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Living Anionic Polymerization of *N,N*-Dimethylacrylamide and Copolymerization with Methyl Methacrylate in the presence of Bulky Aluminum Phenoxide

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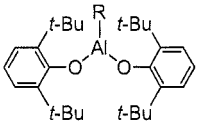
Summary

Anionic polymerization of *N,N*-dimethylacrylamide (DMAAm) was examined in toluene with *tert*-butyllithium (*t*-BuLi)/bis(2,6-di-*tert*-butylphenoxy)ethylaluminum [EtAl(ODBP)$_2$]. In the presence of excess amounts of the aluminum compound over *t*-BuLi, the polymerization proceeded in a living manner. Sequential block copolymerization of DMAAm and methyl methacrylate (MMA) with the same initiator underwent smoothly in both directions, that is, polymerization of MMA by poly(DMAAm) living anions and *vice versa*. Moreover, the copolymerization of an equimolar mixture of DMAAm and MMA proceeded in a monomer-selective manner to give a block-like copolymer; DMAAm was polymerized first followed by MMA polymerization through selective activation of DMAAm by the coordination of EtAl(ODBP)$_2$.

Introduction

In a recent decade, several research groups have studied anionic polymerizations of *N,N*-disubstituted acrylamides [1-7]. Nakahama *et al.* have reported the stereospecific anionic polymerizations of *N,N*-dimethyl- and *N,N*-diethylacrylamides in tetrahydrofuran (THF) by using combinations of proper alkali metal alkyl initiators with diethylzinc or triethylborane additives [3-7].

We have found anionic living polymerizations of (meth)acrylates with combinations of *tert*-butyllithium (*t*-BuLi) and bulky aluminum phenoxides, bis(2,6-di-*tert*-butylphenoxy)alkylaluminum [RAl(ODBP)$_2$, (R = Me, Et, Pr: Scheme 1)], in toluene at low temperatures [8-14]. In particular, one-shot feeding anionic copolymerizations of acrylates and methacrylates proceed in a monomer-selective and living manner at low temperatures to give block-like copolymers [12,13].



R = CH_3 : MeAl(ODBP)$_2$
CH_3CH_2 : EtAl(ODBP)$_2$
$CH_3CH_2CH_2$: Pr(ODBP)$_2$

Scheme 1. Structure of RAl(ODBP)$_2$

In this paper, with the aim of extending the capacity of the initiator system, anionic polymerization of DMAAm as well as copolymerization with MMA were investigated by using above mentioned initiator systems in toluene. *N,N*-dialkylacrylamides and methacrylates usually exhibit much larger reactivity difference in anionic copolymerization as compared with radical copolymerization. Nevertheless, the block copolymerization from poly(DMAAm) anions to MMA and that from PMMA anions to DMAAm proceeded successfully. Moreover, a simple copolymerization of the monomer mixture produced a block-like copolymer through preferential monomer activation by coordination with $RAl(ODBP)_2$.

Experimental

Materials

DMAAm (Kohjin) was purified by drying over CaH_2 and distillation under reduced nitrogen pressure (53.8°C/5.0 Torr), and stored with Molecular Sieves (MS) 4A. MMA was purified by distillation under reduced nitrogen pressure, and dried over CaH_2. Toluene and heptane were purified in the usual manner, and mixed with a small amount of *n*-butyllithium. MMA, toluene, and heptane were distilled under high vacuum just before use. *t*-BuLi in pentane (Aldrich) was used as a heptane solution by replacing the solvent under vacuum. The concentration was determined by titration with 2-butanol using *o*-phenanthrolin as an indicator [15]. $RAl(ODBP)_2$ (R = Me, Et, Pr) were prepared from the reaction of 2,6-di-*tert*-butylphenol and the corresponding trialkylaluminums in toluene at room temperature [10, 16]. Recrystallizations of $RAl(ODBP)_2$ were carried out for several times from heptane (R = Me, Et) or toluene (R = Pr) at −30°C.

