Organocuprates Initiated Anionic Living Polymerization of *tert*-Butyl Methacrylate

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ABSTRACT: We report organocuprates initiated anionic polymerizations of various α,β-unsaturated ester monomers in tetrahydrofuran (THF) under various conditions. It was found that catalysts prepared by reaction of CuI with methyllithium (MeLi) very effectively cause the polymerization of meth(acrylate) monomers. At molar ratio of [MeLi] to [CuI] higher than 2 the polymerization of *t*-butyl methacrylate (TBMA) proceeded quantitatively in THF at 0—45°C to afford high molecular weight poly(*t*-butyl methacrylate) (PTBMA) with extremely narrow molecular weight distribution (MWD) ($M_w/M_n = 1.0_5$— 1.1_7). Initiator efficiency was less than 10% and highest at about [MeLi]/[CuI] = 4.0. The post-polymerization proved the livingness of the polymerization of TBMA caused by lithium methylcuprate in THF at 0 °C. The active species for the polymerization of TBMA was thought to be higher cuprate, such as $Li_2Cu(CH_3)_3$. For the polymerizations of other methacrylates and *t*-butyl acrylate lithium methylcuprate initiators effectively afforded the polymers but with very broad MWD.
KEY WORDS Organocuprates / Living Polymerization / *tert*-Butyl Methacrylate /

Organocuprates are appreciably used in synthetic organic chemistry because of their ability to give very high regioselectivity in conjugate addition reactions to various α,β-unsaturated esters and ketones.[1] Their use as an initiator in the polymerization of analogous vinylic monomers is, thus, of interest.

Organocopper compounds (RCu), prepared by reaction of CuI with stoichiometric amount of alkyllithium, have been reported as polymerization initiators. The first work on the polymerization of vinyl monomers was reported by Bawn and Whitby[2] in 1960, who studied free-radical polymerizations of styrene and acrylonitrile in the presence of RCu(I) as a catalyst. Ikariya and Yamamoto[3] reported that an isolated complex of methyl(trialkylphosphine)copper(I) caused the polymerizations of acrylonitrile and methyl methacrylate (MMA). Lithium organocuprates (R_2CuLi), prepared by the reactions of CuI and two equivalents of alkyllithium, are normally used in stoichiometric amounts in addition reaction, while polymeric products and low molecular weight oligomers have been found as by-products. However, there are few reports where cuprates have been consciously used as ionic polymerization initiators.[4,5] Saegusa *et al.* reported vinyl polymerization of acrylonitrile, methyl acrylate and MMA using cyclopentadienylcopper(I) complexes[6] and Cu_2O-isonitrile system.[7] It was shown by Grigonis *et al.*[8] that benzoxyethyl methacrylate polymerization initiated with lithium di-*n*-butylcuprate ((n-Bu)$_2$CuLi) in toluene affords highly isotactic polymers (5% syndiotactic, 15% heterotactic, and 80% isotactic triad contents). Han *et al.*[9] reported (n-Bu)$_2$CuLi to be an effective initiator for α,β-unsaturated monomers, MMA, acrylonitrile, acrolein, and *N*-acryloylpyrrolidone to afford highly isotactic polymers in toluene. They, however, did not report any evidence related to the molecular weight distribution (MWD) of the polymers and the possibility that the reaction may proceed in a living manner. Day *et al.*[10] demonstrated that the polymerizations of MMA initiated with lithium
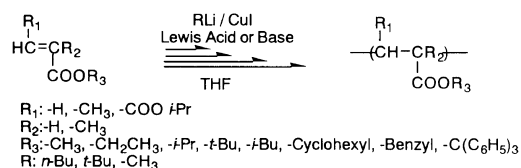
n-butylcyanocuprate and (n-Bu)$_2$CuLi at -78°C proceed in a living manner to afford poly(methyl methacrylate) (PMMA) but with very broad MWD ($M_w/M_n = 1.5$—1.8). The initiator efficiency (f) was found to be less than 4%.

