Full Paper

Termination of Living Anionic Polymerization of Butyl Acrylate with α-(Chloromethyl)acrylate for End-functionalization and Application to the Evaluation of Monomer Reactivity

Yasuhiro Kohsaka, Shoya Ishihara, Tatsuki Kitayama*

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Dr. Yasuhiro Kohsaka
Faculty of Textile Science and Technology, Shinshu University
3-15-1 Tokida, Udeda, Nagano 386-8567, Japan

S. Ishihara, Prof. Dr. Tatsuki Kitayama
Department of Chemistry, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan
E-mail: kitayama@chem.es.osaka-u.ac.jp

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1. Introduction

Since end-functionality[1-3] of macromolecular chains functions as a reactive point for the connection to other macromolecular chains, [4-10] material surface,[1-3,11-13] and biomaterials,[14-16] the control of end-functionality is an important issue along with those of molecular weight and stereoregularity.[17-20] In general, there are two approaches to end-functionalization. The first strategy is a polymerization with functional initiator or terminator.[3] Nowadays, various kinds of initiators and terminators have been developed for anionic,[21,22] cationic,[23-25] and controlled radical polymerization.[26,27] However, as different initiators and terminators must be used for individual functional groups to be introduced, this strategy requires optimization for each polymerization system and thus lacks synthetic versatility. Then, the second strategy is the post-polymerization modification of end-functionality via highly functional-group selective and quantitative 'click' reaction.[1,2, 28, 29] In fact, there are many literatures on the developments of new polymerization agents with clickable groups.[11,30-36] Nevertheless, appropriate choice of initiator (terminator) according to the reactivity of monomer

(polymerization active species) is required for controlling overall polymerization. Thus, versatile initiator and terminator applicable to various monomers are desirable.

We have been interested in the polymerization behavior of α-substituted acrylates,[37-39] and recently have found that α-(halomethyl)acrylate[37] and α-(alkoxymethyl)acrylate[39] functioned as an efficient terminator in stereospecific anionic polymerizations of methyl methacrylate (MMA); the poly(methyl methacrylate) (PMMA) living anion attacks the vinylidene group of the terminators, and the subsequent elimination of halogen atom or alkoxy group generates PMMA with α,β-unsaturated ester moiety at the ω-end. For example, the polymerization initiated by isopropyl α-lithioisobutyrate (Li-iPrIB) in the presence of ethylaluminum bis(2,6-di-$tert$-butylphenoxide) [EtAl(ODBP)$_2$] could be terminated with ethyl α-(chloromethyl)acrylate (ECMA) to afford highly syndiotactic (st-) PMMA with ω-functionality (termination efficiency: $F \sim 99\%$).[37] Furthermore, the incorporated α,β-unsaturated ester moiety allows quantitative post-polymerization modification to incorporate ω-functional groups such as amino, hydroxyl, and carboxylic group via base-catalyzed thiol-ene reactions, one of the widely practiced click reactions.[37]

In general, since a living polymer anion of polyacryate has lower nucleophilicity than that of polymethacrylate, the end-functionalization of polyacrylate living anion through termination is expected to be more difficult. On the other hand, it is reported that polyacrylate living anion can attack to MMA in the presence of EtAl(ODBP)$_2$, because MMA, which has relatively lower reactivity, is activated by the coordination of EtAl(ODBP)$_2$.[40] Inspired from this knowledge, we have envisioned that anionic polymerization of acrylate in the presence of EtAl(ODBP)$_2$ may allow the termination with ECMA. Herein, we report the termination reaction and its application to evaluate the relative reactivity of acrylate to ECMA.

2. Experimental Section

Materials

CH$_2$Cl$_2$ (Wako, super dehydrated grade) was dried over CaH$_2$ and distilled under high vacuum just before use. Toluene (Aldrich, anhydrous grade) dehydrated with red-collared adduct of butyllithium (*n*-BuLi) and 1,1-diphenylethene, and distilled under high vacuum just before use. EtAl(ODBP)$_2$ and methylaluminum bis(2,6-di-*tert*-butylphenoxide) [MeAl(ODBP)$_2$] were prepared according to our previous reports[41] and stored as toluene solutions under nitrogen atmosphere. MMA (Nacalai Tesque), butyl acrylate (*n*BA), and *tert*-butyl acrylate (*t*BA) were fractionally distilled and stored over CaH$_2$. The monomers were distilled over CaH$_2$ under reduced nitrogen pressure just before use. Li-*i*PrIB was prepared and recrystallized in toluene according to our previous report.[42] ECMA was synthesized according to our previous reports.[37] Other reagents were used as purchased without further purification.

