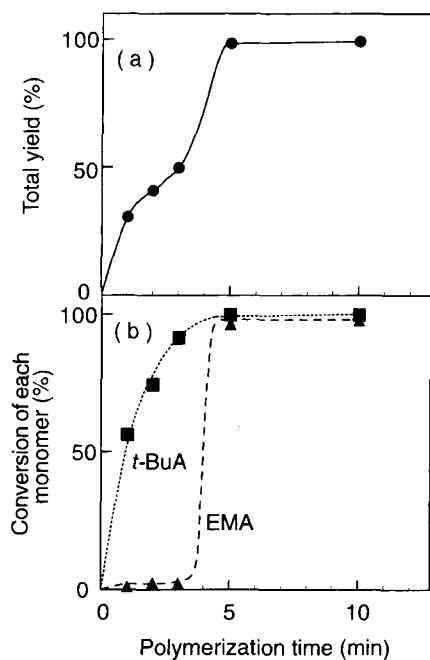


Figure 9. Time course of the copolymerization of *t*-BuA and EMA with *t*-BuLi/MeAl(ODBP)₂ (1/5) at -30°C (*t*-BuA 5.0 mmol, EMA 5.0 mmol, *t*-BuLi 0.2 mmol, toluene 10 mL).

obtained at -60°C (Figure 8a) consists of the unimodal chromatogram corresponding to EMA unit and bimodal one corresponding to *t*-BuA unit. The product obtained at -40°C shows unimodal SEC curve as a whole (Figure 8b). The SEC curves for *t*-BuA unit and EMA unit are almost identical, although the curve for *t*-BuA shows a slight shift at lower molecular weight side, indicating that a small portion of poly(*t*-BuA) anions still failed to propagate further. Nevertheless, the results suggest that increasing the polymerization temperature gives rise to the increase in the block efficiency. In the SEC chromatogram of the product formed at -30°C (Figure 8c), the difference of two SEC curves detected for *t*-BuA and EMA units is negligibly small. Figure 9 illustrates time-conversion plots of the respective monomers in the copolymerization at -30°C , which clearly indicates that *t*-BuA is polymerized first followed by the consumption of EMA in the later stage of the copolymerization. The results suggest that almost all poly(*t*-BuA) anions grow into the block-like copolymer of narrow MWD in a living manner.

Figure 10 shows carbonyl carbon regions of the ¹³C NMR spectra of the copolymers prepared at various temperatures. The spectra of the copolymers obtained at -60°C , -40°C , and -30°C were almost identical to those of mixtures of the corresponding homopolymers, indicating the formation of poly(*t*-BuA) block and poly(EMA) block. Tacticity sensitive peaks, particularly those of EMA units, show temperature dependent changes; for the copolymer formed at -60°C , *mr* peaks are the strongest, that is, the poly(EMA) block is heterotactic, and for those obtained at -40°C and -30°C *rr* peaks become predominant. In sharp contrast, as shown in Figure 10d, the ¹³C NMR spectrum of the copolymer prepared at -20°C displays a different splitting pattern.

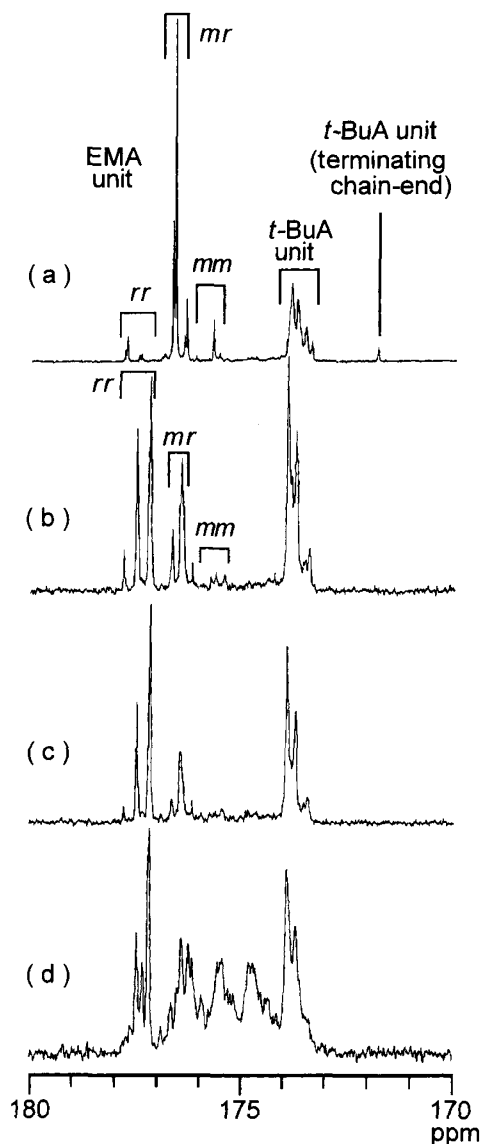


Figure 10. ¹³C NMR spectra of carbonyl carbons of the copolymers of *t*-BuA and EMA prepared in toluene with *t*-BuLi/MeAl(ODBP)₂ (1/5) at (a) -60°C , (b) -40°C , (c) -30°C , and (d) -20°C (*t*-BuA 5.0 mmol, EMA 5.0 mmol, *t*-BuLi 0.2 mmol, toluene 10 mL).

The spectrum was very similar to that of the copolymer prepared by radical polymerization by using AIBN. The signals with very complicated splittings reflect the randomness in comonomer sequences, indicating that the monomer selectivity was lost at -20°C . The results suggest that monomer selectivity either in coordination by MeAl(ODBP)₂ or in propagation reaction is lost at higher temperature in a critical way.

In the present work, it has been shown that the anionic copolymerization of *t*-BuA and EMA with *t*-BuLi/MeAl(ODBP)₂ in toluene at and below -30°C proceeded in a monomer-selective and living manner. The propagating anions react selectively with *t*-BuA which may be activated through the preferential coordination with MeAl(ODBP)₂. Particularly, the copolymerization at -30°C gave a block-like copolymer with narrow MWD. Increase in the polymerization temperature resulted in lower monomer selectivity, and the copolymer formed at

–20°C had the random comonomer sequence. Nevertheless, the copolymer showed narrow MWD, indicating that the livingness of the copolymerization is retained. In other words, the propagations from acrylate anion to methacrylate monomer and *vice versa* proceed smoothly. In conclusion, the comonomer sequence of *t*-BuA and EMA could be successfully controlled from block-like to statistical one by selecting proper polymerization temperature without losing livingness of the polymerization to afford narrow MWD.

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