Living and Monomer-Selective Copolymerization of *n*-Butyl Acrylate and Methyl Methacrylate with the Aid of Bis(2,6-di-*tert*-butylphenoxy)ethylaluminum

Tatsuki KITAYAMA,[†] Masato TABUCHI, Takehiro KAWAUCHI, and Koichi HATADA*

Department of Chemistry, Graduate School of Engineering Science, Osaka University,
1–3 Machikaneyama, Toyonaka, Osaka 560–8531, Japan

*Department of Applied Physics and Chemistry, Fukui University of Technology,
3–6–1 Gakuen, Fukui-shi, Fukui 910–8505, Japan

(Received January 17, 2002; Accepted March 19, 2002)

ABSTRACT: Anionic polymerizations of *n*-butyl acrylate (*n*-BuA) and methyl methacrylate (MMA) in toluene with a combination of *tert*-butyllithium (*t*-BuLi) and bis(2,6-di-*tert*-butylphenoxy)ethylaluminum [EtAl(ODBP)₂] proceed in a living manner at low temperatures. Block copolymerizations of *n*-BuA and MMA with *t*-BuLi/EtAl(ODBP)₂ (1/5 mol/mol) by sequential monomer addition were successful in both directions, that is, from poly(*n*-BuA) anions and from poly(MMA) anions. The conventional copolymerizations of *n*-BuA and MMA with the same initiator in toluene at low temperatures proceeded in a living and monomer-selective fashion; *n*-BuA was polymerized first, followed by the polymerization of MMA by the preformed poly(*n*-BuA) anions to give a block-like copolymer with narrow molecular weight distribution.

KEY WORDS Block Copolymer / Aluminum Bisphenoxide / Anionic Copolymerization / One-shot Block Copolymerization /

Advances in precision polymerization have realized living polymerizations of a variety of monomers, which provide us with a promising way for the preparation of block copolymers with well-defined molecular structures. Poly(alkyl acrylate)s usually have lower glass transition temperature, reflecting higher flexibility, than the corresponding polymethacrylates. Combination of these blocks may give rise to not only high adhesiveness but also elastic property.

The living anionic copolymerization of acrylates and methacrylates has been difficult, because of the large difference in the reactivity as monomer and in the reactivity of propagating anions derived therefrom.^{1,2} Recently, the preparation of block copolymers comprising polyacrylate block and poly(methyl methacrylate) (PMMA) blocks has been reported by several research groups.^{3–14} Maurer *et al.* demonstrated the block polymerization of *n*-butyl acrylate (*n*-BuA) and methyl methacrylate (MMA) with diphenylhexyllithium as an initiator, in the presence of lithium 2-methoxyethoxide, in toluene/tetrahydrofuran (THF) mixtures, but an effort to initiate the polymerization of MMA from living poly(*n*-BuA) anion was not successful.³ Wang *et al.* obtained the diblock and triblock copolymers of 2-ethylhexyl acrylate and MMA with narrow molecular weight distributions (MWDs) by living anionic polymerization with the aid of lithium alkoxyalkoxides in toluene/THF mixtures.¹² Yasuda *et al.* reported the

block copolymerization of *n*-BuA and MMA by using lanthanocenes that afforded high molecular weight polymers, though triblock copolymerizations by sequential addition of monomer gave the mixture of di- and triblock copolymers.^{13,14}

We have reported stereospecific living polymerizations of methacrylates with a combination of *tert*-butyllithium (*t*-BuLi) and bis(2,6-di-*tert*-butylphenoxy)methylaluminum [MeAl(ODBP)₂, **1**] in toluene at low temperature.^{15–23} Recently, it was found that the polymerization of *tert*-butyl acrylate (*t*-BuA), a tertiary acrylate, with the same initiator system in toluene at low temperature proceeded in a living fashion and gave a polymer with narrow MWD.²⁴ Moreover, the copolymerization of *t*-BuA and ethyl methacrylate (EMA) proceeds in a living and monomer-selective manner to give block copolymers with narrow MWD.²⁴ Although the polymerization of primary alkyl acrylates such as *n*-BuA with *t*-BuLi/MeAl(ODBP)₂ gave polymers with broad MWD in low yields, replacing the methyl group in MeAl(ODBP)₂ with ethyl group, *i.e.*, bis(2,6-di-*tert*-butylphenoxy)ethylaluminum [EtAl(ODBP)₂, **2**], drastically improves the control of the polymerization and the polyacrylates with narrow MWD were obtained.²⁵ The initiator *t*-BuLi/EtAl(ODBP)₂ is also effective for syndiotactic living polymerization of alkyl methacrylate.²⁰ Thus, *t*-BuLi/EtAl(ODBP)₂ is an effective initiator for both primary acrylates and

[†]To whom correspondence should be addressed.