Instruments

^{1}H NMR spectra were recorded in CDCl$_3$ (Aldrich) on a Unity Inova 500 spectrometer (Varian) or an ECS-400 spectrometer (JEOL). Chemical shifts in ^{1}H NMR spectra were referred to the signal of tetramethylsilane (TMS). Molecular weights and its distributions of the polymers were determined at 40 °C by size-exclusion chromatography (SEC) using a GPC-900 chromatograph (JASCO) equipped with two SEC columns [Polymer Laboratories, PL-gel, Mixed C (300 mm × 7.5 mm)], using tetrahydrofuran (THF) as an eluent, and calibrated against standard PMMA samples (Shodex, MW: 1.25×10^6, 6.59×10^5, 1.95×10^5, 4.96×10^4, 2.06×10^4, 6.82×10^3, 2.00×10^3).

Polymerization

A typical procedure (Table 1, Run 2): To a glass ampoule filled in dried nitrogen gas passed through MS4A cooled at −78 °C, toluene (5.0 mL), EtAl(ODBP)$_2$ (0.50 mmol), and Li-*i*PrIB (0.10 mmol) were added at room temperature using hypodermic syringes. The reaction mixture was cooled to −60 °C, and the polymerization was started by adding *n*BA (5.0 mmol).

After 1 h, ECMA (0.50 mmol) was added and reacted for 1 h, and the reaction was finally quenched with 5 M HCl aq—MeOH solution. Then the reaction mixture was concentrated and dried under vacuum at 40 °C. The product (0.868 g) was subjected to SEC and NMR analyses.

Evaluation of relative reactivity (*RR*) of *n*BA

A typical procedure (Table 2, Run 1): Anionic polymerization of MMA (2.0 mmol) with Li-*i*PrIB (0.10 mmol) and EtAl(ODBP)$_2$ (0.50 mmol) was conducted in CH$_2$Cl$_2$ at −78 °C in a similar manner to that described above, and a mixture of *n*BA (0.500 mmol) and ECMA (2.05 mmol) was added at −60 °C. After 1 h, the reaction was finally quenched with 5 M HCl aq—MeOH solution.