Dimonie *et al.*[11] have recently carried out a kinetic study on the polymerization of MMA using several types of organocuprates. They prepared syndiotactic-rich PMMA of $M_w/M_n = 1.2$—2.0 at -30——10°C, with relatively high f such as 30—100%. We became interested independently in the fact that Lewis acid-mediated organocopper reagents (n-Bu$_2$CuLi/AlCl$_3$) reacted regioselectively in 1,4-addition with an electron deficient olefin, diethyl fumarate.[12] This monomer could not be polymerized using anionic initiators.[13] We thought that by optimizing the conditions of the polymerization with organocuprates as an initiator, it might be possible to develop a living polymerization of various α,β-unsaturated esters, including methacrylates, acrylates, fumarates, and crotonates.[14] The reaction scheme is shown in Scheme 1. We first investigated the organocuprate initiated polymerization of *t*-butyl methacrylate (TBMA), and applied it to the polymerization of several types of α,β-unsaturated esters.

EXPERIMENTAL

Materials

TBMA and *t*-butyl acrylate (TBA) were supplied from Toagosei Co., Ltd. and diisopropyl fumarate was a gift from NOF Co., Ltd. and MMA, ethyl, isopropyl, iso-

R_1: -H, -CH$_3$, -COO *i*Pr
R_2: -H, -CH$_3$
R_3: -CH$_3$, -CH$_2$CH$_3$, -*i*Pr, -*t*-Bu, -*i*-Bu, -Cyclohexyl, -Benzyl, -C(C$_6$H$_5$)$_3$
R: *n*-Bu, *t*-Bu, -CH$_3$

Scheme 1.

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butyl, cyclohexyl, and benzyl methacrylates, methyl crotonate, diethyl fumarate, and styrene were purchased from Kishida Chemical Co., Ltd. The ester monomers were washed with 5% aq solution of sodium hydrogen sulfite, 5% aq sodium hydroxide, followed by 20% aq sodium chloride to remove hydroquinone inhibitor. The monomers were dried with sodium sulfate overnight and distilled from calcium hydride under a reduced pressure immediately prior to use. Tetrahydrofuran (THF) was refluxed and distilled from the sodium benzophenone solution. Copper iodide (Kojundo Kagaku) was washed by freshly distilled THF with a soxhlet extractor. Methyl-, n-butyl-, t-butyllithium (Aldrich), lithium 2-thienylcyanocuprate (Aldrich), and dilithium methyl-2-cyanocuprate (Aldrich) were used as received. Other chemicals were purified according to standard purification procedures.

Synthesis of Lithium Organocuprates and Polymerization

The experiments were carried out in a 50 mL three-neck reactor fitted with septums. The required amount of CuI was first introduced into the reactor. The reactor was vacuum-dried for 3 h at room temperature and filled with argon. Adequate equivalents of alkyllithium in hexane solution were added slowly to CuI in THF at 0°C. The mixture was maintained at 0°C for 1 h. The polymerizations were carried out by adding monomers to the reaction mixture at various temperatures (-78—$+45$°C) for 30 min. After 30 min, the polymerization was quenched with methanol, and the reaction mixture was poured into a large excess of methanol containing water to precipitate the polymer. The polymers collected by filtration were dried in vacuum. In post-polymerization, by reaction of TBMA and lithium methylcuprate in THF at 0°C for 30 min, the prepolymer of TBMA was quantitatively prepared and an aliquot was sampled out for characterization. To the residual reaction mixture at 0°C, the second feed of TBMA was added and reacted for another 30 min to complete the further polymerization. Block copolymerizations of TBMA with MMA or

TBA were performed in a similar manner. The polymerizations were also carried out under high-vacuum in an all-glass apparatus equipped with the break-seals.[15]

Measurements

Size exclusion chromatography (SEC) for the characterization of molecular weight and its distribution was conducted at 40°C with JASCO PU980 as a pump, JASCO RI-930 as a refractive index detector, and Shodex A-803 + A-804 and A-804 + A-805 as columns. Elution volume was calibrated with a series of polystyrene (Tosoh Co., Japan) standards. ^{1}H NMR spectra were recorded on a JEOL JNM-GX 270 MHz FT-NMR spectrometer in CDCl$_3$ at room temperature.

