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# Monomer-selective living copolymerization of butyl acrylate and methyl methacrylate with a difunctional initiator—a facile synthesis of ABA-type triblock copolymer

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**Abstract**

A difunctional initiator was synthesized through the addition reaction of *tert*-butyllithium (*t*-BuLi) to 1,3-diisopropenylbenzene (DIB) in the presence of triethylamine ($Et_3N$). Under optimized conditions, that is dropwise addition of a mixture of DIB and $Et_3N$ to a stirred toluene solution of *t*-BuLi at 50 °C at a molar ratio of DIB/$Et_3N$/*t*-BuLi = 1/2/2, the difunctional initiator was formed without oligomeriazation of DIB. Copolymerization of butyl acrylate (*n*-BuA) and methyl methacrylate (MMA) with the difunctional initiator in the presence of bis(2,6-di-*tert*-butylphenoxy)ethylaluminum [EtAl(ODBP)$_2$] in toluene at low temperature proceeded in a monomer-selective manner; *n*-BuA is polymerized first, followed by MMA polymerization, to form an ABA-type triblock copolymer [PMMA-*block*-poly(*n*-BuA)-*block*-PMMA], which exhibits microphase separation.


*Keywords:* Aluminum bisphenoxide; Thermoplastic elastomer; Microphase separation

## 1. Introduction

Block copolymers comprising polymer blocks of different properties, such as solubility and glass transition temperature ($T_g$), have received much attention from the viewpoint of materials applications including compatibilizers in polymer blends and thermoplastic elastomers [1,2]. Living anionic polymerization is one of the most promising ways to design the molecular architecture and synthesize well-defined block copolymers. A typical example of useful block copolymers synthesized anionically is polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) known as a thermoplastic elastomer.

Difunctional initiators are of considerable interest for facile preparation of ABA-type triblock copolymers, which involves addition of monomer A to difunctional living polymers of B. Although, triblock copolymers can be prepared with monofunctional initiators using sequential monomer addition process, use of difunctional initiators provides us with the more facile process for the preparation of triblock copolymers. Among the difunctional initiators so far studied, we have focused our attention on the diadduct derived from butyllithiums and *m*-diisopropenylbenzene (*m*-DIB) in non-polar solvents. *m*-DIB exhibits a rather low ceiling temperature, like α-methylstyrene. Under chosen conditions, it reacts with butyllithiums but does not undergo polymerization, as reported by several authors [3–14]. Foss et al. earlier obtained an efficient diinitiator by the addition of *sec*-butyllithium (*s*-BuLi) to *m*-DIB (*s*-BuLi/*m*-DIB = 2/1) in the presence of 0.1 molar equivalent of triethylamine ($Et_3N$) per lithium site as a promoter [3]. Beinert et al. reported that they have successfully prepared a difunctional initiator from *m*-DIB and *s*-BuLi in benzene. However, the initiator solution was in fact an equimolar mixture of *s*-BuLi and a monoaddition product [4]. Fetters et al. added equimolar quantities of $Et_3N$ to *s*-BuLi and attained quantitative yield of an efficient difunctional initiator with excellent stability [5]. Lutz et al. reported that they have prepared a difunctional initiator from *m*-DIB and *s*-BuLi in benzene. As the diadduct yield increases, it soon becomes insoluble [6]. Cameron and Buchan, however, claimed that the lithiation reaction led to a mixture of di- and polyfunctional initiators rather than to a pure difunctional

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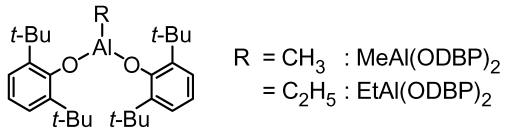



Scheme 1.

initiator [7]. Hogen-Esch et al. have revisited the problem and concluded that the addition of *s*-BuLi to *m*-DIB in a 2/1 molar ratio in benzene produces a nearly perfect difunctional compound, though the precipitation was observed [8]. Yu et al. have prepared a difunctional initiator from *m*-DIB and *s*-BuLi or *t*-BuLi in the presence of $Et_3N$ in benzene or cyclohexane [9–13]. The diadduct polymerized styrene and butadiene as a monofunctional initiator in non-polar solvents, and reacted as a difunctional initiator in polar solvents such as tetrahydrofuran (THF) [11]. Jou et al. also reported that the diadduct prepared from a 2/1 molar ratio of *n*-BuLi to *m*-DIB in hexane solution. This organolithium compound did not react as a difunctional initiator in cyclohexane [14].