Polymerization

All the polymerizations were carried out in glass ampoules filled with dried nitrogen passed through MS 4A cooled at −78°C. *t*-BuLi solution was added to $RAl(ODBP)_2$ in toluene at polymerization temperature. The polymerization reaction was initiated by adding the monomer slowly to the mixture at polymerization temperature, and quenched by adding methanol at the polymerization temperature. For the polymerization of DMAAm, the reaction mixture was poured into a large amount of diethyl ether and the precipitated polymer was collected by centrifugation, washed with the ether. For the copolymerization, the reaction mixture was poured into a large amount of hexane, and the precipitated copolymer was collected by centrifugation. Collected homopolymers and copolymers were dried under high vacuum at 40°C.

Measurements

Number-average molecular weight (M_n) and molecular weight distribution (MWD) were determined by size exclusion chromatography (SEC) using a PU-980 chromatograph (JASCO) equipped with SEC columns PLgel Mixed-C (Polymer Laboratories: 7.5 mm × 300 mm × 2, maximum porosity 3×10^6), and an RI-930 detector (JASCO) using $CHCl_3$ as an eluent at 40°C at the flow rate of 0.8 mL/min. SEC chromatograms were calibrated against standard PMMA samples (Shodex).

^{1}H and ^{13}C NMR spectra of the homopolymers and copolymers were measured in 1,1,1,3,3,3-hexafluoro-propan-2-ol (HFIP) / C_6D_6 (95/5, v/v) at 55°C by using a Unity-Inova 500 spectrometer (Varian). The solvent peaks were used as internal standards as 4.33 ppm [^{1}H, $(CF_3)_2$**C**H**O**H] and 128.0 ppm (^{13}C, $\mathbf{C}_6\mathbf{D}_6$), respectively. ^{13}C NMR measurements of the monomers in the presence or absence of EtAl(ODBP)$_2$ in toluene-d_8 at 0°C were performed by using an AL-400 spectrometer (JEOL). The CD_3 signal of the solvent was used as an internal standard as 20.4 ppm.

Results and discussion

Polymerization of DMAAm with t-BuLi/ bis(2,6-di-tert-butylphenoxy)alkylaluminum [RAl(ODBP)$_2$]

Table 1 summarizes the results of the anionic polymerizations of DMAAm in toluene with *t*-BuLi/RAl(ODBP)$_2$. Though the polymerization with *t*-BuLi alone at 0°C gave a polymer quantitatively (Run 1), MWD of the polymer was very broad. In contrast, when *t*-BuLi was used in combination with excess amounts of EtAl(ODBP)$_2$, the polymerizations gave narrow MWD polymers quantitatively (Runs 3-6). When EtAl(ODBP)$_2$ was used 5 folds to *t*-BuLi, the MWD of the obtained polymer became narrowest. These results suggest that EtAl(ODBP)$_2$ is effective for the control of the polymerization of DMAAm as in the cases of polymerizations of acrylates [12-14] and methacrylates [8-11]. The polymerization at –20°C for 24 hr gave the polymer almost quantitatively (Run 9), but no polymer was obtained at –40°C (Run 10). The MWD's of the polymers obtained at 20°C (Run 8) and 40°C (Run 7) were broader, suggesting occurrence of some side reactions such as back-biting termination. When MeAl(ODBP)$_2$ was used in place of EtAl(ODBP)$_2$, the MWD's of the obtained polymers became broader than those formed with EtAl(ODBP)$_2$, though the temperature dependences of polymer yields and MWD's were similar. The better control of polymerization by EtAl(ODBP)$_2$ over MeAl(ODBP)$_2$, has been reported for ethyl and butyl acrylates [14]. Use of PrAl(ODBP)$_2$ did not improve the MWD of the polymer (Run 14).