R = CH₃ : MeAl(ODBP)₂ **1**

C₂H₅ : EtAl(ODBP)₂ **2**

methacrylates.

Based on these findings, we pursued the preparation of diblock copolymers of *n*-BuA and MMA with *t*-BuLi/EtAl(ODBP)₂ in toluene at low temperature by sequential addition of monomer. Also examined was copolymerization of *n*-BuA and MMA which expectedly proceeds in a living and monomer-selective fashion to give a block copolymer.

EXPERIMENTAL

Materials

n-BuA (Tokyo Chemical Industry) and MMA (Nacalai Tesque) were purified by distillation, dried over calcium dihydride and vacuum-distilled just before use. Toluene and heptane were purified in the usual manner, mixed with a small amount of *n*-butyllithium, and distilled under high vacuum. *t*-BuLi in pentane, obtained commercially (Nacalai Tesque), 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.²⁶ 2,6-Di-*tert*-butylphenol, obtained commercially (Tokyo Chemical Industry), was fractionally distilled, and used as a heptane solution. Triethylaluminum (Kishida Chemical) was used as a heptane solution. EtAl(ODBP)₂ was prepared from 2,6-di-*tert*-butylphenol (2 equivalent) and triethylaluminum (1 equivalent) in toluene at room temperature for 24 h and recrystallized three times from heptane at -20°C.^{18,19,27,28} The EtAl(ODBP)₂ was dissolved in toluene and used for the polymerization reaction.

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 EtAl(ODBP)₂ in toluene at polymerization temperatures at a molar ratio of [EtAl(ODBP)₂]/[*t*-BuLi] = 5. The polymerization reaction was initiated by adding the monomer or monomer mixture slowly to the initiator solution. After prescribed reaction period the reaction was quenched by adding a small amount of methanol containing aq. 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.

Measurements

¹H NMR spectra were measured in chloroform-*d* at 55°C for compositional analysis and in dimethyl sulfoxide-*d*₆/nitrobenzene-*d*₅ (3/1 vol/vol) at 100°C for end-group analysis, using a JEOL JNM400 spectrometer operated at 400 MHz or a Varian Unity Inova 500 spectrometer at 500 MHz. ¹³C NMR spectra were recorded on the Varian Unity Inova 500 spectrometer at 125 MHz. Number-average molecular weight ($\overline{M}_n$), determined by ¹H NMR spectroscopic end-group analysis, was calculated from the *tert*-butyl signal (0.85 ppm) of the initiator fragments. Molecular weight distributions (MWDs) were determined by size exclusion chromatography (SEC) using a JASCO TRI ROTAR-V chromatograph equipped with Shodex SEC columns KF-806L × 2 (8 mm *i.d.* × 300 mm) using THF as an eluent at 40°C. SEC chromatograms were calibrated against standard PMMA samples (Shodex).

RESULTS AND DISCUSSION

Sequential Block Copolymerization of *n*-BuA and MMA

The block copolymerization of *n*-BuA and MMA with *t*-BuLi/EtAl(ODBP)₂ was examined in toluene at -60°C in two ways; one from poly(*n*-BuA) anion to poly(*n*-BuA)-*block*-PMMA and the other from PMMA anion to PMMA-*block*-poly(*n*-BuA). The second monomers were added to the polymerization mixtures after completion of the polymerizations of the first monomers. Upon the addition of the second monomers, the polymerization mixtures were colored yellow due to the complex formation between the monomers and EtAl(ODBP)₂, and the copolymerizations proceeded further. The results are shown in Table I. In all the cases the block copolymerizations of *n*-BuA and MMA proceeded quantitatively with high initiator efficiency for both the first and second blocks, and MWDs of the block copolymers were narrow.

