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Living polymerization of primary alkyl acrylates with *t*-butyllithium/bulky aluminum Lewis acids

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Abstract

Anionic polymerizations of primary alkyl acrylates such as ethyl acrylate (EA) and *n*-butyl acrylate (*n*-BuA) with *tert*-butyllithium (*t*-BuLi) in the presence of bis(2,6-di-*tert*-butylphenoxy)alkylaluminums were carried out in toluene. The polymerizations with *t*-BuLi/bis(2,6-di-*tert*-butylphenoxy)ethylaluminum at low temperatures gave syndiotactic-rich polymers with narrow molecular weight distribution (MWD) in high yields, while those with *t*-BuLi/bis(2,6-di-*tert*-butylphenoxy)methylaluminum gave polymers with broader MWD in lower yields. The monomer addition experiment revealed the livingness of the former polymerizations. The initial monomer concentration and polymerization temperature were found to affect the MWD and the stereoregularity of the obtained polymers.

Keywords: Bis(2,6-di-*tert*-butylphenoxy)ethylaluminum; Chain end cyclization; Syndiotactic polyacrylate

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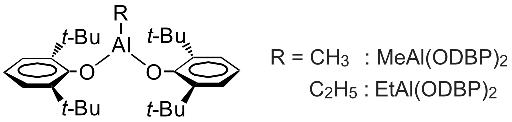
1. Introduction

In the last decade several research groups have studied living polymerizations of alkyl acrylates by using combined initiators comprising initiator components and stabilizers [1–14], which overcome the difficulty in controlling the reaction. An early example of the combined initiators is a combination of alkyllithium and lithium chloride (LiCl), which is effective for living polymerization of a bulky alkyl acrylate, *tert*-butyl acrylate (*t*-BuA) [4–6], in tetrahydrofuran (THF). However, the combination of *t*-BuLi/LiCl is not effective for the polymerization of primary alkyl acrylates. Later it was reported that some primary alkyl acrylates, such as ethyl acrylate (EA) and *n*-butyl acrylate (*n*-BuA) could be polymerized in a living manner by diphenylmethyllithium as an initiator, in the presence of chelating $\mu-\sigma$ type ligands, i.e. polydentate lithium alkoxides, in toluene/THF mixtures at low temperatures [14]. The living polymerizations of such primary alkyl acrylates have also been realized by using rare-earth metal complexes in THF, giving high molecular weight polymers [15].

We have found stereospecific living polymerizations of alkyl methacrylates with a combination of *tert*-butyllithium (*t*-BuLi) and bis(2,6-di-*tert*-butylphenoxy)methylaluminum [MeAl(ODBP)$_2$, (Scheme 1)] in toluene at low temperatures [16–24]. Recently, we also found that living polymerization of *t*-BuA with the same initiator in toluene at low temperature proceeds in a living manner and gives a polymer with narrow molecular weight distribution (MWD) [25–27]. 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 (−30 to −40 °C). The monomer selectivity was lost at −20 °C but the living nature was kept and a random copolymer of *t*-BuA and EMA with narrow MWD was obtained [27].

This paper reports the anionic polymerization of primary alkyl acrylates with combinations of *t*-BuLi and bis(2,6-di-*t*-butylphenoxy)alkylaluminums [RAl(ODBP)$_2$] in toluene at low temperatures. The polymerization of EA and *n*-BuA



Scheme 1.

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with *t*-BuLi/MeAl(ODBP)$_2$ gave polymers with broad MWD in low yields. Replacing methyl group in MeAl(ODBP)$_2$ with ethyl group [bis(2,6-di-*t*-butylphenoxy)-ethylaluminum, EtAl(ODBP)$_2$, (Scheme 1)] drastically changed the behavior of the polymerization and gave syndiotactic-rich polymers with narrow MWD. The effects of other polymerization conditions on the MWD and the stereoregularity of the obtained polymers were also examined.

2. Experimental section

2.1. Materials

EA and *n*-BuA (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*-phenanthrolin as an indicator [28]. Trimethylaluminum and triethylaluminum were used as heptane solutions. EtAl(ODBP)$_2$ was prepared from 2,6-di-*t*-butylphenol and triethylaluminum in toluene at room temperature [19,20, 29], and recrystallized several times from heptane at -30 °C. Preparation of MeAl(ODBP)$_2$ was made essentially in the same way as that for EtAl(ODBP)$_2$.