RESULTS AND DISCUSSION

Influence of Types of Alkyllithium

The results of the polymerization of TBMA using various alkylcuprates are listed in Table I. Lithium homocuprates as initiators caused the polymerization to afford quantitatively poly(t-butyl methacrylate) (PTBMA), irrespective of the alkyllithium species used (runs 1—3). In contrast, no polymerization of TBMA occurred when lithium 2-thienylcyanocuprate (LTCC) was used as initiator (run 4). The initiator efficiency (f), calculated assuming lithium dialkylcuprate (R$_2$CuLi) as an active species, and MWD of resulting PTBMA strongly depended on the alkyllithium. The value of f was relatively high (40—60%) when using lithium butylcuprates (runs 1, 2), but considerably low (3.0% at 0°C) when using lithium methylcuprate (run 3). In the latter system MWD was significantly narrow ($M_w/M_n = 1.1_3$). The polymerization results using (n-Bu)$_2$CuLi were almost consistent with those reported by Day et al.,[10] who studied the polymerization of MMA. We note here in particular that the methyllithium-CuI initiator systems gave PTBMA with a narrow MWD and investigated various conditions to optimize the polymerization.

Table I. Polymerizations of TBMA using organocuprates prepared from various alkyllithiums[a]

Run	RLi	[CuI]/mmol	[RLi]/mmol	[RLi]/[CuI]	[TBMA]/mmol	Temp/°C	Conv./%	M_n[b]/10^3	M_w/M_n[b]	f/%[c]
1	n-BuLi	0.47	0.99	2.0	9.37	0	97.7	7.5	1.5$_9$	3$_7$
2	t-BuLi	0.42	0.85	2.0	18.0	-78	98.5	9.4	1.3$_2$	6$_4$
3	MeLi	0.47	1.05	2.2	9.37	0	100	99	1.1$_3$	2$_9$
4	LTCC[d]	—	—	—	9.37	0	0	—	—	0

[a] Polymerizations were carried out in 10 mL THF for 30 min. [b] Determined by SEC calibrated with a series of polystyrene standards. [c] Initiator efficiency calculated by the equation, $f(\%) = (W \times \text{Conv.}(\%))/([\text{CuI}] \times M_n)$, where W is weight of TBMA in feed. [d] Lithium 2-thienylcyanocuprate, 0.42 mmol.

Table II. Polymerizations of TBMA using lithium methylcuprates at various temperatures[a]

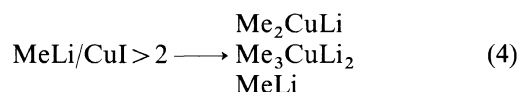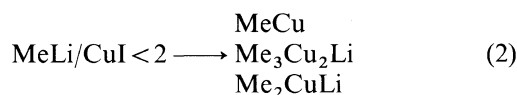| Run	[CuI]/mmol	[MeLi]/mmol	[RLi]/[CuI]	[TBMA]/mmol	THF/mL	Temp/°C	Conv./%	M_n[b]/10^3	M_w/M_n[b]	f/%[c]
1	0.47	0.94	2.0	9.14	10.0	-78	0	—	—	0
2	0.47	1.93	4.1	9.14	10.0	-78	0	—	—	0
3	0.47	1.93	4.1	9.14	10.0	-48	4.5	14	1.9$_6$	0.8$_9$
4	0.47	2.0	4.0	7.92	10.0	-21	100	73	1.3$_0$	3$_3$
5	0.47	1.88	4.0	9.14	10.0	0	100	44	1.0$_5$	6$_3$
6	0.47	1.93	4.1	9.14	10.0	22	100	32	1.0$_7$	8$_6$
7	0.49	2.10	4.3	12.5	20.0	45	99	76	1.1$_7$	4$_7$

[a] Polymerizations were carried out for 30 min. [b] Determined by SEC calibrated with a series of polystyrene standards. [c] Initiator efficiency calculated by the equation, $f(\%) = (W \times \text{Conv.}(\%)) / ([\text{CuI}] \times M_n)$, where W is weight of TBMA in feed.

