SHORT COMMUNICATIONS

Anionic Polymerization of Methacrylate Having Hindered Phenolic Group with Unprotected Hydroxyl Function

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Usually, the anionic polymerization of a monomer bearing a functional reactive group requires the protection of this group prior to the polymerization process. As a consequence, the deprotection reaction necessarily follows, making it more troublesome than an ideal one-step polymerization, although versatile protection–deprotection methods have been developed.¹

Recently, we reported the preparation of heterotactic poly(alkyl methacrylate)s with narrow molecular weight distributions (MWDs) by *t*-butyllithium (*t*-BuLi)/bis(2,6-di-*t*-butylphenoxy)methylaluminum [MeAl(ODBP)₂].^{2–4} In the first report,² we described the polymerization of methyl methacrylate (MMA) with *t*-BuLi in the presence of a fivefold excess of a 1 : 1 mixture of MeAl(ODBP)₂ and 2,6-di-*t*-butylphenol, which was formed by the reaction of (CH₃)₃Al and the phenol in a 1 : 3 molar ratio. The fact that a heterotactic PMMA was obtained, even in the presence of a fivefold excess of this phenol over the initiator *t*-BuLi, motivated our interest in polymerizing anionically a monomer with a hydroxyl group with steric hindrance similar to the case of 2,6-di-*t*-butylphenol.

In this study, we investigate the possibility of polymerizing anionically 3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)propyl methacrylate (DBHPPMA) in which the neighboring *t*-butyl groups around the hydroxyl function may provide a steric hindrance sufficient for its protection in regard of the anionic initiators and propagating species.

EXPERIMENTAL

Materials

The synthesis procedure of DBHPPMA is shown in Scheme 1. The starting material, tetrakis[3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)propanoyloxymethyl]methane (trade name IRGANOX 1010, Ciba-Geigy), is a kind gift from Kasho Co. (Osaka). In 125 ml of tetrahydrofuran (THF) was dissolved 50.0 g (42.5 mmol) of the starting material. LiAlH₄ (6.62 g, 174.4 mmol) in 100 ml

of THF was slowly added to the solution of IRGANOX 1010 under nitrogen at room temperature. As the reduction reaction proceeded, the solution thickened and thus additional amounts of solvent were added to reach finally 400 ml of THF.

Scheme 1.

The consumption of the starting ester was followed by infrared spectroscopy, observing the carbonyl absorption band at 1710 cm⁻¹. When a high conversion was attained, the mixture was quenched by dropwise addition of water, and the solvent was evaporated under vacuum and replaced by diethyl ether. The ether solution was then washed with aqueous sodium chloride and dried over MgSO₄. Evaporation of the solvent gave a solid product, 3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)propanol (yield 94.4%), which was used for the next reaction without purification.

To synthesize DBHPPMA, 4.99 g (18.9 mmol) of the diol were dissolved in 35 ml of diethyl ether together with a 1.2 molar equivalent of triethylamine. The reaction was started with the slow addition of a 1.1 molar equivalent of methacryloyl chloride and carried out at room temperature for 24 hours. The yield was determined by high performance liquid chromatography (HPLC) on a silica-gel column (250 mm × 10 mm, Develosil 100-5, Nomura Chemical Co., Ltd.) with chloroform as an eluent. When stopped, the reaction was 78% in yield. The recrystallization from diethyl ether at 0°C led to almost pure DBHPPMA, as checked by HPLC analysis (mp 59.5–61.0°C, lit. 58–60°C⁵; ¹H NMR data (CDCl₃, 35°C) 1.42 ppm (s, 18H), 1.94 ppm (s, 3H), 1.99 ppm (dt, 2H), 2.62 ppm (t, 2H), 4.17 ppm (t, 2H), 5.02 ppm (s, 1H), 5.52 ppm (s, 1H), 6.09 ppm (s, 1H), 6.97 ppm (s, 2H)).

After being dried under vacuum at room temperature, DBHPPMA was placed in an ampoule filled with dry nitrogen and freshly vacuum-distilled toluene was added

to obtain the monomer solution. This solution was dried over Molecular Sieves 4A. For polymerization, the supernatant monomer solution was transferred to the initiator solution by a hypodermic syringe.

Toluene was purified in the usual manner, mixed with butyllithium and then distilled under high vacuum. *t*-BuLi in pentane, obtained commercially, was used as a heptane solution by replacing the solvent under vacuum. The concentration was determined by titration with butan-2-ol (1.20M) using *o*-phenanthroline as an indicator.⁶ MeAl(ODBP)₂ was prepared from 2,6-di-*t*-butylphenol and trimethylaluminum in toluene at room temperature, and recrystallized several times from hexane at -78°C .