We have reported living polymerizations of alkyl methacrylates with a combination of *t*-BuLi and bis(2,6-di-*tert*-butylphenoxy)methylaluminum [$MeAl(ODBP)_2$, Scheme 1] in toluene at low temperatures [15–25]. We also found that polymerization of *tert*-butyl acrylate (*t*-BuA) with the same initiator system in toluene at low temperatures proceeds in a living manner and give a polymer with narrow molecular weight distribution (MWD) [26]. Since the initiator system is effective both for methacrylate and acrylate polymerizations, we have examined the anionic copolymerization of *t*-BuA and ethyl methacrylate (EMA), and found that the copolymerization proceeds in a monomer-selective and living manner at low temperatures [26]. On the contrary, polymerizations of primary alkyl acrylates such as *n*-BuA with *t*-BuLi/$MeAl(ODBP)_2$ gave polymers with broad MWD in low yields. However, replacing the methyl group in $MeAl(ODBP)_2$ with an ethyl group, bis(2,6-di-*tert*-butylphenoxy)ethylaluminum [$EtAl(ODBP)_2$, Scheme 1], drastically improved the control of the polymerization to afford polymers with narrow MWD [27]. Moreover, the anionic copolymerization of *n*-BuA and methyl methacrylate (MMA) proceeds in a monomer-selective and living manner and gives PMMA-*block*-poly(*n*-BuA) [28]. Based on these findings, we reexamine synthesis of the difunctional initiator from *t*-BuLi and *m*-DIB with the aim of obtaining an ABA-type triblock copolymer, PMMA-*block*-poly(*n*-BuA)-*block*-PMMA, through one-shot copolymerization of *n*-BuA and MMA.

Poly(*n*-BuA) has low $T_g$. Hence, the block copolymer of primary alkyl acrylate and MMA is a good candidate of thermoplastic elastomers with better resistance to UV irradiation and thermal degradation, in compararison with SBS elastomers. Recently, syntheses of triblock copolymers comprising poly(*n*-BuA) and PMMA blocks have been reported by other workers [29–32].

## 2. Experimental

### 2.1. Materials

*n*-BuA and MMA (Tokyo Chemical Industry Co. Ltd) were purified by distillation dried over $CaH_2$, and then vacuum-distilled just before use. Toluene and heptane were purified in a usual manner, mixed with a small amount of *n*-butyllithium, and distilled under high vacuum. *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*-phenanthrolin as an indicator [33]. *m*-Diisopropenylbenzene (Aldrich) was dried over $CaH_2$ for 1 day, and distilled. Triethylamine was dried over $CaH_2$, and then vacuum-distilled just before use. $EtAl(ODBP)_2$ was prepared from 2,6-di-*tert*-butylphenol (2 equiv.) and triethylaluminum (1 equiv.) in toluene at room temperature for 24 h [18,19,34–36], and recrystallized three times from heptane at −25 °C. $EtAl(ODBP)_2$ thus prepared was dissolved in toluene and used for the polymerization reaction.

### 2.2. Polymerization

All the polymerizations were carried out in glass ampoules filled with dried nitrogen passed through Molecular Sieves 4A cooled at −78 °C. Syringes and needles steel capillaries were used in order to transfer solvent, monomer, and initiator. Difunctional anionic initiator was synthesized by the addition reaction of *t*-BuLi to *m*-DIB. Under optimized conditions, the difunctional initiator was formed without oligomeriazation of *m*-DIB. A typical procedure is described in the following. A mixture of *m*-DIB (1.5 mmol) and triethylamine ($Et_3N$) (3.0 mmol) was added dropwise to a stirred toluene solution of *t*-BuLi (3.0 mmol/3.0 ml) at 50 °C. The initiator was used for the polymerization and copolymerization of (meth)acrylates. The difunctional anionic initiator was added to $EtAl(ODBP)_2$ in toluene at the polymerization temperature. The polymerization reaction was initiated by adding the monomer or the mixture of monomers slowly to the initiator solution with stirring. Polymerization was terminated by adding methanol containing aqueous HCl at the polymerization temperature. The reaction mixture was concentrated to dryness under reduced pressure. The residue was dissolved in chloroform, and the solution was extracted with dilute aqueous HCl and subsequently with water. The polymer was recovered by evaporating the solvent and dried under vacuum. For the copolymerization, the reaction mixture was poured into a large amount of methanol, and the precipitated polymer was collected by filtration, washed successively with methanol, diluted aqueous HCl, water and methanol, and dried under vacuum.