3.   Results and Discussion

Termination of Living Anionic Polymerization of Butyl Acrylate

Anionic polymerization of *n*BA with Li-*i*PrIB and EtAl(ODBP)$_2$ was conducted in toluene at −60 °C for 1 h, and then ECMA was added to the reaction mixture (**Scheme 1**). **Figure 1** shows the ^{1}H NMR spectrum of the resulting polymer. Besides the signals of the monomeric units (signals labeled **1-6**), signal **α** (4.94 ppm) assignable to the isopropyl methine proton at the α-end group is clearly observed, which can be used as an internal standard for quantitative analyses of polymer structures. Olefinic proton signals **ω1** (5.51 ppm) and **ω2** (6.15 ppm) are assignable to the ω-end unit formed by the termination reaction of the living poly(*n*BA) anions with ECMA through addition-elimination (S$_N$2') mechanism (**Scheme 1**), similarly to the case of MMA polymerization.[37] The ethoxyl methylene signal **ω3** (4.19 ppm) is also observed, further confirming the assignments. Thus, the termination efficiency (*F*) can be determined from the relative intensity of **ω1** to **α**. The results of polymerization were summarized in **Table 1**.
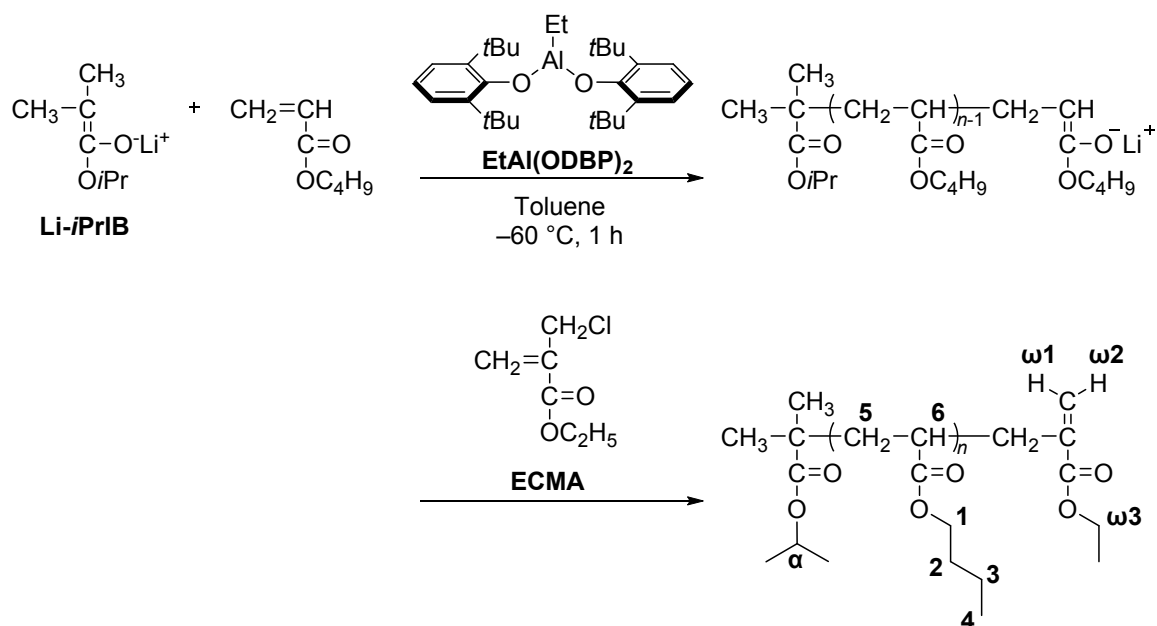
Scheme 1. Termination of living anionic polymerization of acrylates with ECMA.
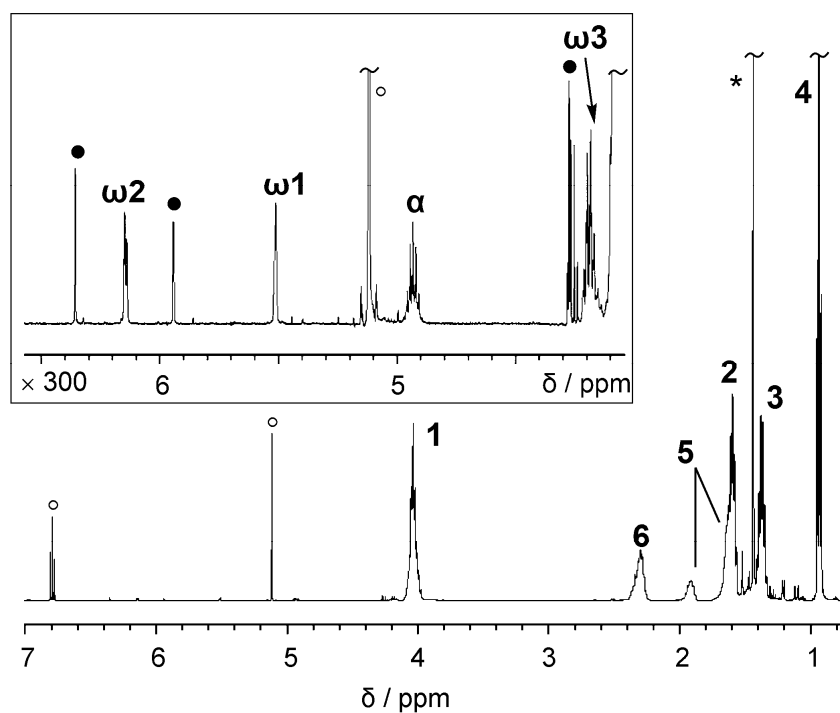

Figure 1. ^{1}H NMR spectra of poly(nBA) (Table, 1, Run 2) (500 MHz, CDCl$_3$, 55 °C). ●: ECMA, °: 2,6-di-*tert*-butylphenol, *: H$_2$O. Other labels on signals correspond to those shown in Scheme 1.

Table 1. Termination of living anionic polymerization of acrylates with ECMA.