Effects of Polymerization Temperature

Table II shows the polymerization results of TBMA using lithium methylcuprates at various temperatures. The polymerization of TBMA did not occur at $-78°C$ (runs 1, 2) but did occur slowly at $-48°C$ to afford PTBMA with very broad MWD ($M_w/M_n = 1.9_6$) (run 3). At $-21°C$, the polymerization proceeded to quantitatively afford PTBMA but with relatively broad MWD ($M_w/M_n = 1.3_0$). It should be noted, however, that above $0°C$ the polymerizations afford PTBMA with very narrow MWDs (runs 5—7) and the initiator efficiency increases with temperature up to $22°C$. Even at $45°C$, the polymerization proceeded quantitatively to afford the polymer with a relatively narrow MWD ($M_w/M_n = 1.1_7$) (run 7).[16,17]

Influence of the Ratio of [MeLi] to [CuI]

Ashby et al.[18,19] reported that the composition of lithium methylcuprates varies with solvent, temperature, and molar ratio of methyllithium to CuI, as follows:

$$MeLi/CuI = 1 \longrightarrow MeCu \tag{1}$$

$$MeLi/CuI < 2 \longrightarrow \begin{array}{c} MeCu \\ Me_3Cu_2Li \\ Me_2CuLi \end{array} \tag{2}$$

$$MeLi/CuI = 2 \longrightarrow Me_2CuI \tag{3}$$

$$MeLi/CuI > 2 \longrightarrow \begin{array}{c} Me_2CuLi \\ Me_3CuLi_2 \\ MeLi \end{array} \tag{4}$$

The reactivity of these lithium methylcuprates for alkyl halides decreases in the order, $RLi > R_3CuLi_2 > R_2CuLi > R_3Cu_2Li > RCu$, where R is an alkyl group.[18,19] Table III shows the polymerization results of TBMA using lithium methylcuprates prepared at various mole ratios of methyllithium to CuI at $0°C$, together with the results of the control experiments using MeLi and 1,1-diphenyl-3-methylpentyllithium (DPPL) as initiator. At the molar ratio, [MeLi]/[CuI] higher than 2, the polymerizations of TBMA quantitatively afforded PTBMAs with very narrow MWDs (runs 4—7). The initiator efficiency increased and MWD correspondingly decreased with molar ratio up to about 4. Compared with the polymerization results using MeLi (run 8) and DPPL (run 9) at $0°C$, one might reasonably expect

relatively high regioselectivity and stability of the lithium methylcuprates active chain-end in the polymerization at $0°C$.

In [MeLi]/[CuI] < 2.0, there may exist three methylcuprates in THF, MeCu, Me_3Cu_2Li, and Me_2CuLi. Since MeCu does not cause the polymerization of TBMA (runs 1, 2), Me_3Cu_2Li and Me_2CuLi may cause the polymerization. However, initiator efficiency was very low ($f = 0.69\%$) and the polymer with a broad MWD was obtained (run 3). Therefore, Me_3Cu_2Li and Me_2CuLi species are thought not so good to control the polymerization of TBMA in THF at $0°C$

At [MeLi]/[CuI] > 2.0, there are three active species, Me_2CuLi, Me_3CuLi_2, and MeLi in the following equilibrium.[18]

$$1/4(MeLi)_4 + 1/2(Me_2CuLi)_2 \underset{}{\overset{K}{\rightleftharpoons}} Me_3CuLi_2 \tag{5}$$

Ashby et al.[18,19] determined, using NMR, the equilibrium constant, K to be $0.12\,L\,mol^{-1}$ in THF at $-5°C$. Indeed, we confirmed the existence of free methyllithium in [MeLi]/[CuI] > 2.0 by Gilman test.[20] Since MeLi itself was not a good active species (run 8) in THF at $0°C$, we suppose that the active species of the polymerization of TBMA is Me_3CuLi_2. According to Ashby's formulation, we calculated the concentration of Me_3CuLi_2 and thereby, effective initiator efficiency (f_{eff}), based on the assumption that Me_3CuLi_2 is an active species for the polymerization of TBMA at $0°C$. The values of f_{eff} are listed in Table III. Interestingly, f_{eff} changed very little with methyllithium concentration to lie around $55 \pm 9\%$, except for run 7. More data are needed to conclude what is actually an active species of the polymerization of TBMA and why f_{eff} decreases at [MeLi]/[CuI] higher than 6.