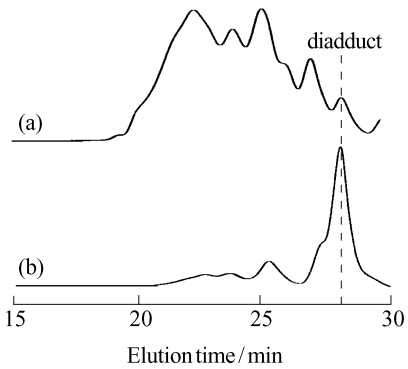



Fig. 1. SEC curves of the reaction products of *t*-BuLi (3.0 mmol) and *m*-DIB (1.5 mmol) in toluene (3.0 ml) at 20 °C for 2 h (a), further increased up to 50 °C for 2 h (b).

### 2.3. Measurements

Two different size exclusion chromatography (SEC) instruments have been used. One equipped with Shodex SEC columns K-2001 × 2 (20 mm i.d. × 300 mm) using chloroform as an eluent was used to characterize the products from the reaction of *m*-DIB and *t*-BuLi. Molecular weights of the polymers and their distributions were determined by another SEC system 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 (MW: $1.577 \times 10^6$, $7.45 \times 10^6$, $1.74 \times 10^5$, $2.02 \times 10^4$, $5.72 \times 10^3$, $1.85 \times 10^3$, Shodex). Conversion was determined by using a HEWLETT PACKARD HP6890 series gas chromatography (GC) system equipped with Cross-linked 5% PH ME Siloxane (HP-5) capillary column of 30 m length and 0.32 mm diameter. GC–mass (GC–MS) spectra were recorded on a JEOL MS-DX303HF mass spectrometer (electron ionization method). $^1$H and $^{13}$C NMR spectra were measured at 55 or 35 °C using a Varian Unity INOVA 500 spectrometer. Transmission electron micrograph (TEM) was measured as follows. Sample films were prepared by heat press molding of the copolymers at 230 °C and annealed at 140 °C for 66 h. The SEC measurements of the annealed samples confirmed no degradation of the samples. The ultra-thin sections were stained with 10 wt% $H_2O$/methanol (50/50 v/v) solution of PTA [12-tungsto(VI)phosphoric acid, *n*-hydrate] and observed by a transmission electron microscope H-7100 FA (Hitachi, Ltd.) at an acceleration voltage of 75 kV.

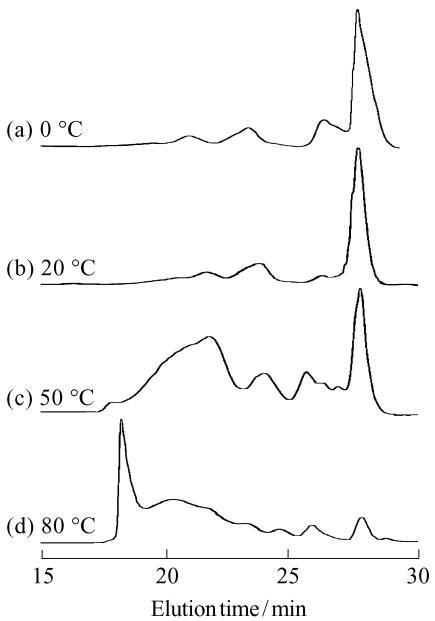



Fig. 2. SEC curves of the reaction products of *t*-BuLi, $Et_3N$ and *m*-DIB in toluene at several temperatures for 2 h. *m*-DIB was added dropwise to a toluene solution of a 1:1 mixture of *t*-BuLi and $Et_3N$.

## 3. Results and discussion

### 3.1. Synthesis of difunctional initiator

Previously, the difunctional initiator has been synthesized by the stoichiometric reaction of *m*-DIB with two molar equivalents of *s*-BuLi or *n*-BuLi in the presence or absence of $Et_3N$ in cyclohexane, benzene or hexane [3–14]. In these literatures, however, there were equivocal and conflict points, which insisted us to reinvestigate the synthesis and the potential use of the difunctional initiator particularly in toluene which is the same as the polymerization solvent.