Run[a)	Monomer (equiv.[b))	*Conv.* /%[c)	M_n[d)	M_w/M_n[d)	*F* /%[e)
1	*n*BA (50)	100	13300	1.11	78
2	*n*BA (50)	100	12600	1.13	75
3	*n*BA (50)	100	12500	1.12	74
4[f)	*n*BA (50)	100	12100	1.12	80
5	*t*BA (30)	100	6000	1.11	29

[a) Polymerization was conducted in toluene (5.0 mL) with BA (5.0 mmol) at –60 °C for 1 h and terminated with ECMA for 1 h: [Li-*i*PrIB]$_0$ / [EtAl(ODBP)$_2$] / [ECMA] = 1 / 5 / 5.
[b) Equivalent to Li-*i*PrIB.
[c) Estimated by ^{1}H NMR spectroscopy (400 MHz, CDCl$_3$, 30 °C).
[d) Estimated by SEC (THF, 40 °C, PMMA standards).
[e) Estimated by ^{1}H NMR spectroscopy (500 MHz, CDCl$_3$, 55 °C).
[f) Terminating reaction was conducted for 24 h.

The polymerization and terminating reactions were repeated three times under the same conditions (Runs 1-3). In any case, the termination efficiencies were *ca.* 75%. It slightly increased to 80% by the extension of reaction time from 1 h to 24 h (Run 4).[43-45] The termination efficiencies are lower than that in the polymerization of MMA ($F \sim 99\%$)[37], probably due to the lower reactivity of polyacrylate living anion. The same termination experiment for *t*BA (Run 5) resulted in much lowertermination efficiency (29%) than that for *n*BA.