Polymerization

Polymerizations of DBHPPMA were carried out in glass ampoules filled with dried nitrogen passed through Molecular Sieves 4A cooled at -78°C . The reactions were initiated by adding slowly the toluene solution of the monomer to a solution of the initiator at -78°C and were terminated by adding methanol containing a small amount of aqueous HCl (1M) at the polymerization temperature. The solvent was removed under vacuum, and the residue was dissolved in chloroform. A small fraction of this chloroform solution was subjected to ¹H NMR analysis after filtration and replacement of the solvent by deuterated chloroform. Polymer yields were calculated from the intensities of vinylidene proton signals of the monomer and the signals of the hydroxy protons of both the monomer and polymer. The rest of the chloroform solution was filtered. The resulting poly(DBHPPMA) was then separated by GPC from both the unreacted DBHPPMA and the phenolic compound resulting from the hydrolysis of MeAl(ODBP)₂ in the termination process. The GPC fractionation was performed using a Shodex GPC column K2003 (300 mm $\times$ 20 mm). Chloroform of the polymer solution thus obtained was evaporated and replaced with benzene for freeze-drying. The polymer was dried under vacuum at room temperature. Its number-average molecular weight ($\bar{M}_n$) was calculated from the intensities of the hydroxy proton signal (4.94 ppm) and the signal of *t*-butyl protons of the initiator fragment at the polymer chain-end (0.88 ppm) in the ¹H NMR spectrum measured in chloroform-*d* at 55°C or in nitrobenzene-*d*₅ at

110°C (cf. Figure 1).

Measurements

Molecular weights of the polymers and their distributions were determined by GPC using a JASCO TRI ROTAR-V chromatograph equipped with Shodex GPC columns K-80M (300 mm $\times$ 8 mm) and K-802.5 (300 mm $\times$ 8 mm) using chloroform as an eluent. The GPC chromatograms were calibrated against standard polystyrene samples.

Tacticities of the polymers were determined from ¹³C NMR spectra measured in nitrobenzene-*d*₅ at 110°C on a JEOL JNM-GX500 spectrometer at 125 MHz.

RESULTS AND DISCUSSION

Table I shows the results of anionic polymerization of DBHPPMA in toluene at -78°C initiated with several initiator systems. Though the initiator efficiencies were less than unity, poly(DBHPPMA) did form in all the experiments, with the exception of run 2 where *t*-BuLi was the initiator. Polymerization with *t*-BuMgBr, which is known to initiate isotactic living polymerization of MMA,⁷ gave a poly(DBHPPMA) with multimodal MWD in 97.5% yield. The initiator efficiency, *f*, estimated from the yield and $\bar{M}_n$ determined by end-group analysis by ¹H NMR spectroscopy was 0.74, much lower than that in the case of polymerization of MMA (*f* $\approx$ 1.0).

Polymerization with *t*-BuLi, a stronger Lewis base than *t*-BuMgBr, gave no polymer. The acidic proton of the phenolic group of the monomer probably quenches the initiator in the initiation step. Nevertheless, polymerization of DBHPPMA with this initiator was made possible upon the addition of an aluminum compound. Indeed, polymerization with *t*-BuLi/(*n*-Bu)₃Al (1/3) (run 3) gave a polymer in a low yield (38.5%) but the MWD was fairly narrow ($\bar{M}_w/\bar{M}_n = 1.11$), suggesting that quenching of the polymerization reaction should occur mostly in the initiation step, but not during the propagation process. Tacticity of the polymer is predominantly syndiotactic, as in the case of the polymerization of other alkyl methacrylates with this initiator.⁸ Determination of tacticity is described later.

Polymerization with *t*-BuLi/MeAl(ODBP)₂ (run 4) gave a polymer with narrow MWD (1.08) in a higher

Table I. Polymerization of DBHPPMA with several initiators in toluene at -78°C

Run	Initiator	Time	Yield	$\bar{M}_n$	$\bar{M}_n$	$\frac{\bar{M}_w}{\bar{M}_n}$ ^b	<i>f</i> ^c	Tacticity/% ^d		
		h	% ^a	(Calcd)	(NMR)			<i>mm</i>	<i>mr</i>	<i>rr</i>
1	<i>t</i> -BuMgBr ^e	48	97.5	9450	12720	3.03	0.74	82.6	11.8	5.6
2	<i>t</i> -BuLi ^f	72	~ 0	—	—	—	—	—	—	—
3	<i>t</i> -BuLi/(<i>n</i> -Bu) ₃ Al ^e	72	38.5	3770	9400	1.11	0.40	1.5	13.2	85.3
4	<i>t</i> -BuLi/MeAl(ODBP) ₂ ^g	24	57.3	4220	12560	1.08	0.34	40.0	49.5	10.5
5	<i>t</i> -BuLi/MeAl(ODBP) ₂ ^{g,h}	24	86.6	6360	16350	1.30	0.39	0.0	16.5	83.5
6	PEMA anion/MeAl(ODBP) ₂ ⁱ	72	59.4 ^j	9930 ^k	10260 ^k	1.13	0.99 ^j	38.7 ^j	52.5 ^j	8.8 ^j