2.2. Polymerization

All the polymerizations were carried out in glass ampoules filled with dried nitrogen passed through Molecular Sieves 4Å cooled at -78 °C. *t*-BuLi was added to EtAl(ODBP)$_2$ in toluene at the polymerization temperature at a molar ratio of *t*-BuLi/EtAl(ODBP)$_2 = 1/5$. The polymerization reaction was initiated by adding the monomer slowly to the initiator solution with stirring. 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. 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-*tert*-butylphenol resulting from the hydrolysis of EtAl(ODBP)$_2$ was removed from the polymeric product by size exclusion chromatography (SEC) using a Shodex SEC column K-2003 (20 mm i.d. × 300 mm) with chloroform as an eluent.

2.3. Measurements

Molecular weights of the polymers and their distributions were determined by 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 polystyrene samples.

^{1}H NMR spectra of the polymers were measured in chloroform-*d* at 55 °C using a JEOL JNM AL400 spectrometer. Diad tacticities of the polymers were determined from ^{1}H NMR signals of the main-chain methylene protons. For poly(*n*-BuA), *racemo* methylene proton signals are overlapped with the signal due to β-methylene protons in the ester group, and thus the peak intensity of one of the *meso* methylene proton signals (1.9 ppm) is compared with that of the main-chain methine proton (2.3 ppm) to estimate the *meso* diad content. Number-average molecular weight ($\bar{M}_n$) was also determined from the intensities of the ^{1}H NMR signal (0.85 ppm) of *t*-butyl group of the initiator fragment at the chain-end and of the methine proton signal due to the monomer units.

3. Results and discussion

3.1. Polymerization with t-BuLi/bisphenoxyalkylaluminum [RAl(ODBP)$_2$]

In the previous paper [27], we reported that the combination of *t*-BuLi and MeAl(ODBP)$_2$ initiates a living polymerization of *t*-BuA in toluene at low temperatures. First the polymerizations of EA and *n*-BuA were carried out with *t*-BuLi/MeAl(ODBP)$_2 = 1/5$ in toluene at -60 °C. As shown in Table 1, the polymers were obtained in about 70% yields and had broad MWDs, indicating the occurrence of some side reaction. When EtAl(ODBP)$_2$ was used in place of MeAl(ODBP)$_2$, the polymerization smoothly proceeded, completed within 0.5 h, and gave polymers with somewhat narrow MWD (<1.14). The ($\bar{M}_n$) values, determined by ^{1}H NMR end-group analysis, were close to those expected from the reacted monomer-to-initiator molar ratio. The syndiotacticities of the polymers were higher with EtAl(ODBP)$_2$ than with MeAl(ODBP)$_2$. The results suggest that a slight increase in the bulkiness of the substituent of aluminum atom displays significant effect on the polymerization behavior. A similar effect of the alkyl group in RAl(ODBP)$_2$ was observed in the living polymerization of ethyl methacrylate in toluene at low temperature; the polymerization with *t*-BuLi/MeAl(ODBP)$_2$ gave a heterotactic polymer and that with *t*-BuLi/EtAl(ODBP)$_2$ a syndiotactic polymer [21].

The effect of the concentrations of initial monomer and initiator on the polymerization behavior was examined. The results are shown in Table 2. The $\bar{M}_n$ of the resulting polymer increases with increasing initial monomer

Table 1
Polymerization of EA and n-BuA with t-BuLi/bis(2,6-di-t-butylphenoxy)alkylaluminum [RAl(ODBP)$_2$] in toluene at -60 °C

Bis(phenoxyalkyl)aluminum	Monomer	Time (h)	Yield (%)	$\bar{M}_n$		$\bar{M}_w/\bar{M}_n$ [a]	Tacticity [b] (%)		N(enol) [c]
				Calcd	NMR		m	r	
–	EA	5	100	5100	8800	18.2	87	13	–
–	n-BuA [d]	5	100	6500	7900	20.5	82	18	–
MeAl(ODBP)$_2$	EA	24	69	3500	3900	1.77	47	53	0.43
MeAl(ODBP)$_2$	n-BuA	0.5	71	4600	5000	1.49	48	52	0.35
EtAl(ODBP)$_2$	EA	0.5	100	5100	6000	1.09	32	68	0.03
EtAl(ODBP)$_2$	n-BuA	0.5	96	6200	7600	1.14	37	63	0.08

Monomer 5 mmol, t-BuLi 0.1 mmol, toluene 5 ml, t-BuLi/RAl(ODBP)$_2$ = 1/5 mol/mol.