Figure 1 shows the SEC curves of poly(DMAAm) prepared with *t*-BuLi/EtAl(ODBP)$_2$ (1/5, mole ratio) in toluene at 0°C. When a fresh monomer was charged into the system where the first batch of the monomer was consumed (dotted line), the added monomer was smoothly polymerized, and *Mn* of the polymers increased further (solid line). These results indicate the living nature of this polymerization system.

Diad tacticity of poly(DMAAm) was estimated from CH_2 proton NMR signals [1]. The polymers obtained with *t*-BuLi/EtAl(ODBP)$_2$ and *t*-BuLi/PrAl(ODBP)$_2$ were slightly rich in racemo (*r*) diad and those with *t*-BuLi/MeAl(ODBP)$_2$ were slightly rich in meso (*m*) diad. Thus, the alkyl groups in the aluminum bisphenoxides apparently affect the stereospecificity but at a limited level.

Table 1. Polymerization of DMAAm with *t*-BuLi / $RAl(ODBP)_2$ in toluene [a]

Run	R	Al/Li	Temp/°C	Time/hr	Yield/%	$Mn/10^3$	Mw/Mn	Tacticity/%	
								m	*r*
1	–	None	0	2	100	105	9.30	84	16
2	Et	1	0	2	81	8.60	5.02	62	38
3	Et	3	0	12	100	5.56	1.20	48	52
4	Et	5	0	3	100	5.22	1.13	42	58
5	Et	5	0	12	100	5.21	1.12	42	58
6	Et	10	0	12	97	5.35	1.15	41	59
7	Et	5	40	3	55	5.67	1.26	40	60
8	Et	5	20	3	100	5.03	1.41	39	61
9	Et	5	–20	24	93	4.13	1.18	44	56
10	Et	5	–40	48	0	–	–	–	–
11	Me	5	0	3	100	7.57	1.35	62	38
12	Me	5	–20	24	100	7.36	1.33	60	40
13	Me	5	–40	48	0	–	–	–	–
14	Pr	5	0	12	100	5.56	1.31	41	59

a DMAAm 10 mmol, *t*-BuLi 0.2 mmol, toluene 10 mL.

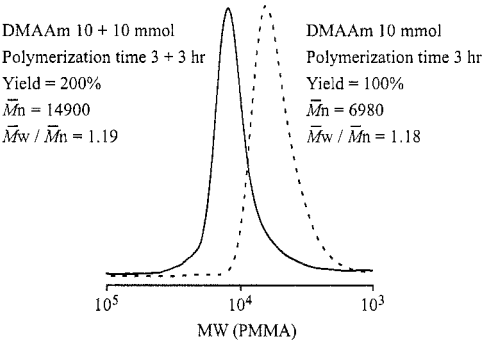


Figure 1. SEC curves of poly(DMAAm) prepared with *t*-BuLi/$EtAl(ODBP)_2$ in toluene at 0°C: *t*-BuLi 0.2 mmol, $EtAl(ODBP)_2$ 1.0 mmol, toluene 10 mL.

Copolymerization of DMAAm and MMA with t-BuLi/ $EtAl(ODBP)_2$

Sequential block copolymerizations of DMAAm and MMA with *t*-BuLi/$EtAl(ODBP)_2$ (1/5, mole ratio) were examined in toluene at 0°C in two different ways; the polymerization of MMA by poly(DMAAm) anions and the polymerization of DMAAm by PMMA anions. Figure 2 shows the SEC curves of the obtained block copolymers together with those of the prepolymers of DMAAm and MMA. As shown in Figures 2a and 2c, SEC curves of the obtained copolymers exhibited unimodal peaks shifted from the prepolymer to higher molecular weight side. The results indicate that both of poly(DMAAm) and PMMA anions initiated the counterpart monomers.