Figure 1 shows the SEC curves of the block copolymers, and those of the prepolymers. The copolymers finally obtained exhibited unimodal SEC curves, in which the peak due to each prepolymer was scarcely observed, indicating the livingness of the sequential copolymerizations of *n*-BuA and MMA. In anionic polymerization, *n*-BuA is more reactive than MMA, and PMMA anion is more reactive than poly(*n*-BuA) anion. Thus the successful block copolymerization

Table I. Sequential block copolymerization of *n*-BuA and MMA with *t*-BuLi/EtAl(ODBP)₂ in toluene at -60°C ^a

Run	Polymer	Time h	Conversion/%		$\overline{M}_n^b$	$\frac{\overline{M}_w}{\overline{M}_n}^c$
			<i>n</i> -BuA	MMA		
1	Poly(<i>n</i> -BuA)	0.5	97.1	—	7600	1.14
2	Poly(<i>n</i> -BuA)- <i>block</i> -PMMA	0.5+6	94.7	100	12200	1.12
3	PMMA	6	—	99.9	5900	1.09
4	PMMA- <i>block</i> -poly(<i>n</i> -BuA)	6+3	98.4	100	12800	1.10

^aMonomer 5 mmol (each), *t*-BuLi 0.1 mmol, Al/Li = 5, toluene 5 mL. ^bDetermined by ¹H NMR. ^cDetermined by SEC (calibrated against PMMA standards).

Figure 1. SEC curves of the block copolymers of *n*-BuA and MMA and these prepolymers prepared with *t*-BuLi/EtAl(ODBP)₂ (1/5 mol/mol) in toluene at -60°C (*n*-BuA 5 mmol, MMA 5 mmol, *t*-BuLi 0.1 mmol, toluene 5 mL). Dotted line (---); prepolymer, solid line (—); block copolymer.

from PMMA anion to *n*-BuA monomer is not surprising as far as PMMA anion is living. However, the block copolymerization from poly(*n*-BuA) anion to MMA requires a mechanism which compensates the lower reactivity of poly(*n*-BuA) anion and of MMA monomer. EtAl(ODBP)₂ is therefore presumed to coordinate with MMA as a Lewis acid to enhance its reactivity against the poly(*n*-BuA) anion.

Monomer-Selective Copolymerization of *n*-BuA and MMA

As described in the previous paper,²⁴ the copolymerization of *t*-BuA and EMA with *t*-BuLi/MeAl(ODBP)₂ in toluene at -30°C proceeds in a living and monomer-selective fashion and gave a block-like copolymer with narrow MWD, comprising a poly(*t*-BuA) block as the first block and a poly(EMA) block as the second. To examine whether the monomer-selective copolymerization takes place for the pair of *n*-BuA and MMA with *t*-BuLi/EtAl(ODBP)₂, the copolymerization of *n*-BuA

Table II. Copolymerization of *n*-BuA and MMA with *t*-BuLi/EtAl(ODBP)₂ in toluene by one-shot feeding of the monomers^a

Run	Temp. $^{\circ}\text{C}$	Time	Conversion/%		$\overline{M}_n^b$	$\frac{\overline{M}_w}{\overline{M}_n}^c$
			<i>n</i> -BuA	MMA		
5	-60	5 min	69.4	0.7	5300	1.06
6	-60	10 min	98.5	10.9	8100	1.06
7	-60	20 min	99.3	34.4	9500	1.08
8	-60	6 h	98.5	97.7	13200	1.09
9	-40	6 h	100	100	12500	1.09
10	-20	1 h	100	100	15500	1.18
11	0	1 h	100	100	20400	1.27
12 ^d	-60	24 h	84.2	1.7	6900	23.8
13 ^e	60	24 h	100	100	12000 ^c	3.71

^aMonomer 5 mmol (each), *t*-BuLi 0.1 mmol, Al/Li = 5, toluene 10 mL. ^bDetermined by ¹H NMR. ^cDetermined by SEC (calibrated against PMMA standards). ^dCopolymerization with *t*-BuLi alone. ^eRadical copolymerization with AIBN (0.1 mmol) in toluene (5 mL).

and MMA was conducted in toluene at -60°C (run 8, Table II). Figure 2a shows ¹H NMR spectrum of the product, together with those obtained with *t*-BuLi alone and with AIBN. The copolymerization with *t*-BuLi alone (run 12, Table II) gave a polymer with broader MWD. ¹H NMR analysis revealed that the polymer consisted of *n*-BuA units almost exclusively with a few MMA units (Figure 2b). The results suggest that *n*-BuA anion did scarcely attack MMA monomer as discussed in the previous section, and the MMA units might be incorporated through the initiation with *t*-BuLi and subsequent propagation until the MMA anions thus formed attack *n*-BuA.

In sharp contrast, the copolymerization with *t*-BuLi/EtAl(ODBP)₂ gave a copolymer with narrow MWD quantitatively, which consisted of both monomer units as seen from its ¹H NMR spectrum (Figure 2a). The spectrum is almost a superpose of those of poly(*n*-BuA) and PMMA, differing evidently from that of the copolymer obtained by radical mechanism (Figure 2c) which should consist of randomly distributed comonomer sequences. These spectral features suggest that the copolymer obtained with *t*-BuLi/EtAl(ODBP)₂ may consist of long blocks of *n*-BuA and MMA.