[a] Determined by SEC.

[b] Determined from ^{1}H NMR signals of methylene protons.

[c] The amount of enol unit per chain determined from the peak intensities of the enol proton, I(enol), and t-butyl group signal, I(t-Bu); $N(\text{enol}) = [I(\text{enol})/I(t\text{-Bu})] \times 9$.

[d] Toluene 10 ml.

concentration at the same initiator concentration (runs 1–3 in Table 2). The $\bar{M}_n$ (NMR) of the polymer agreed roughly with the calculated value. The polymer obtained at the initial monomer concentration of 2.0 mol/l (run 3) had rather broad MWD as compared with those at lower concentrations (runs 1 and 2). Even in the cases where the ratio of initial monomer to initiator was constant, the MWD became broader with increasing initial monomer concentration (runs 4–6). The fractions of *racemo* diad of the polymers increased with decreasing initial monomer concentration. The results suggest that the monomer concentration affects the coordination of EtAl(ODBP)$_2$ with the propagating species and changes their behavior including stereospecificity.

3.2. Living nature of polymerization of EA with t-BuLi/EtAl(ODBP)$_2$

The polymerization of EA with t-BuLi/EtAl(ODBP)$_2$ was carried out in toluene at -60 °C. After completion of the polymerization (30 min after initiation), the same molar amount of EA (5 mmol) was added again to the polymerization mixture. Fig. 1 shows the plots of the $\bar{M}_n$ and MWD against the polymer yield. Even after the second addition of the monomer, the polymerization proceeded quantitatively and the $\bar{M}_n$ increased in proportion to the polymer yield, maintaining narrow MWD (<1.11). The results clearly indicate the living nature of this polymerization system. Moreover, it was supposed that the first monomer was consumed after 2–3 min, as the yield of the polymerization after 1 min was 69%. However, the polymerization system was kept at -60 °C for 30 min till the second addition of the monomer. The results suggest that the propagating species in the polymerization of EA at -60 °C are very stable for a long time. The stability may be due to the prevention of the autotermination reaction of the propagating species by the coordination of EtAl(ODBP)$_2$.

Anionic polymerization of alkyl acrylates is often complicated by undesirable termination reactions [1–3]. Such termination reactions occur through three main pathways: termination reaction with monomer ester group, intermolecular termination reaction with ester groups of another polymer chain and intramolecular termination with the antepenultimate ester group of the same chain

Table 2
Polymerization of EA with t-BuLi/EtAl(ODBP)$_2$ in toluene at -60 °C, effect of the concentration of monomer and t-BuLi

Run no.	Monomer (mol/l)	t-BuLi (mol/l)	Time (h)	Yield (%)	$\bar{M}_n$		$\bar{M}_w/\bar{M}_n$ [a]	Tacticity [b] (%)	
					Calcd	NMR		m	r
1	0.5	0.02	0.5	100	2500	3200	1.10	24	76
2	1.0	0.02	0.5	100	5100	6000	1.09	32	68
3	2.0	0.02	3	99	10 000	12 700	1.35	42	58
4	0.5	0.01	0.5	100	5100	7200	1.07	24	76
5	1.0	0.02	0.5	100	5100	6000	1.09	32	68
6	2.0	0.04	0.5	98	5000	6000	1.35	39	61

t-BuLi/EtAl(ODBP)$_2$ = 1/5 mol/mol, toluene 5 ml.

[a] Determined by SEC.

[b] Determined from ^{1}H NMR signals of methylene protons.

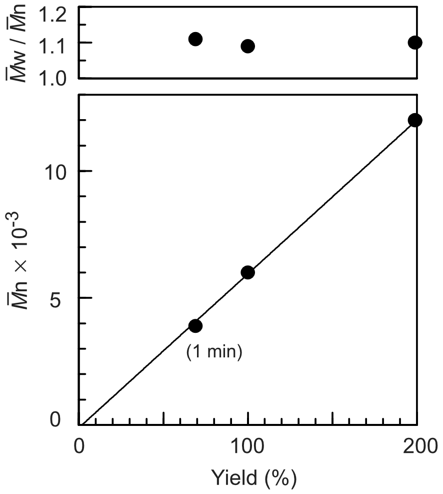


Fig. 1. Polymerizations of EA with *t*-BuLi/EtAl(ODBP)$_2$ (1/5) in toluene at − 60 °C [EA 5 mmol (each 1st and 2nd), *t*-BuLi 0.1 mmol, EtAl(ODBP)$_2$ 0.5 mmol, toluene 5 ml].