Evaluation of Relative Reactivity of Butyl Acrylate

Although the terminating reaction did not proceed quantitatively, it was found that the incorporated vinylidene group at the ω-end had different ^{1}H NMR chemical shifts from that in *st*-PMMA chain-end.[37] **Figure 2** shows the ^{1}H NMR spectra of poly(*n*BA) and *st*-PMMA terminated with ECMA. The vinylidene signal **ω1M** of *st*-PMMA (5.48 ppm) was observed at 0.03 ppm higher magnetic field than that of poly(*n*BA), whereas **ω2M** of *st*-PMMA (6.17 ppm) was at lower magnetic field than **ω2**. Besides, **ω2** split two peaks,[46] while **ω2M** is a singlet. Thus, these signals of ω-ends reflect the penultimate monomeric units.
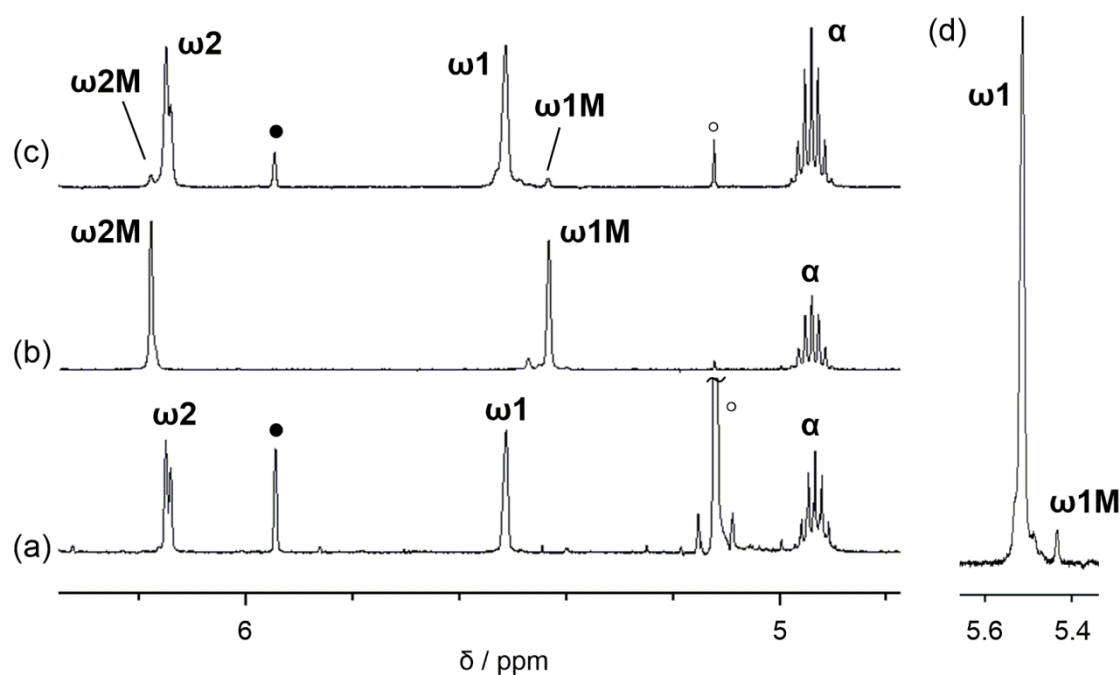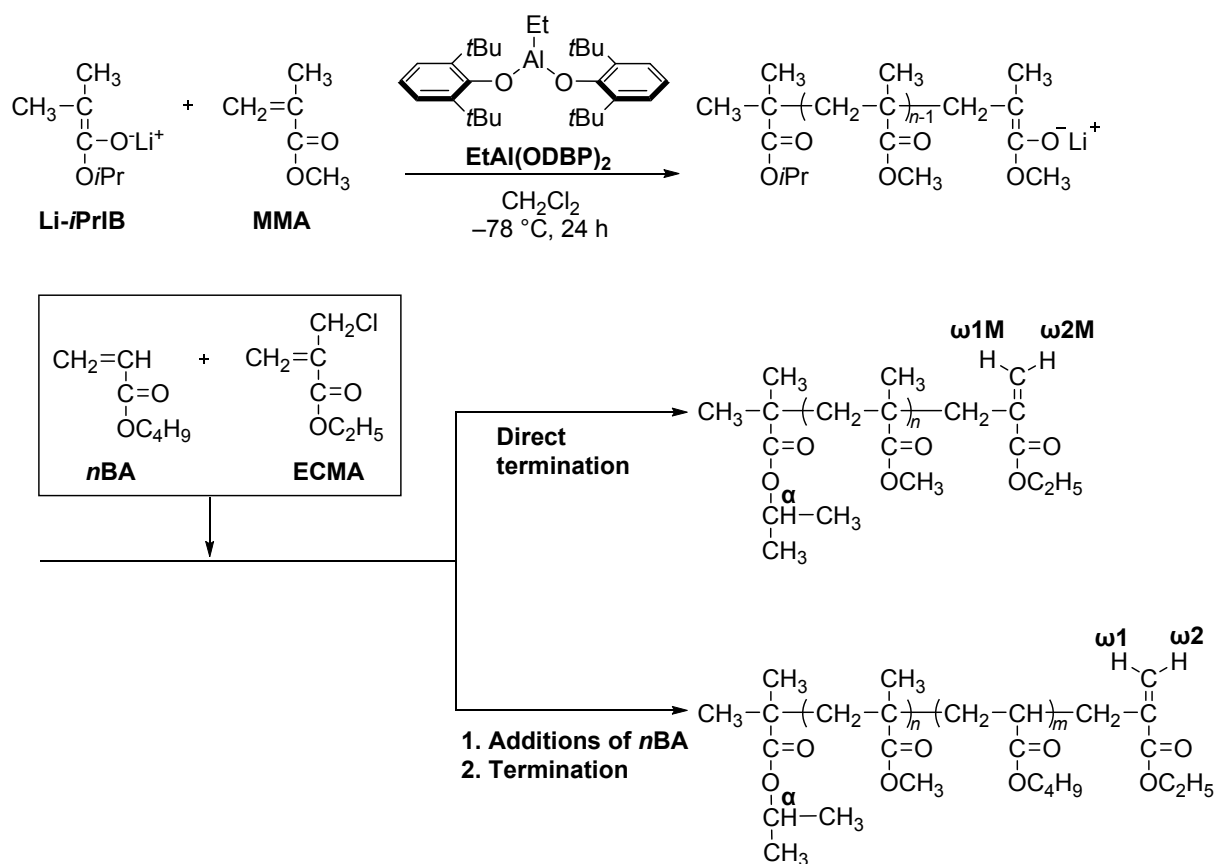
Figure 2. ^{1}H NMR spectra of (a) poly(*n*BA) and (b) *st*-PMMA, both terminated with ECMA, (c) the product of the reaction of *st*-PMMA living anion with a mixture of ECMA and *n*BA, and (d) its expansion for **ω1** and **ω1M** signals (500 MHz, CDCl₃, 55 °C).
●: ECMA, °: 2,6-di-*tert*-butylphenol. Other labels on signals correspond to those in Scheme 2.

Scheme 2. Competitive reaction of *st*-PMMA living anion: Termination with ECMA (above) and block copolymerization with *n*BA (below).