Figure 3 shows the time-conversion plots for

Figure 2. ^1H NMR spectra of copolymers of *n*-BuA and MMA prepared in toluene with *t*-BuLi/EtAl(ODBP) $_2$ at -60°C (run 8) (a), with *t*-BuLi (run 12) (b), and with AIBN at 60°C (run 13) (c).

each monomer in the copolymerization with *t*-BuLi/EtAl(ODBP) $_2$ in toluene at -60°C (runs 5–8). The results indicate that the polymerization of *n*-BuA proceeds preferentially, completed within 10 min, and then the polymerization of MMA by the formed poly(*n*-BuA) anions followed. The consumption of MMA took much longer time than that of *n*-BuA but the reaction proceeded quantitatively. The data shown in Figure 3, together with the NMR spectral data in Figure 2, clearly indicate that the copolymerization proceeds in a monomer-selective fashion. Thus the copolymerization should give a block-like copolymer through the monomer-selective copolymerization.

Figure 4 illustrates the change of SEC curves of the copolymer prepared with *t*-BuLi/EtAl(ODBP) $_2$ at 5 min, 10 min and 6 h. The molecular weights of the products smoothly increased as the polymerization proceeded, while their MWDs were kept narrow. The results mean that the copolymerization is not only

Figure 3. Time course of the copolymerization of *n*-BuA and MMA with *t*-BuLi/EtAl(ODBP) $_2$ (1/5 mol/mol) in toluene at -60°C (*n*-BuA 5 mmol, MMA 5 mmol, *t*-BuLi 0.1 mmol, toluene 10 mL).

Figure 4. SEC curves of the copolymers of *n*-BuA and MMA prepared with *t*-BuLi/EtAl(ODBP) $_2$ (1/5 mol/mol) in toluene at -60°C (*n*-BuA 5 mmol, MMA 5 mmol, *t*-BuLi 0.1 mmol, toluene 10 mL). Dotted line (---); polymerization time 5 min, broken line (---); 10 min, solid line (—); 6 h.

monomer-selective but also living.

In the case of the copolymerization of *t*-BuA and EMA with MeAl(ODBP) $_2$ which proceeds in a monomer-selective and living fashion at and below -30°C , the monomer-selectivity was lost at and above -20°C , where a copolymer consisted of random monomer sequences was formed.²⁴ To examine temperature dependence of the copolymerization of *n*-BuA and MMA with *t*-BuLi/EtAl(ODBP) $_2$ in regard to monomer selectivity and livingness, the copolymerization was carried out in temperature range from 0 to -60°C , and the results are summarized in Table II (runs 8–11). Though a slight broadening of MWD of the copolymer was observed for the copolymerization at 0°C , the copolymerizations of *n*-BuA and MMA proceeded quantitatively to give copolymers with narrow

Figure 5. 125 MHz ^{13}C NMR spectra of carbonyl carbons of the copolymers of *n*-BuA and MMA prepared by one-shot feeding of the monomers with *t*-BuLi/EtAl(ODBP) $_2$ in toluene at -60°C (a), -40°C (b), -20°C (c), 0°C (d), and that prepared with AIBN at 60°C (e).

MWDs. Figure 5 shows carbonyl carbon regions of the ^{13}C NMR spectra of the copolymers prepared at $-60 \sim 0^\circ\text{C}$ by the one-shot feeding copolymerization, together with that of the radically prepared copolymer. The latter shows complicate split signals in the chemical shift range from 174 to 178 ppm, reflecting random comonomer sequences. The spectra of the anionically prepared copolymers were much simpler and almost identical to those of mixtures of the corresponding homopolymers, indicating the formation of poly(*n*-BuA) and PMMA blocks. Thus the monomer selectivity is kept in this temperature range at least up to 0°C .

It should be noted that the MWD of the copolymer obtained at -60°C was slightly narrower than that obtained by the sequential block copolymerization at -60°C (*cf.* Table I). In the sequential block copolymerization, there might be a chance that a small fraction of poly(*n*-BuA) anions are deactivated before the second feed of MMA monomer, which should be attributed to the relatively short lifetime of the living poly(*n*-BuA) anions even at -60°C . In contrast, in the

monomer-selective copolymerization, MMA monomer exists from the beginning of the reaction in the same medium where the poly(*n*-BuA) anions are formed, and thus supplied to the anions without time lag. Thus the present copolymerization system is not only more facile but also more effective than the sequential block copolymerization.