Since it is of great importance to estimate the stability of the active chain end for proof of the livingness of polymerization, post-polymerization was carried out. After the first polymerization of TBMA with lithium methylcuprate ([MeLi]/[CuI] $= 4.0$) in THF at $0°C$ for 30 min, the second feed of TBMA was added to the reaction mixture and reacted for another 30 min to complete the polymerization. The postpolymer was quantitatively obtained after quenching. From the SEC chromatogram of the postpolymer shown in Figure 1, the peak of the prepolymer disappeared completely and

Table III. Polymerizations of TBMA using lithium methylcuprates prepared at various [MeLi]/[CuI] ratios at $0°C$[a]

| Run	[CuI]/mmol	[MeLi]/mmol	[RLi]/[CuI]	[TBMA]/mmol	Conv./%	$M_n^b/10^3$	M_w/M_n^b	$f/\%^c$	$f_{eff.}/\%^d$
1	0.47	0.40	0.85	9.14	0	—	—	0	—
2	0.47	0.53	1.1	9.14	0	—	—	0	—
3	0.47	0.76	1.62	13.15	84.2	48_5	1.3_4	0.6_9	—
4	0.47	1.05	2.2	9.37	100	99	1.1_3	$2._9$	4_6
5	0.47	1.45	3.1	9.14	100	72	1.1_0	$3._9$	6_2
6	0.47	1.88	4.0	9.14	100	44	1.0_5	$6._3$	5_6
7	0.47	2.89	6.1	9.14	100	67	1.1_2	$4._2$	$5._7$
8[e]	0.0	0.43 (MeLi)	—	9.14	7.3	47_3	1.5_0	0.0_5	—
9[e]	0.0	1.30 (DPPL)	—	9.14	98	3.4	1.4_6	2_9	—

[a] Polymerizations were carried out in 10 mL THF for 30 min. [b] Determined by SEC calibrated with polystyrene standards. [c] Initiator efficiency calculated by the equation, $f(\%) = (W \times Conv.(\%))/([CuI] \times M_n)$, where W is weight of TBMA in feed. [d] Effective initiator efficiency calculated by the equation, $f_{eff}(\%) = (W \times Conv.(\%))/([Me_3CuLi_2] \times M_n)$, where $[Me_3CuLi_2]$ was calculated using equilibrium constant, $K = 0.12\,L\,mol^{-1}$ in THF at $-5°C$, reported by Ashby and Watkins.[18] [e] Control experiments with MeLi and 1,1-diphenyl-3-methylpentyllithium (DPPL) as initiator in THF at $0°C$.

the peak of the postpolymer shifted to the higher molecular weight side. The resulting postpolymer possessed the expected molecular weight and a narrow MWD ($M_w/M_n = 1.0_8$). Consequently, it is evident that the propagating end produced by the cuprate initiator is stable in THF at 0°C at least for 30 min and initiates further polymerization of TBMA.

Effects of Lewis Acids and Bases

One characteristic of Lewis acid and base mediated organocuprates is the effective 1,4-addition with sterically hindered α,β-unsaturated esters and ketones with which normal organocuprates do not react.[12,21,22] Therefore, we investigated the effects of Lewis acids and bases on the polymerization of TBMA initiated by lithium methylcuprates. The polymerization results are presented in Table IV. Contrary to our expectation, the polymerizations failed to occur in the presence of Lewis acid (runs 1—3), except for triethylaluminum (run 4). The addition of Lewis bases caused polymerization but initiator efficiency decreased and MWD broadened (runs 5—8). Therefore, we could not find any positive effect of the additives on the polymerization of TBMA at 0°C.
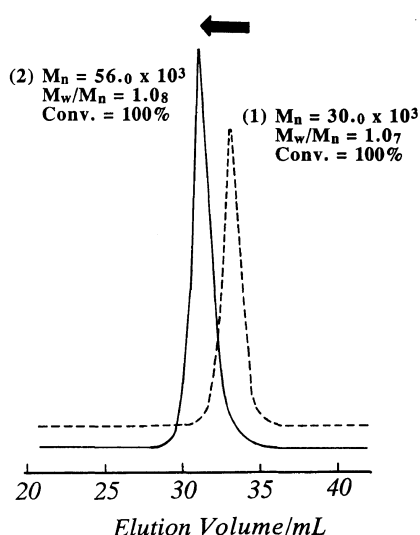
Figure 1. SEC curves of PTBMA obtained at 0°C: first polymerization (broken lines) (1), M_n (obsd) = 30×10^3, $M_w/M_n = 1.0_7$, [MeLi]/[CuI] = 4.0, Conv. = 100%, $f = 6._0$%; second polymerization (solid line) (2), M_n (obsd) = 56×10^3, $M_w/M_n = 1.0_8$, Conv. = 100%, M_n (calcd) = 57×10^3 (the second monomer was added 30 min after the first addition).