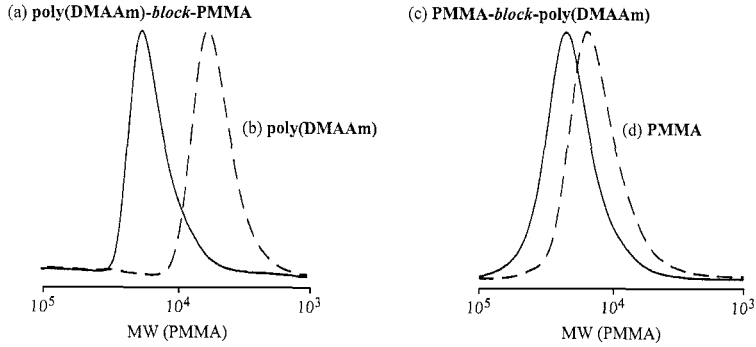


Figure 2. SEC curves of poly(DMAAm)-*block*-PMMA (a), poly(DMAAm) (b), PMMA-*block*-poly(DMAAm) (c), and PMMA (d): DMAAm and MMA 10 mmol, *t*-BuLi 0.2 mmol, $EtAl(ODBP)_2$ 1.0 mmol, toluene 10 mL, temperature 0°C, polymerization time MMA 12 hr, DMAAm 3 hr, yields 100% in all cases.

Figure 3a shows time conversion plots of the one-shot feeding copolymerization of an equimolar mixture of DMAAm and MMA with *t*-BuLi/$EtAl(ODBP)_2$ in toluene at 0°C. The results indicate that DMAAm polymerized first followed by the MMA consumption in the later stage of the copolymerization while MWD of the products were kept narrow. Figure 3b displays SEC curves of the copolymers formed at 1 hr, 3 hr, and 12 hr. The smooth shift of the unimodal peak suggest that almost all poly(DMAAm) anions grow into the block-like copolymer in a living manner. The copolymerization of DMAAm and MMA with *t*-BuLi alone ($[DMAAm]_0/[MMA]_0/[t\text{-BuLi}]_0$= 25/25/1, mole ratio), gave a copolymer with broader MWD (M_w/M_n = 3.14) with the conversions of DMAAm 100% and that of MMA 28%. The results suggest that the addition of $EtAl(ODBP)_2$ is inevitable for the successful one-shot copolymerization of these monomers.

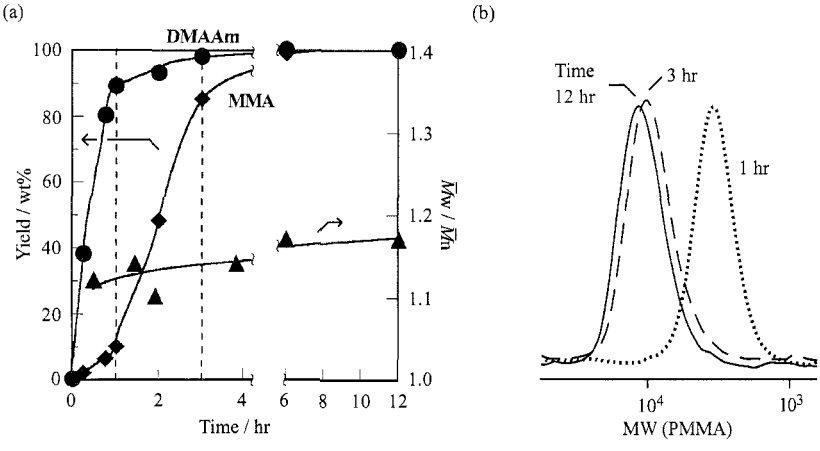


Figure 3. Time conversion plots of yield and M_w/M_n for the one-shot feeding copolymerization of DMAAm and MMA in toluene at 0°C (a) and SEC curves of the copolymers obtained for 1, 3, and 12 hr (b). [DMAAm and MMA 5 mmol, *t*-BuLi 0.2 mmol, $EtAl(ODBP)_2$ 1.0 mmol, toluene 10 mL]

Figure 4 shows the ^{13}C NMR spectra of carbonyl carbons of the copolymers obtained by one-shot feeding copolymerization for 12 hr (*cf.* Figure 3), together with those of sequentially copolymerization, poly(DMAAm)-*block*-PMMA (*cf.* Figure 2a). The spectrum of the one-shot feeding copolymer (Figure 4a) was similar to that of the sequentially prepared block copolymer (Figure 4b), indicating the formation of the block-like copolymer by the one-shot feeding copolymerization.