The NMR spectroscopic features described above motivated us to conduct the following experiment for evaluating the relative reactivity of nBA to ECMA against the methacrylate-type anion in the presence of the aluminum Lewis acid, EtAl(ODBP)$_2$; a mixture of nBA and ECMA was added to the PMMA living anion prepared with Li-iPrIB and EtAl(ODBP)$_2$ (**Scheme 2**). If ECMA reacts with PMMA living anion directly, PMMA possessing vinylidene terminal will be generated. On the other hand, if the anion adds one or more n-BA before the termination with ECMA, it affords a copolymer carrying nBA units at ω-end side adjacent to the terminal unsaturated unit. Figure 2c shows the ^{1}H NMR spectrum of the resulting polymer. Apparently, a set of signals, **ω1** and **ω2**, are strongly observed together with small signals, **ω1M** and **ω2M**. The fraction of the PMMA living anion reacted with ECMA was estimated as 4.9% from the relative intensity of **ω1M** to **α** (Figure 2d).[47] On the assumption that the rest of the PMMA living anion reacted with nBA, the relative reactivity (*RR*) of nBA in reference to ECMA can be estimated as follows;

$$RR = [\text{Selectivity to } n\text{BA}] / [\text{Selectivity to ECMA}] \times ([n\text{BA}]_0 / [\text{ECMA}]_0) \qquad (1)$$

Here, $[n\text{BA}]_0$ and $[\text{ECMA}]_0$ are initial concentrations of nBA and ECMA, respectively. The experiments were repeated at the feed ratio of nBA and ECMA, 4.10 and 2.22, ~~three times~~ and the results were summarized in **Table 2.** Although errors in NMR integration of the smaller signals for **ω1M** and **ω2M** might magnify difference in *RR* values as expected from the calculation based on equation (1), the deviation of the estimated *RR* values for Entries 1-3 and Entries 4-6 is reasonably small (average value 85, standard deviation 7.2 %), indicating that the results were independent of the feed ratio of nBA and ECMA.[48] When the amount of nBA was doubled (Entries 7 and 8), however, the estimated *RR* values were slightly increased. Since the reaction of nBA and PMMA living anion is much faster than the termination, the consumed nBA changes the balance of nBA / ECMA before complete consumption of PMMA living anion. This effect should be suppressed when a sufficient amount of nBA is

used, and thus the data by Entries 7 and 8 might be closer to the true value. In conclusion, however, it is apparent that *n*BA has at least 80 times higher reactivity than ECMA.

Table 2. Evaluation of relative reactivity of *n*BA to ECMA.

Entry[a]	Feed		Selectivity[c] /%		RR[d] (*n*BA)
	*n*BA (mmol)	$[ECMA]_0 / [nBA]_0$[b]	*n*BA[b]	ECMA[b]	
1	0.50	4.10	95.1	4.9	80
2	0.50	4.10	95.9	4.1	96
3	0.50	4.10	95.5	4.5	87
4	0.50	2.22	97.3	2.7	81
5	0.50	2.22	97.3	2.7	81
6	0.50	2.22	97.4	2.6	83
7	1.0	2.22	97.9	2.1	103
8	1.0	2.22	98.0	2.0	109
Average					90

[a] A mixture of *n*BA and ECMA was reacted at −60 °C with PMMA living anion, prepared with Li-*i*PrIB (0.10 mmol) / EtAl(ODBP)$_2$ (0.50 mmol) and MMA (2.0 mmol) in CH$_2$Cl$_2$at −78 °C.
[b] Determined from the mass of ECMA and *n*BA.
[c] Selectivities to ECMA were estimated as an intensity ratio of **ω1M** relative to **α** in ^{1}H NMR spectrum (500 MHz, CDCl$_3$, 55 °C, Figure 3c), while the residues from 100% were presumed as reacted with BA.
[d] Relative reactivity estimated according to equation (1).

To describe the reactivity of vinyl monomers, *Q* and e values in *Q*-e scheme and the ^{13}C NMR chemical shift values of β-carbons[49] are often used as a measure. However, there are little differences between *n*BA and ECMA in both their *e* values (*n*BA: 0.85[50], ECMA: 0.91[51]) and ^{13}C chemical shift values (*n*BA: 128.9 ppm,[52] ECMA: 128.1 ppm[53]), and thus these measures do not appropriately account for the much larger *RR* of *n*BA than that of ECMA. In the anionic polymerization in the presence of aluminum Lewis acids, like EtAl(ODBP)$_2$, it has been postulated that the aluminum compounds stabilize the propagating anions so as to require monomer activation through coordination to the carbonyl group of the monomers[40,41]. Therefore, the *RR* obtained in this experiment should reflect such a monomer activation effect as well as the moderated reactivity of the stabilized propagating anion, and could be regarded as a more practical measure of monomer reactivity in the anionic polymerization system employed. In a copolymerization of *n*BA and MMA, the monomer

activation is selective for sterically less demanding nBA, which leads to monomer-selective living copolymerization to afford block-like copolymers.[40] In the case of nBA and ECMA, nBA should be coordinated by EtAl(ODBP)$_2$ preferentially so as to bring about such a great differences in the RR between nBA and ECMA.