Polymerization of α,β-Unsaturated Esters

The polymerization results of various α,β-unsaturated esters initiated by lithium organocuprates in THF are listed in Table V. When [RLi]/[CuI] is higher than 2, the initiators initiated the polymerization of methyl, ethyl, isopropyl, isobutyl, cyclohexyl, benzyl, and triphenylmethyl methacrylates to give polymers with broad MWDs ($M_w/M_n = 1.5$—2.2) (runs 1—12). The initiators also effectively initiated the polymerization of TBA and styrene to afford polymers with very broad MWDs ($M_w/M_n = 1.7$—2.7) (runs 13—16, 24). The cuprate initiators, however, could not initiate the polymerizations of methyl crotonate, and diethyl and diisopropyl fumarates, irrespective of the presence or absence of Lewis acid (runs 17—22). The feature to be noted in the polymerizations of methacrylates other than TBMA is that polymerizations proceeded with relatively higher initiator efficiency (e.g., for MMA, $f = 27$% at 0°C, run 4), implying that the other cuprates presented in eq 3—5 may also be active species for the polymerization of MMA. The tacticity of PMMA prepared in THF at 0°C (run 4 in Table V) was estimated to be 1.8% isotactic, $38._7$% heterotactic, and $59._5$% syndiotactic in triad, by ^{1}H NMR measurement.

Syntheses of block copolymer of TBMA with MMA or TBA were carried out by the sequential polymerization of TBMA followed by MMA or TBA in THF at 0°C. From the SEC chromatogram of PTBMA-*block*-PMMA shown in Figure 2(a), it was observed that the peak of prepolymer, PTBMA disappeared and the peak of the block copolymer appeared at the higher molecular weight side, in addition to the appearance of a new peak in the lower molecular weight side. The polymer in the region of lower molecular weight side was considered the PMMA homopolymer most probably formed by the initiation with Me_2CuLi remaining in the reaction medium. We successfully carried out peak separation of the SEC chromatogram into two components, high molecular weight ($M_n = 99._5 \times 10^3$, $M_w/M_n = 1.2_1$) and low molecular weight ($M_n = 52 \times 10^3$, $M_w/M_n = 1.3_2$), respectively.

The ratio of MMA successfully incorporated into block copolymer to total MMA polymerized, x, is calculated by

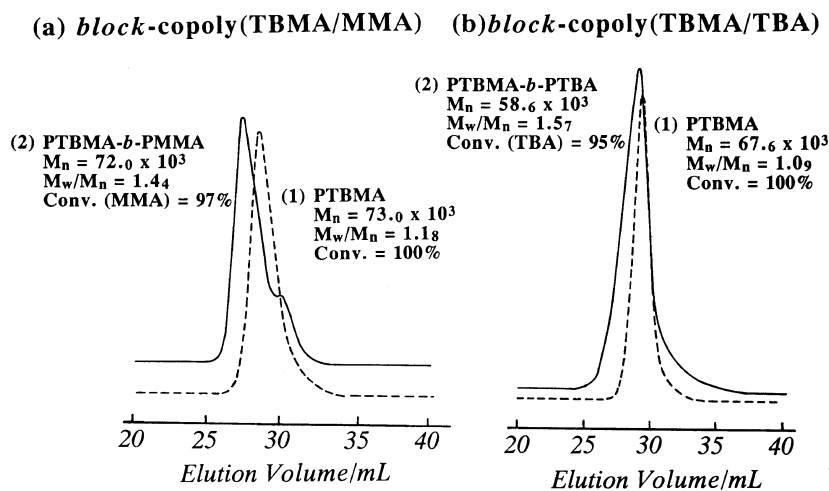**Table IV.** Polymerizations of TBMA using lithium methylcuprates in the presence of Lewis acid and base at 0°C[a]

Run	[CuI]/mmol	[RLi]/[CuI]	Additives	Conv./%	$M_n^b/10^3$	M_w/M_n^b	$f/\%^c$
1	0.47	2.2	BF_3OEt_2	0	—	—	0
2	0.47	2.2	Me_3SiCl	0	—	—	0
3	0.47	2.2	$AlCl_3$	0	—	—	0
4	0.47	2.2	$AlEt_3$	64	29_6	1.3_1	$0._6$
5	0.47	2.2	Ph_3P	85	14_0	1.1_4	$1._7$
6	0.47	2.2	TMEDA	100	40_5	1.1_2	0.7
7	0.47	4.1	TMEDA	95	70	1.2_9	$3._8$
8	0.47	2.2	2,2'-Bipyridine	100	59_9	1.3_3	0.5