(backbiting reaction). The backbiting reaction has already been well explained by other observations [2,3]; it forms a keto or an enol structure at the chain end (Scheme 2). ^{1}H NMR spectrum of the poly(EA) prepared with MeAl(ODBP)$_2$ at − 60 °C (Fig. 2(A)) shows two small signals at 12.20 and 12.45 ppm, that should be assigned to enol protons [6]. Splitting of the peaks may be due to stereochemistry of the six-membered ring structure formed at the chain end. The number of the enol protons per chain, *N*(enol), was estimated from the relative peak intensity of the enol proton, *I*(enol), and *t*-butyl group signal, *I*(*t*-Bu), as:

$$N(\text{enol}) = [I(\text{enol})/I(t\text{-Bu})] \times 9$$

The *N*(enol) of the poly(EA) was found to be 0.43, indicating that substantial amount of polymer chains terminated through the backbiting. On the contrary, the spectrum of the poly(EA) prepared with EtAl(ODBP)$_2$ shows much smaller ones (Fig. 2(B)), from which *N*(enol) was estimated to be 0.03. Similar results were also observed for the polymerizations of *n*-BuA is shown in Table 1. The results suggests that EtAl(ODBP)$_2$ coordinates with the propagation species to prevent them from the backbiting reaction. Thus the polymerization with EtAl(ODBP)$_2$ proceeds in a predominantly living manner.

3.3. Temperature dependence of polymerization reaction

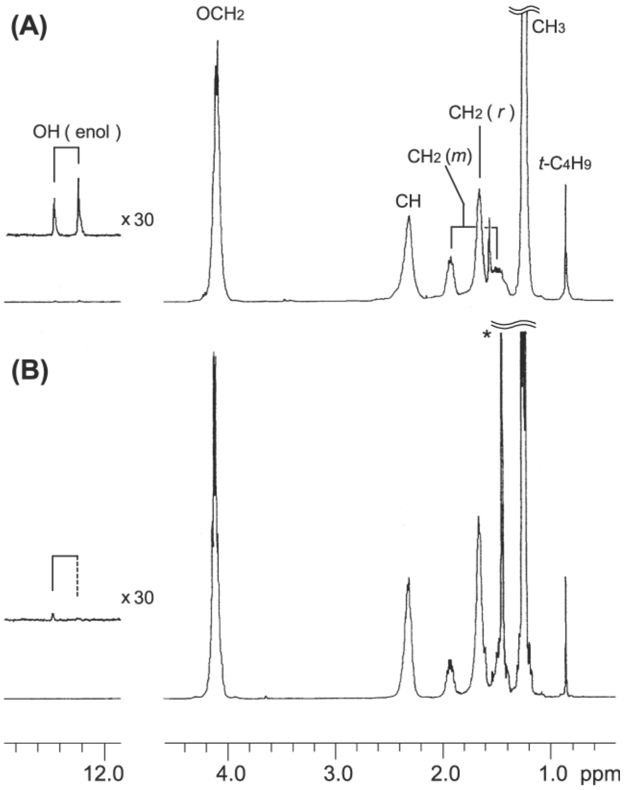
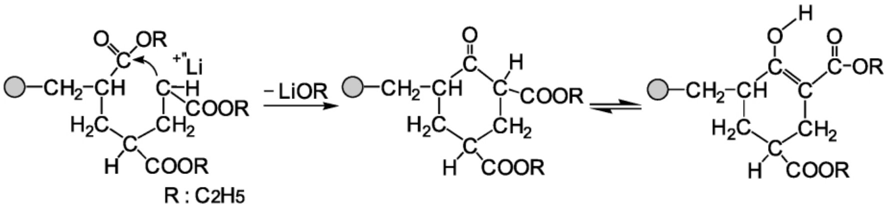


Fig. 2. ^{1}H NMR spectra of poly(EA) prepared with (A) *t*-BuLi/MeAl(ODBP)$_2$ and (B) *t*-BuLi/EtAl(ODBP)$_2$ in toluene at − 60 °C (400 MHz, CDCl$_3$, 55 °C). (*) Signal due to CH$_3$ protons of 2,6-di-*tert*-butylphenol derived from EtAl(ODBP)$_2$.