4. Conclusion

End-clickable polyacrylates were prepared by the anionic polymerization in the presence of EtAl(ODBP)$_2$ and termination with ECMA. The termination efficiency was up to 80% for poly(nBA), although that for poly(tBA) was low (29%). As the ^{1}H NMR signals of the terminal vinylidene groups were so sensitive to the penultimate monomeric units to provide information on the competition of propagation with nBA and termination with ECMA from PMMA living anion. As a result, the relative reactivity of nBA to ECMA could be estimated at least 80 times higher. As this relative reactivity reflects the effect of activation by EtAl(ODBP)$_2$, it describes more realistic polymerization behavior of monomers than other conventional evaluation.

Abstract

Poly(n-butyl acrylate) [poly(nBA)] with clickable vinylidene group at the terminal end was prepared through the anionic polymerization on the presence of bulky aluminum Lewis acid and termination with ethyl α-(chloromethyl)acrylate (ECMA) with the termination efficiency of 80% at a maximum. The incorporated terminal group showed characteristic ^{1}H NMR signals differing from those of poly(methyl methacrylate) (PMMA), that is the signals were sensitive to the penultimate monomeric unit. A mixture of nBA and ECMA was reacted with PMMA living anion, and the terminal structure of the resulting polymer was investigated.

From the content of PMMA directly terminated with ECMA in the overall resulting polymers, the relative reactivities of *n*BA to ECMA are estimated as at least 80.

Abbreviations

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[43]   Since the polymerization system was known living (described in Ref. 40), we expected the residual 25% remained unreacted and finally quenched with HCl solution after the reaction with ECMA. However, since the terminal proton NMR signal was overlapped with butyl signals, the direct observation was difficult.

[44]   It should be noted that an attempt of the termination at temperatures higher than −60 °C might be not effective, as the propagating species underwent self-termination reaction through 'back-biting' to the carbonyl group in the penpenultimate unit.

[45]   The unimodal SEC curves indicated that the formed vinylidene group at the terminal end was not involved in the reaction with the residual living anion, probably due to the bulkiness of the substituents of the vinylidene group. Similar results were observed in our previous work on the termination of the anionic polymerization of MMA (see Ref. 37).

[46]   Similarly to the terminal vinylidene signals of PMMA terminated with ECMA (see Ref. 37), the two peaks might reflect the stereochemical diads around the terminal end, although the overlapping of these two peaks prevent the detailed analysis.

[47]   The relative intensity of **ω1M** to **ω1** was inherently not agreed with that of **ω1M** to **α,** since the termination efficiency for poly(nBA) living anion is not 100%, while the termination of the PMMA living anion with ECMA proceeds quantitatively, as reported previously.

[48]   A similar experiment was also tried for 1:20 mixture of nBA and ECMA. However, gelation accompanied with exotherm occurred, which was not observed in other Entries. A similar phenomenon was observed on mixing ECMA and EtAl(ODBP)$_2$ in CH$_2$Cl$_2$ at ambient temparature, and thus we suspected the large amount of ECMA caused an unexpected side reaction.

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FIGURE FOR ToC_ABSTRACT

Poly(*n*-butyl acrylate) with clickable vinylidene group at the terminal end was prepared through the living anionic polymerization in the presence of aluminum additives and terminating reaction with ethyl α-(chloromethyl)acrylate. The terminating reaction was applied to evaluate the relative reactivity of *n*-butyl acrylate in the anionic polymerization system through the competition of propagation and termination.

Y. Kohsaka, S. Ishihara, T. Kitayama*

Termination of Living Anionic Polymerization of Butyl Acrylate with α-(Chloromethyl)acrylate for End-functionalization and Application to the Evaluation of Monomer Reactivity

ToC figure ((Please choose one size: 55 mm wide × 50 mm high **or** 110 mm wide × 20 mm high. Please do not use any other dimensions.))