^a Determined by ¹H NMR. ^b Determined by GPC. ^c Initiator efficiency given by the ratio $\bar{M}_n(\text{Calcd})/\bar{M}_n(\text{NMR})$. ^d Determined from ¹³C NMR signals of main-chain quaternary carbon, except run 3 (carbonyl carbon) and run 6 (α -methyl carbon). ^e Monomer 2.9 mmol, initiator 0.1 mmol, toluene 4.5 ml. ^f Monomer 0.5 mmol, initiator 0.045 mmol, toluene 0.5 ml. ^g Monomer 2.2 mmol, initiator 0.1 mmol, toluene 2.5 ml. ^h At 0°C . ⁱ The PEMA anion was prepared under the following conditions: EMA 3.0 mmol, *t*-BuLi 0.15 mmol, toluene 4 ml, at -78°C for 12 h. Then DBHPPMA (4.9 mmol) was added. PEMA block: yield 100%, $\bar{M}_n(\text{NMR})$ 2690, *f* = 0.89. ^j Values for the poly(DBHPPMA) block. ^k Values for the copolymer.

Figure 1. ^1H NMR spectrum measured in nitrobenzene- d_5 at 110°C of poly(DBHPPMA) formed with $t\text{-BuLi/MeAl(ODBP)}_2$ in toluene at -78°C (run 4 in Table I). * Signals due to the solvent. † Signal due to benzene remaining in the sample.

Figure 2. Partial ^1H NMR spectra measured in nitrobenzene- d_5 at 110°C of poly(DBHPPMA)s formed with (a) $t\text{-BuMgBr}$ (run 1 in Table I), (b) $t\text{-BuLi}/(n\text{-Bu})_3\text{Al}$ (run 3), and (c) $t\text{-BuLi/MeAl(ODBP)}_2$ (run 4).

yield (57.3%) than the previous cases even with shorter polymerization time. Figure 1 shows the ^1H NMR spectrum of the polymer, where the singlet signal of the phenolic hydroxyl group clearly appears at 4.94 ppm. Figures 2a, 2b, and 2c are the partial spectra of poly(DBHPPMA)s obtained with $t\text{-BuMgBr}$, $t\text{-BuLi}/(n\text{-Bu})_3\text{Al}$, and $t\text{-BuLi/MeAl(ODBP)}_2$, respectively. The signals of the main-chain methylene protons appear in the range of 1.7 ppm to 2.6 ppm with the overlap of the signal due to methylene protons, $\text{CH}_2(\text{c})$, of the ester group. The polymer obtained with $t\text{-BuMgBr}$ (Figure 2a) shows a typical AB quartet signal due to the meso methylene protons of isotactic polymethacrylate chain. On the contrary, poly(DBHPPMA) obtained with $t\text{-BuLi}/(n\text{-Bu})_3\text{Al}$ (1/3) (Figure 2b) is syndiotactic as revealed by the singlet signal of the main-chain methylene protons at 2.17 ppm. As for poly(DBHPPMA) formed

Figure 3. Main-chain quaternary carbon resonances in ^{13}C NMR spectra measured in nitrobenzene- d_5 at 110°C of poly(DBHPPMA)s formed with (a) $t\text{-BuMgBr}$ (run 1 in Table I), (b) $t\text{-BuLi}/(n\text{-Bu})_3\text{Al}$ (run 3), and (c) $t\text{-BuLi/MeAl(ODBP)}_2$ (run 4).

with $t\text{-BuLi/MeAl(ODBP)}_2$, the main-chain methylene proton signals show more complicated splitting (Figure 2c) owing to the lower stereoregularity of this polymer; this will be described later. From the results mentioned above, the α -methyl proton signals at 1.52 ppm (Figure 2a) and 1.29 ppm (Figure 2b) could be ascribed to the mm and rr triads, respectively, mr triad signal being partly hidden in the strong t -butyl signal (Figure 2c).