The addition reaction of *t*-BuLi (2 equiv.) to *m*-DIB (1 equiv.) was examined in toluene. Fig. 1(a) shows the SEC curve of reaction products of *t*-BuLi and *m*-DIB in toluene at 20 °C for 2 h. The product is apparently a mixture of oligomers, though it contains the diadduct, whose peak is observed at the elution time of 28 min. When the temperature was raised to 50 °C and kept for 2 h, the product showed the SEC curve seen in Fig. 1(b), in which the diadduct became a major product, suggesting the occurrence of depropagation of the oligomeric anions formed at 20 °C. These results indicate that the addition reaction of *m*-DIB and *t*-BuLi is a quasi-equilibrium process, as Yu et al. have reported previously [10].

To optimize the reaction temperature, the reaction of *t*-BuLi and *m*-DIB was carried out in toluene at several temperatures from 0 to 80 °C. The reaction at 50 °C gave the highest content of the diadduct, while at 80 °C the content became even lower, probably due to hydrogen abstraction from the solvent. At 0 °C, the reaction itself did not take place owing to the non-polar solvent medium. Though the reaction at 50 °C gave the diadduct, it was contaminated with oligomers and, moreover, the product mostly precipitated out in toluene.

Several literatures reported the use of $Et_3N$ in the synthesis of the diadduct anion of *m*-DIB [3,5,7,11–14]. Accordingly, *m*-DIB was added dropwise to a toluene solution of a 1:1 mixture of *t*-BuLi and $Et_3N$ at several

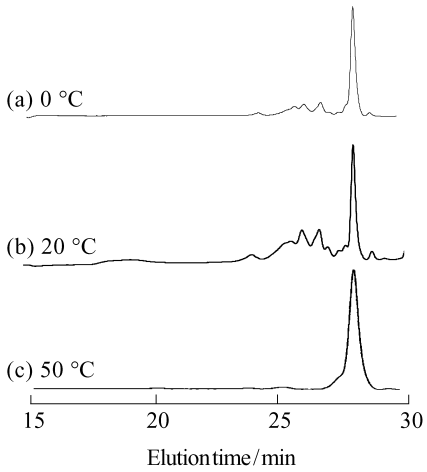



Fig. 3. SEC curves of the reaction products of *t*-BuLi, $Et_3N$ and *m*-DIB in toluene at several temperatures for 2 h. A 1:2 mixture of *m*-DIB and $Et_3N$ was added dropwise to a toluene solution of *t*-BuLi.

temperatures to examine the optimal conditions. The reactions were quenched by adding methanol containing aqueous HCl, and the reaction mixtures were subjected to SEC analysis. The results are shown in Fig. 2. The diadduct was formed in a better yield at 20 °C rather than 50 °C, where oligomerization took place in a considerable extent. When *m*-DIB is added to the *t*-BuLi/$Et_3N$ mixture, the anions formed might be activated by $Et_3N$ present in excess over the diadduct anions, and the oligomerization might be

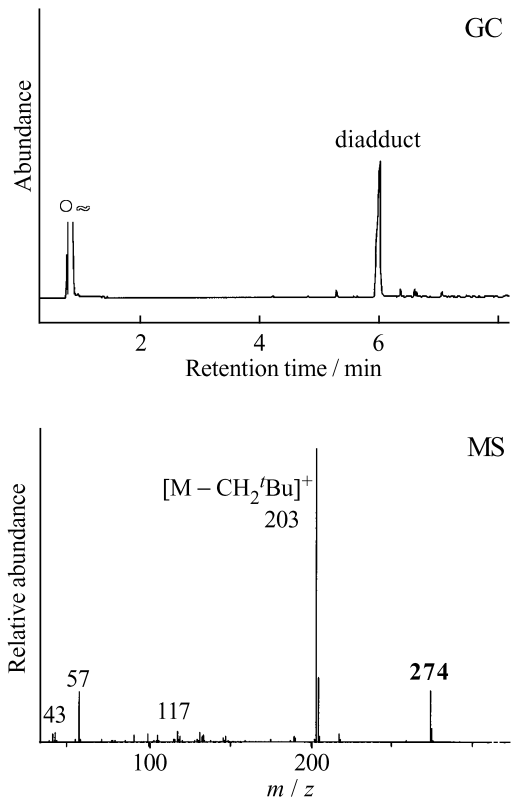



Fig. 4. GC–MS (electron ionization method) analysis of fractionated main peak.