[a] Polymerizations were carried out in 10 mL THF for 30 min. [TBMA] = 9.37 mmol. The catalysts of 0.47 mmol were added to the initiator solution. [b] Determined by SEC calibrated with polystyrene standards. [c] Initiator efficiency calculated by the equation, $f(\%) = (W \times \text{Conv.}(\%))/([CuI] \times M_n)$, where W is weight of TBMA in feed.

Table V. Polymerizations of α,β-unsaturated esters, $CH(R_1)=C(R_2)COOR_3$ using lithium methylcuprates[a]

Run	R_1	R_2	R_3	[M]/mmol	CuI/mmol	[MeLi]/[CuI]	Temp./°C	Conv./%	$M_n{}^{b}/10^3$	$M_w/M_n{}^{b}$	$f/\%{}^{c}$
1	H	CH_3	$CH_3{}^{d}$	16	0.47	2.0	0	0	—	—	0
2	H	CH_3	CH_3	16	0.47	2.3	0	$56._3$	31	1.5_4	$6._2$
3	H	CH_3	CH_3	14.1	0.47	4.1	−58	$21._4$	18_2	1.4_3	0.3_5
4	H	CH_3	CH_3	16.5	0.47	4.1	0	$89._3$	11_7	1.9_4	2_7
5	H	CH_3	CH_3	11.8	0.47	4.1	19	$86._0$	5.5	1.7_8	3_9
6	H	CH_3	Ethyl	13.2	0.47	3.9	0	$80._0$	6.5	2.1_6	3_9
7	H	CH_3	i-Pr	14.1	0.47	4.1	0	$96._0$	—	—	—
8	H	CH_3	i-Bu	10.3	0.47	3.7	0	$95._0$	13	2.1_5	2_3
9	H	CH_3	CyH^{e}	12.1	0.47	4.07	0	$98._0$	—	—	—
10	H	CH_3	Benzyl	11.3	0.47	4.98	0	74.3	—	—	—
11	H	CH_3	$C(Ph)_3$	11.3	0.47	2.0	0	0	—	—	—
12	H	CH_3	$C(Ph)_3$	11.3	0.47	4.0	0	$98._5$	—	—	—
13	H	H	t-Bu	10.4	0.47	1.9	0	$76._8$	36	1.6_6	$6._6$
14	H	H	t-Bu^{f}	22.1	0.36	2.0	−78	$25._9$	14_{30}	1.7_2	$0._1$
15	H	H	t-Bu	10.4	0.47	4.1	0	$64._0$	$19._3$	2.1_1	$9._9$
16	H	H	t-Bu	10.4	0.47	4.1	19	$53._0$	$12._3$	2.1_5	1_3
17	CH_3	H	CH_3	14.1	0.47	2.0	0	0	—	—	0
18	CH_3	H	$CH_3{}^{g}$	14.1	—	—	0	0	—	—	0
19	COOEt	H	Ethyl	14.1	0.47	2.0	0	0	—	—	0
20	COOEt	H	Ethyl^{h}	14.1	—	—	−78—0	0.	—	—	0
21	COOEt	H	Ethyl	14.1	0.47	4.0	0	0	—	—	0
22	COOi-Pr	H	i-Pr	14.1	0.47	2.0	0	0	—	—	0
23	styrene			18.7	0.47	2.0	0	0	—	—	0
24	styrene			18.7	0.47	4.36	0	$98._0$	$27._0$	2.6_5	1_5

[a] Polymerizations were carried out in 10 mL THF for 30 min. [b] Determined by SEC calibrated with olystyrene standards. [c] Initiator efficiency calculated by the equation, $f(\%)=(W\times\text{Conv.}(\%))/([\text{CuI}]\times M_n)$, where W is weight of the monomer in feed. [d] In 10 mL toluene. [e] Cyclohexyl. [f] THF = 20 mL. [g] Dilithium methyl-2-cyanocuprate, 0.47 mmol. [h] $Bu_2CuLi\cdot BF_3$, 0.47 mmol.