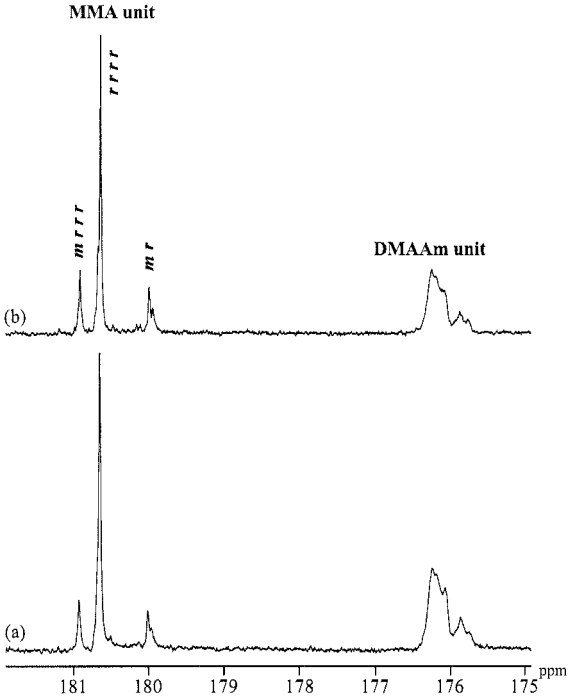


Figure 4. 125 MHz ^{13}C NMR spectra of carbonyl carbons in the copolymers of DMAAm and MMA, measured in HFIP/C_6D_6 (95/5) at 55°C. Copolymer (a) was obtained by one-shot feeding copolymerization for 12 hr (*cf.* Figure 3) and copolymer (b) was obtained by sequential copolymerization (*cf.* Figure 2a).

As depicted by the results of the sequential copolymerizations (*cf.* Figure 2), both of DMAAm and MMA anions are able to add the counterpart monomers. Nevertheless, the copolymerization proceeds with high monomer selectivity. In the aluminum Lewis acid-assisted anionic polymerizations of carbonyl-containing vinyl monomers, it has been suggested that the coordination of the aluminum compounds to the monomers enhances the reactivity of the monomers toward nucleophilic propagating species [17]. To examine the selectivity of monomer coordination by $EtAl(ODBP)_2$, ^{13}C NMR spectra of DMAAm and/or MMA in the presence or absence of $EtAl(ODBP)_2$ were measured in toluene-d_8 at 0°C. Carbonyl carbons of DMAAm and MMA showed signals at 165.0 and 167.0 ppm, respectively (Figure 5a). In the spectrum of DMAAm/$EtAl(ODBP)_2$ (1/1, mole ratio) (Figure 5b), a part of C=O signals of DMAAm shifted to 168.6 ppm due to the coordination of $EtAl(ODBP)_2$. In the spectrum of MMA/$EtAl(ODBP)_2$ (1/1, mole ratio) (Figure 5c), all the C=O signals of MMA shifted to 173.9 ppm by the coordination of $EtAl(ODBP)_2$. When the ^{13}C NMR

spectra of DMAAm/MMA/EtAl(ODBP)$_2$ (1/1/1, mole ratio) were measured (Figure 5d), the signals due to the coordinated DMAAm and free MMA were observed. The results suggest that the selective coordination and activation of DMAAm by EtAl(ODBP)$_2$, which as depicted in Scheme 2, may play a key role in the monomer-selective living copolymerization of DMAAm and MMA.