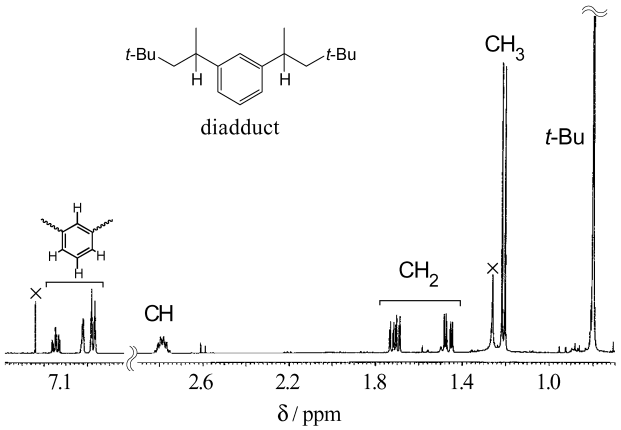



Fig. 5. $^1$H NMR spectrum of diadduct of *m*-DIB and *t*-BuLi ($CDCl_3$ at 35 °C).

promoted. Thus, we examined the reversed addition order of $Et_3N$, that is, a 1:2 mixture of *m*-DIB and $Et_3N$ was added to a stirred toluene solution of *t*-BuLi. Fig. 3 shows the SEC curves of the reaction products prepared at several temperatures. At 50 °C, the difunctional initiator was formed without oligomerization of *m*-DIB almost exclusively.

The structure of the diadduct was confirmed by GC–MS and $^1$H NMR analysis of the hydrocarbon derivative. The main peak in the SEC chromatogram was identified as the diadduct by GC–MS (Fig. 4). $^1$H NMR spectrum indicates complete consumption of the double bond and is in perfect agreement with the expected diadduct structure (Fig. 5).

### 3.2. *Polymerization of n*-butyl *acrylate with difunctional initiator/EtAl(ODBP)$_2$*

The polymerization of *n*-BuA with the difunctional initiator, in combination with the bulky aluminum bisphenoxide, $EtAl(ODBP)_2$, was carried out in toluene at −60 and −40 °C. We used two kinds of initiator solution, one was the initiator synthesized by adding *m*-DIB to a toluene solution of a 1:1 *t*-BuLi-$Et_3N$ complex at 20 °C [**I**] (Fig. 2), the other by adding the mixture of *m*-DIB and $Et_3N$ to a stirred toluene solution of *t*-BuLi at 50 °C [**II**] (Fig. 3). The results are shown in Table 1. The poly(*n*-BuA) prepared

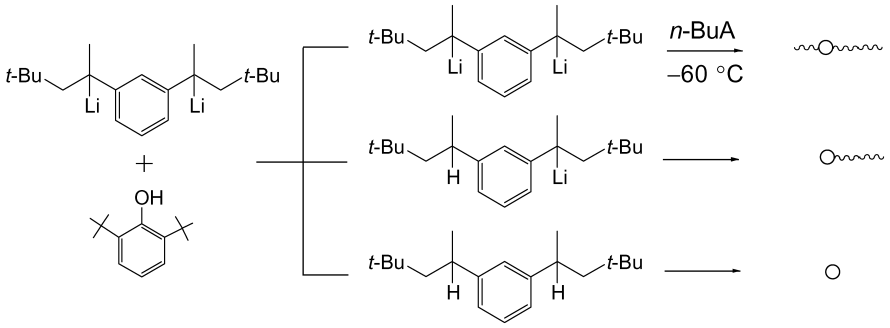
Table 1
Polymerization of *n*-BuA with difunctional initiator/$EtAl(ODBP)_2$ in toluene

| Initiator[a] | Temperature (°C) | $\bar{M}_n$[a] | $\bar{M}_w/\bar{M}_n$[b] |
|---|---|---|---|
| **I** | −40 | 9800 | 3.41 |
| | −60 | 8600 | 2.33 |
| **II** | −40 | 10,500 | 1.58 |
| | −60 | 9700 | 1.17 |

*n*-BuA 5 mmol, difunctional initiator 0.1 mmol, $EtAl(ODBP)_2$ 1 mmol, toluene 5 ml.

[a] **I**; see Fig. 2, **II**; see Fig. 3.

[b] Determined by SEC (calibrated against standard PMMA samples).




Scheme 2.