(a) block-copoly(TBMA/MMA)   (b)block-copoly(TBMA/TBA)

(2) PTBMA-b-PMMA
$M_n = 72.0 \times 10^3$
$M_w/M_n = 1.4_4$
Conv. (MMA) = 97%

(1) PTBMA
$M_n = 73.0 \times 10^3$
$M_w/M_n = 1.1_8$
Conv. = 100%

(2) PTBMA-b-PTBA
$M_n = 58.6 \times 10^3$
$M_w/M_n = 1.5_7$
Conv. (TBA) = 95%

(1) PTBMA
$M_n = 67.6 \times 10^3$
$M_w/M_n = 1.0_9$
Conv. = 100%

20 25 30 35 40
Elution Volume/mL

20 25 30 35 40
Elution Volume/mL

Figure 2. (a) SEC curves of block copolymer of TBMA with MMA: first polymerization of TBMA (broken lines) (1), M_n (obsd) = 73×10^3, $M_w/M_n = 1.1_8$, [MeLi]/[CuI] = 4.1_8, Conv. = 100%, $f=6._4$; second polymerization of MMA (solid line) (2), M_n (obsd) = 72×10^3, $M_w/M_n = 1.4_4$, Conv. (MMA) = 97%, M_n (calcd) = 123×10^3 (the second MMA monomer was added 30 min after the first addition). (b) SEC curves of block copolymer of TBMA with TBA: first polymerization of TBMA (broken lines) (1), M_n (obsd) = $67._6 \times 10^3$, $M_w/M_n = 1.0_9$, [MeLi]/[CuI] = 4.1_1, Conv. = 100%, $f=7._8$; second polymerization of TBMA (solid line) (2), M_n (obsd) = $58._6 \times 10^3$, $M_w/M_n = 1.5_7$, Conv. (TBA) = 95%, M_n (calcd) = 112×10^3 (the second TBA monomer was added 30 min after the first addition).

$$x(\%) = \frac{S_{\text{PTBMA-}b\text{-PMMA}}\left(\dfrac{dn}{dc}\right)_{\text{PMMA}} W_{\text{MMA}}\theta_{\text{MMA}} - S_{\text{PMMA}}\left(\dfrac{dn}{dc}\right)_{\text{PTBMA}} W_{\text{TBMA}}\theta_{\text{TBMA}}}{S_{\text{PTBMA-}b\text{-PMMA}}\left(\dfrac{dn}{dc}\right)_{\text{PMMA}} W_{\text{MMA}}\theta_{\text{MMA}} + S_{\text{PMMA}}\left(\dfrac{dn}{dc}\right)_{\text{PMMA}} W_{\text{MMA}}\theta_{\text{MMA}}} \times 100 \tag{6}$$

where S is the area of SEC chromatogram, (dn/dc), the excess refractive index increment in THF,[23] W, the weight of monomer in feed, and θ, the conversion, and the subscripts correspond to the respective monomers, polymers, and block copolymer. We determined x to be 61%. In other words, 61% of MMA is successfully

block-copolymerized and 39% of MMA is polymerized by reinitiation with the cuprates to afford the PMMA homopolymer. M_n of the block copolymer is calculated to be $10_4 \times 10^3$, based on the fact that 61% of MMA is polymerized by the living PTBMA anions. The M_n is in good agreement with M_n observed for the block

copolymer. This implies that the broadening of MWD in the homopolymerization of MMA initiated by lithium methylcuprates (Table V), is due to slow initiation rate and/or multiple active species.

On the other hand, from the SEC chromatogram of PTBMA-*block*-poly(TBA) shown in Figure 2(b) it was deduced that significant termination and propagation reactions with multiple active species may occur during the polymerization of TBA in THF at 0°C.

This study demonstrates that lithium methylcuprate-initiated polymerizations of TBMA proceed in a living manner in THF at 0—45°C. At [MeLi]/[CuI] higher than 2 the polymerization afforded PTBMA with very narrow MWD ($M_w/M_n = 1.05$—1.1_7). The initiator effectively polymerized other methacrylates, TBA, and styrene to afford polymers but with broad MWDs. The active species for the TBMA polymerization was supposed to be Me_3CuLi_2. The initiator was not effective for the polymerizations of crotonates and fumarates.

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