For the quantitative tacticity determination of these polymers, ^{13}C NMR spectra were measured. The main-chain quaternary carbon clearly exhibits triad splitting as shown in Figure 3. Comparing the spectra of both the isotactic and syndiotactic poly(DBHPPMA)s, we could then assign the mm and rr triad signals, and consequently the remaining mr triad signal as indicated in the figure. The assignments were made at triad level for the main-chain quaternary carbon signals, while they show further splittings due to longer tactic sequences. The results of the quantitative determination of tacticity are included in Table I.

Tacticity of poly(DBHPPMA) formed with $t\text{-BuLi/MeAl(ODBP)}_2$ is rather unusual; the mm triad content balances the mr triad content, whereas typical alkyl methacrylates such as MMA and ethyl methacrylate (EMA) give heterotactic polymers under the same conditions.^{2,3}

DBHPPMA polymerizes with $t\text{-BuLi/MeAl(ODBP)}_2$ even at 0°C to give poly(DBHPPMA) in good yield. In this experiment, the addition of the monomer was done at -78°C . After completion of the addition, the polymerization temperature was raised to 0°C . The broader MWD of this poly(DBHPPMA) ($\bar{M}_w/\bar{M}_n = 1.30$), as compared to that of the polymer formed at -78°C (1.08), suggests the possibility of hydrogen abstraction at 0°C . However, the MWD remains comparable to that of poly(EMA) synthesized at 0°C with $t\text{-BuLi/MeAl(ODBP)}_2$.³ Tacticity of poly(DBHPPMA) initiated with

t-BuLi/MeAl(ODBP)₂ strongly depends on the polymerization temperature, as in the case of EMA and MMA.³ Indeed, poly(DBHPPMA) polymerized at -78°C (Table I, run 4) has a majority of *mr* triads (49.5% of *mr* triads), but poly(DBHPPMA) obtained at 0°C (Table I, run 5) is a syndiotactic-rich polymer (83.5% of *rr* triads). A similar temperature dependence of stereospecificity has been observed for the polymerization of EMA; below -60°C , heterotactic poly(EMA) is obtained, and in the temperature range from -60°C to 30°C , syndiotactic poly(EMA) is formed.

If the lower initiator efficiency of *t*-BuLi/MeAl(ODBP)₂ is due to the reaction between strongly basic *t*-BuLi and the hydroxyl group of the monomer, the initiation with a methacrylate type anion is expected to give a better result. Thus, polymerization of DBHPPMA with oligo(EMA) anion obtained with *t*-BuLi/MeAl(ODBP)₂ was carried out in toluene at -78°C . The block copolymer formed had a narrow MWD ($\bar{M}_w/\bar{M}_n = 1.13$) and the initiator efficiency for the poly(DBHPPMA) block was almost quantitative (Table I, run 6). Tacticity of the poly(DBHPPMA) block (run 6, Table I) was determined from the ^{13}C NMR signals of the α -methyl carbon by assuming the tacticity of the poly(EMA) block to be the same as that of poly(EMA) synthesized under conditions identical to those for the synthesis of poly(EMA) living anion used as the initiator in run 6.

As was mentioned in the introduction, the presence of a fivefold excess of a 1 : 1 mixture of MeAl(ODBP)₂ and 2,6-di-*t*-butylphenol over *t*-BuLi did not inhibit polymerization of MMA.² In the case of DBHPPMA polymerization, the phenol group and the methacrylate inherently exist in a 1 : 1 molar ratio. To examine the effect of the free phenol on the polymerization, we carried out polymerization of MMA with *t*-BuLi/MeAl(ODBP)₂ in the presence of an equimolar amount of 2,6-di-*t*-butylphenol to MMA. A heterotactic poly(MMA) did form but with a very low initiator efficiency (less than 10%).

The MWD of the PMMA thus formed is larger than that of poly(DBHPPMA) obtained under identical conditions, suggesting that some quenching of the reaction takes place not only during the initiation process but also during the propagation in such a system. These results indicate that the sterically protected phenolic group is less troublesome when it is attached to the monomer.

In conclusion, a monomer with a sterically protected hydroxyl group can be anionically polymerized without the need of protection as far as the reactivity of the propagating anion is modified by proper selection of initiator such as *t*-BuLi/MeAl(ODBP)₂. Though the strongly basic initiator, *t*-BuLi, is partly quenched with the hydroxyl group of the monomer, the rest of the initiator survives and initiates the polymerization to form methacrylate anions. The resulting anions are stabilized through the coordination by MeAl(ODBP)₂, and propagate in a living manner to give the functional polymers with narrow MWD, without being quenched with the hydroxyl group of the hindered phenol, at least at -78°C . Further experiments will be carried out in the near future.

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