Table 2
One-shot copolymerization of *n*-BuA and MMA with difunctional initiator/EtAl(ODBP)$_2$ in toluene at −40 °C

| Run | Al/Li | Time (min) | Conversion[a] (%) | | $\bar{M}_n$[b] | $\bar{M}_w/\bar{M}_n$[b] |
|---|---|---|---|---|---|---|
| | | | *n*-BuA | MMA | | |
| 1 | 42 | 2 | 14.3 | Trace | 42,700 | 1.20 |
| 2 | 42 | 3 | 30.0 | Trace | 83,200 | 1.23 |
| 3 | 42 | 15 | 100 | 24.6 | 17,8300 | 1.26 |
| 4 | 42 | 180 | 100 | 100 | 20,8000 | 1.17 |
| 5[c] | 42 | 180 | 100 | 100 | 28,0000 | 1.08 |
| 6[c] | 25 | 180 | 100 | 100 | 23,5000 | 1.20 |

*n*-BuA 3.75 mmol, MMA 1.25 mmol, difunctional initiator 0.006 mmol, toluene 5 ml.
[a] Determined by GC.
[b] Determined by SEC (calibrated against standard PMMA samples).
[c] *n*-BuA 22.5 mmol, MMA 7.5 mmol, difunctional initiator 0.036 mmol, toluene 30 ml.

under condition [**II**] had much narrower MWD than that formed under condition [**I**]. Thus, the purity of the initiator is essentially important for the control of this polymerization reaction.

Several reports claim that the diadduct dianion of *m*-DIB functions as a monofunctional initiator in non-polar solvents. To investigate the functionality of the diadduct anion as the initiator in combination with EtAl(ODBP)$_2$, the polymerization of *n*-BuA was carried out in toluene at −60 °C with the diadduct quenched partially with 2,6-di-*tert*-butylphenol, which is expected to be a mixture of the dianion, monoanion and fully quenched neutral hydrocarbon (Scheme 2). Fig. 6 shows the SEC curve of poly(*n*-BuA). The product showed a bimodal SEC curve, in which the peak-top molecular weight of the higher molecular weight side is about two times larger than that of the lower one. The results suggest that the dianion works as a difunctional initiator to form the doubled molecular weight polymer.

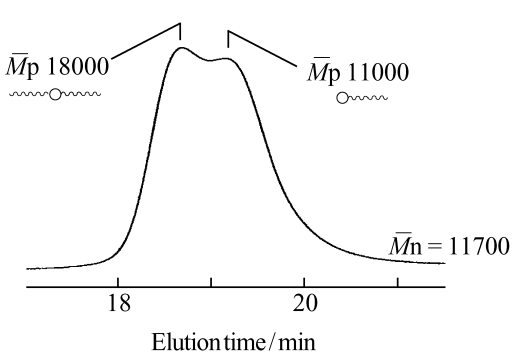


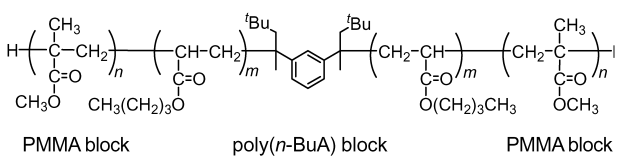

Fig. 6. SEC curve of poly(*n*-BuA) prepared with difunctional initiator quenched partially with 2,6-di-*tert*-butylphenol ($M_p$: peak-top molecular weight, calibrated against standard PMMA samples).

### 3.3. Copolymerization of n-BuA and MMA with difunctional initiator/EtAl(ODBP)$_2$—one-shot feeding synthesis of ABA-type triblock copolymer

An ABA-type triblock copolymer comprising poly(*n*-BuA) block as a middle segment (B) and PMMA blocks as end segments (A) may be used as a thermoplastic elastomer, since poly(*n*-BuA) is a soft segment to form rubbery domains and PMMA blocks are hard segments to form glassy domains expected to act as physical cross-links [29–32].

As described in Section 1, we have reported that the copolymerization of *n*-BuA and MMA with *t*-BuLi/EtAl(ODBP)$_2$ proceeds in a living and monomer-selective manner to afford block-like copolymers [28]. When the difunctional initiator is used in the place of *t*-BuLi, an ABA-type triblock copolymer is expected to form as depicted in Scheme 3. Thus, a mixture of *n*-BuA and MMA was added to difunctional initiator/EtAl(ODBP)$_2$ in toluene at −40 °C. The results of the copolymerization shown in Table 2 indicate that the copolymerization apparently proceeded in two steps; *n*-BuA was polymerized first, and, after almost all *n*-BuA was consumed, MMA started to be polymerized. Fig. 7 shows changes of SEC traces of the product, which clearly demonstrate that the copolymerization proceeded in a living manner to give the copolymer with MWD kept narrow.

$^{13}$C NMR spectrum of the copolymer is shown in Fig. 8,




Scheme 3. ABA-type triblock copolymer prepared with difunctional initiator/EtAl(ODBP)$_2$.