The polymerization EA and *n*-BuA with *t*BuLi/EtAl(ODBP)$_2$ were carried out at various temperatures and the results are summarized in Table 3. All of the polymerizations proceeded quantitatively. However, the poly(EA)s prepared at − 20 and 0 °C have broad MWD (> 1.6). The ^{1}H NMR spectra of the polymers obtained in the temperature range showed that the intensities of enol proton signals increased with increasing polymerization temperature. The fraction of the enol structure in the polymer chain was determined as the ^{1}H NMR peak intensity of the enol protons relative to *t*-butyl group signal and is shown in percentage in Table 3. The polymers formed at − 20 and 0 °C contained the enol units in 0.03 and 0.07, respectively, suggesting the enhanced backbiting reaction at higher temperatures. Compared with EA, the polymerization of *n*-BuA in the temperature range from − 60 to − 20 °C gave polymers with narrower MWD. The polymer formed at − 20 °C showed $\bar{M}_w/\bar{M}_n$ value of 1.14 though the fraction of the enol unit increased to 0.26. This probably



Scheme 2.

Table 3
Polymerization of EA and *n*-BuA with *t*-BuLi/EtAl(ODBP)$_2$ in toluene at various temperatures

Monomer	Temperature (°C)	Time (h)	Yield (%)	$\bar{M}_n$		$\bar{M}_w/\bar{M}_n$[a]	Tacticity[b] (%)		*N*(enol)[c]
				Calcd	NMR		*m*	*r*	
EA	−60	0.5	100	2600	3200	1.10	24	76	0.03
	−40	0.5	100	2600	3200	1.15	40	60	0.07
	−20	0.5	99	2500	3400	1.61	45	55	0.24
	0	0.5	98	2500	6000	1.70	44	56	0.64
n-BuA	−78	48	100	6500	7300	1.23	28	72	0
	−60	0.5	97	6300	7600	1.14	37	63	0.08
	−40	0.5	100	6500	6800	1.11	44	56	0.10
	−20	0.5	100	6500	9300	1.14	47	53	0.26

EA 2.5 mmol, *n*-BuA 5 mmol, *t*-BuLi 0.1 mmol, EtAl(ODBP)$_2$ 0.5 mmol, toluene 5 ml.

[a] Determined by SEC.

[b] Determined by ^{1}H NMR.

[c] The amount of enol unit per chain determined from the peak intensities of the enol proton, *I*(enol), and *t*-butyl group signal, *I*(*t*-Bu); $N(\text{enol}) = [I(\text{enol})/I(t\text{-Bu})] \times 9$.

means that a part of the enol units is formed after the polymerization is completed. The difference in the structure of the ester alkyl group of acrylate affects the coordination of EtAl(ODBP)$_2$ to the propagating species and changes the degree of backbiting reaction during the propagation.

3.4. Tacticity of the polyacrylates

Tacticity of the polymers was determined by the ^{1}H NMR spectra. The signals of the main-chain methylene protons in the range 1.4–2.0 ppm clearly exhibit the splittings due to the diad tacticity as shown in Fig. 2. EtAl(ODBP)$_2$ gives the polyacrylates with higher fractions of *racemo* diad than MeAl(ODBP)$_2$ (Table 1). Polymerizations with *t*-BuLi in the absence of the aluminum phenoxides give isotactic polymers in non-living manner [30] while those in the presence of the phenoxides provide syndiotactic-rich polymers in a living manner (Table 1). The results suggest that the coordination of the phenoxide, particularly EtAl(ODBP)$_2$, gives *racemo* selectivity to the propagating species and also prevent them from backbiting reaction.

As mentioned in the previous sections, the fractions of *racemo* diads increased with decrease in the polymerization temperature and monomer concentration (Tables 2 and 3). A similar tendency is observed in the anionic and radical polymerization of methacrylates [31]. Particularly, the polymerizations of methyl and ethyl methacrylates with *t*-BuLi/EtAl(ODBP)$_2$ in toluene at −78 °C give syndiotactic polymers while those with *t*-BuLi/MeAl(ODBP)$_2$ give heterotactic polymers [21]. In both stereospecific polymerizations, the coordination of the aluminum compound to the propagating chain end and to the monomers are considered to be important factors for the stereocontrol of the polymerization. The results suggest that the steric demand near the aluminum center of the Lewis acids is critical for the stereoregulation in the polymerizations of methacrylate and acrylate. The increase of syndiotacticity at lower temperature suggests that the more strongly coordinates the phenoxide with the propagating species, the better controlled the stereospecificity is. Further investigation is now under way to extend the present results to higher level of stereoregulation without loosing the living nature of the polymerization.

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