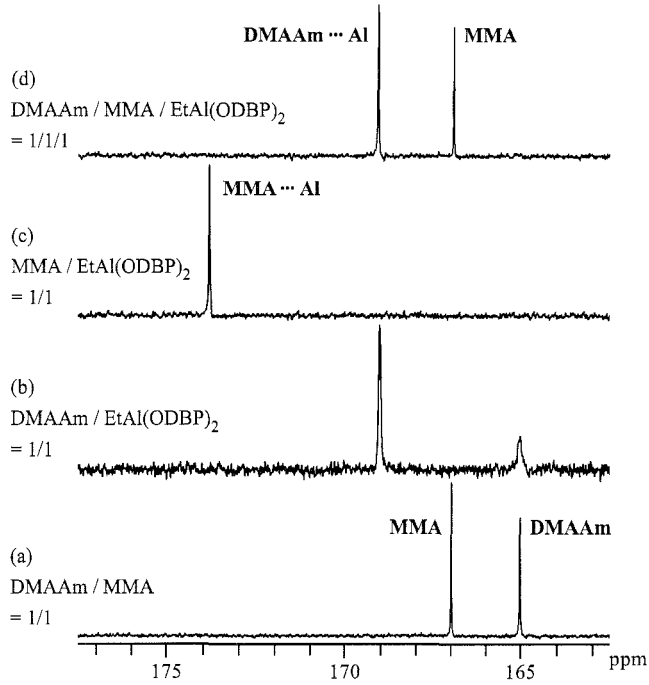
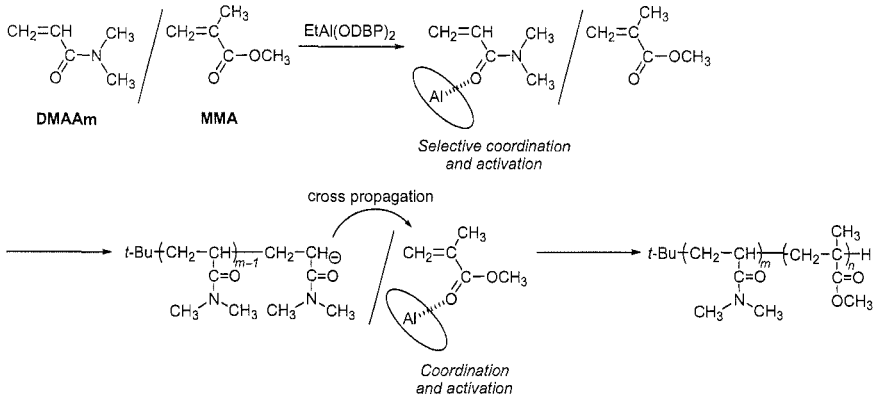


Figure 5. 100 MHz ^{13}C NMR spectra of carbonyl carbons of DMAAm/MMA (a), DMAAm (b) or MMA (c) /EtAl(ODBP)$_2$ (1/1, mole ratio), and DMAAm/MMA/EtAl(ODBP)$_2$ (1/1/1, mole ratio) (d), measured in toluene-d_8 at 0°C.



Scheme 2. Monomer-selective copolymerization of DMAAm and MMA through preferential coordination and activation of DMAAm by EtAl(ODBP)$_2$

Conclusions

Anionic polymerization of DMAAm with *t*-BuLi in toluene was successfully controlled by the addition of the bulky aluminum phenoxides to provide the polymerization systems with a living nature. Sequential copolymerizations of DMAAm and MMA with *t*-BuLi/EtAl(ODBP)$_2$ (1/5, mole ratio) in toluene underwent smoothly in both directions to give block copolymers. Moreover, the one-shot feeding copolymerization of DMAAm and MMA with this initiating system proceeded in a monomer-selective manner to give a block-like copolymer with narrow MWD; DMAAm polymerized first followed by the MMA consumption in the later stage of copolymerization, through preferential coordination and activation of DMAAm by EtAl(ODBP)$_2$.

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