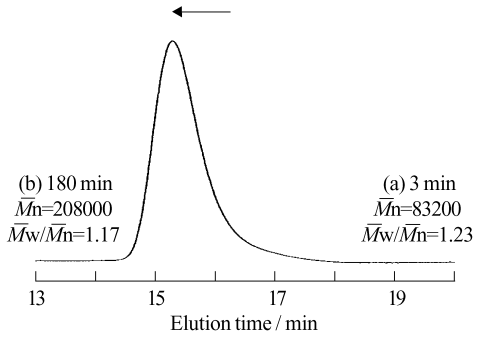



Fig. 7. SEC curves of the copolymers of *n*-BuA and MMA prepared with difunctional initiator/EtAl(ODBP)$_2$ in toluene at −40 °C for 3 min (a) (run 2 in Table 2) and for 180 min (b) (run 4 in Table 2).

which is almost a superpose of the spectra of the corresponding homopolymers, and does not show evident peaks due to *n*-BuA–MMA sequence expected to be observed at around 175.0–177.0 ppm. The result means that the copolymer consists of PMMA block and poly(*n*-BuA) block.

The morphology of the ABA-type triblock copolymer was studied by transmission electron microscopy (TEM) for cast film samples before and after annealing (Fig. 9). The TEM images of the sample prepared with difunctional initiator/EtAl(ODBP)$_2$ (Al/Li = 42) in toluene at −40 °C (run 5 in Table 2) clearly indicate microphase-separated texture (brighter zone: poly(*n*-BuA), darker zone: PMMA). As shown in Fig. 9(b), PMMA domain partly melt-fused after annealed at 140 °C for 66 h. Fig. 10 shows the morphology of the triblock copolymer prepared under the condition that the amount of EtAl(ODBP)$_2$ is reduced (Al/Li = 25) (run 6 in Table 2). In this case, PMMA domains were formed with better uniformity and kept stable even after annealed. This difference of thermal stability of the domain structure might result from the fraction of taper segment between poly(*n*-BuA) block and PMMA blocks, which may be affected by an amount of EtAl(ODBP)$_2$. The taper segment is expected to be incorporated into

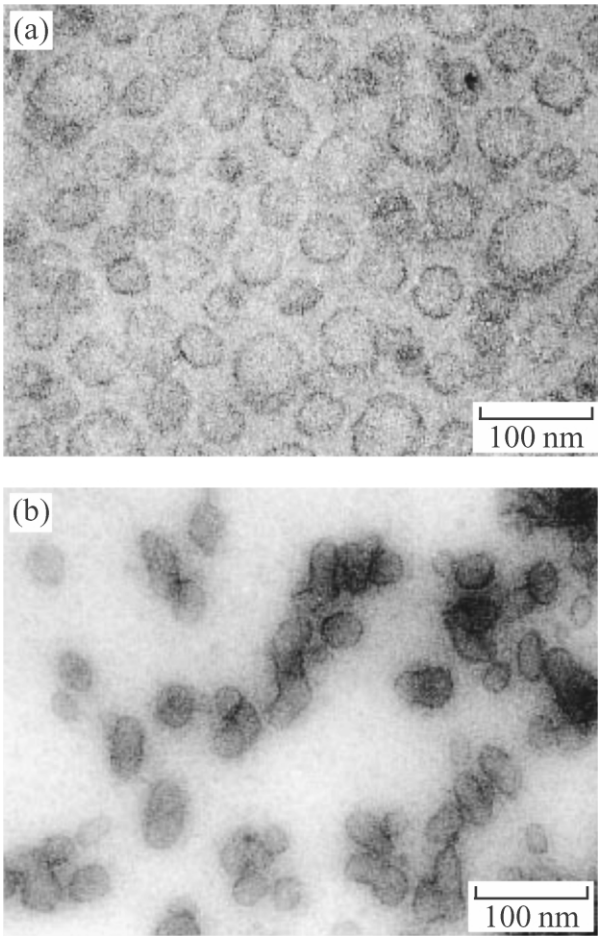



Fig. 9. TEM of PMMA-*block*-poly(*n*-BuA)-*block*-PMMA prepared with difunctional initiator/EtAl(ODBP)$_2$ (Al/Li = 42) in toluene at −40 °C (run 5 in Table 2) before (a), and after annealed at 140 °C for 66 h (b).

poly(*n*-BuA) anions firstly formed in the copolymerization when the amount of *n*-BuA monomer remained becomes smaller than that of EtAl(ODBP)$_2$ and thus MMA monomer is also activated with an excess of EtAl(ODBP)$_2$. Under such circumstance, both the monomers activated may be