REFERENCES

1. R. Fayt, R. Forte, C. Jacobs, R. Jérôme, T. Ouhadi, Ph. Teyssié, and S. K. Varshney, *Macromolecules*, **20**, 1442 (1987).
2. R. Forte, T. Ouhadi, R. Fayt, R. Jérôme, and Ph. Teyssié, *J. Polym. Sci., Part A: Polym. Chem.*, **28**, 2233 (1990).
3. A. Maurer, X. Marcarián, A. H. E. Müller, C. Navarro, and B. Vuillemin, *Polym. Prepr., (Am. Chem. Soc., Div. Polym. Chem.)*, **38**(1), 467 (1997).
4. Y. Hosokawa, M. Kuroki, T. Aida, and S. Inoue, *Macromolecules*, **24**, 824 (1991).
5. C. Jacobs, S. K. Varshney, J. P. Hautekeer, R. Fayt, R. Jérôme, and Ph. Teyssié, *Macromolecules*, **23**, 4024 (1990).
6. S. K. Varshney, C. Jacobs, J. P. Hautekeer, R. Jérôme, R. Fayt, and Ph. Teyssié, *Macromolecules*, **24**, 4997 (1991).
7. S. K. Varshney, R. Jérôme, Ph. Bayard, C. Jacobs, R. Fayt, and Ph. Teyssié, *Macromolecules*, **25**, 4457 (1992).
8. J.-S. Wang, R. Jérôme, Ph. Teyssié, and S. K. Varshney, *Macromolecules*, **26**, 2386 (1993).
9. J.-S. Wang, R. Jérôme, Ph. Bayard, and Ph. Teyssié, *Macromolecules*, **27**, 4608 (1994).
10. J.-S. Wang, R. Jérôme, Ph. Bayard, L. Baylac, M. Patin, and Ph. Teyssié, *Macromolecules*, **27**, 4615 (1994).
11. J.-S. Wang, R. Jérôme, Ph. Bayard, M. Patin, and Ph. Teyssié, *Macromolecules*, **27**, 4635 (1994).
12. J.-S. Wang, R. Jérôme, Ph. Bayard, and Ph. Teyssié, *Macromolecules*, **27**, 4908 (1994).
13. E. Ihara, M. Morimoto, and H. Yasuda, *Macromolecules*, **28**, 7886 (1995).
14. H. Yasuda, E. Ihara, and M. Morimoto, *Polym. Prepr., (Am. Chem. Soc., Div. Polym. Chem.)*, **35**(2), 532 (1994).
15. T. Kitayama, Y. Zhang, and K. Hatada, *Polym. J.*, **26**, 868 (1994).
16. T. Kitayama, Y. Zhang, and K. Hatada, *Polym. Bull.*, **439**, 32 (1994).
17. T. Kitayama, S. He, Y. Hironaka, and K. Hatada, *Polym. Prepr., Jpn.*, **44**, 153 (1995).
18. T. Kitayama, T. Hirano, and K. Hatada, *Polym. J.*, **28**, 61 (1996).
19. T. Kitayama, T. Hirano, Y. Zhang, and K. Hatada, *Macromol. Symp.*, **107**, 297 (1996).
20. T. Kitayama, T. Hirano, and K. Hatada, *Tetrahedron*, **53**, 15263 (1997).
21. T. Hirano, T. Kitayama, and K. Hatada, *Polym. J.*, **30**, 736 (1998).
22. T. Hirano, H. Yamaguchi, T. Kitayama, and K. Hatada, *Polym. J.*, **30**, 767 (1998).
23. T. Kitayama and K. Hatada, "New Macromolecular Archi-

- ecture and Functions”, M. Kamachi and A. Nakamura, Ed., Springer-Verlag GmbH & Co., Berlin, 1996, p 31.
24. T. Kitayama, M. Tabuchi, and K. Hatada, *Polym. J.*, **32**, 796 (2000).
25. M. Tabuchi, T. Kawauchi, T. Kitayama, and K. Hatada, *Polymer*, in press.
26. S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 195 (1965).
27. K. Maruoka, T. Itoh, M. Sakura, K. Nonoshita, and H. Yamamoto, *J. Am. Chem. Soc.*, **110**, 3588 (1988).
28. A. P. Shreve, R. Mulhaupt, W. Fultz, J. Calabrese, W. Robbins, and S. D. Ittel, *Organometallics*, **7**, 409 (1988).