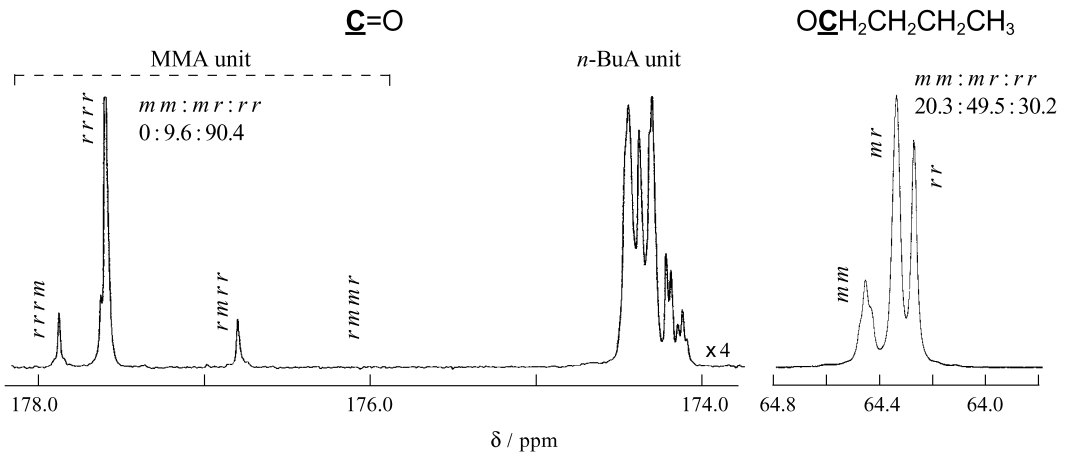



Fig. 8. $^{13}$C NMR spectra of $-OCH_2-$ (*n*-BuA unit) and carbonyl carbons of PMMA-*block*-poly(*n*-BuA)-*block*-PMMA prepared with difunctional initiator/EtAl(ODBP)$_2$ in toluene at −40 °C.

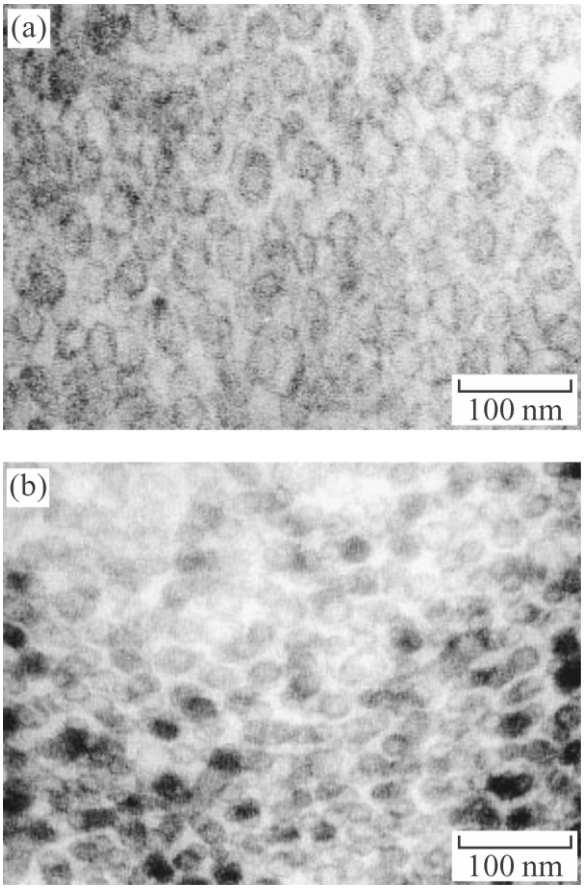



Fig. 10. TEM of PMMA-*block*-poly(*n*-BuA)-*block*-PMMA prepared with difunctional initiator/EtAl(ODBP)$_2$ (Al/Li = 25) in toluene at −40 °C (run 6 in Table 2) before (a), and after annealed at 140 °C for 66 h (b).

incorporated into the propagating chain to form a mixed monomer sequence, whose composition changes gradually from *n*-BuA unit to MMA unit to form the taper segment. The length of the taper segment should be affected by the amount of EtAl(ODBP)$_2$, and the polymer formed at Al/Li = 25 may have shorter taper segment than that formed at Al/Li = 42. The difference of thermal stability of domain structure may be ascribed to the difference in the taper segment length, and affect physical property of the polymer as an elastomer.

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