SHORT COMMUNICATIONS

# Anionic Polymerization of Methyl Methacrylate with Lithium *N*-Benzyltrimethylsilylamide

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End-functional polymers have attracted much attention since they can be used for constructing more elaborated polymer chain architectures.[1] Living polymerization, the concept of which was first proposed by Szwarc[2] in 1956, is one of the most promising ways to introduce a functional group at the polymer chain-end.[3] Another means to obtain end-functional polymers is to polymerize a monomer with an initiator which comprises a functional group or its precursor group.[4]

We have found stereospecific and living polymerization of methacrylates; isotactic-specific one with *tert*-butylmagnesium bromide (*t*-BuMgBr),[5, 6] syndiotactic-specific one with *tert*-butyllithium (*t*-BuLi)/trialkylaluminum (R$_3$Al),[7, 8] and heterotactic-specific one with *t*-BuLi and bis(2,6-di-*tert*-butylphenoxy)methylaluminum [MeAl(ODBP)$_2$].[9–17] More recently, we have reported that *t*-BuLi/bis(2,6-di-*tert*-butylphenoxy)ethylaluminum [EtAl(ODBP)$_2$] initiating system was effective for syndiotactic-specific living polymerization of methacrylates[13] and acrylates.[18] In all these cases, obtained polymers have *t*-Bu group at the initiating chain-end of each polymer molecule.

Lithium dialkylamides (R$_2$NLi) such as lithium diisopropylamide (LDA) have been known as useful anionic initiators for methacrylate polymerizations.[19–22] Antoun *et al.* reported that LDA/lithium chloride (LiCl) was an effective initiating system for anionic polymerization of methyl methacrylate (MMA) in tetrahydrofuran (THF) and generated PMMA with narrow molecular weight distribution (MWD) in high initiator efficiency (> 0.9).[20] The obtained polymer has the tertiary amino group at the chain end, which is less feasible for further chemical modification than primary and secondary amino groups, however. Kubo *et al.* reported that polymerization of MMA with *N,N'*-
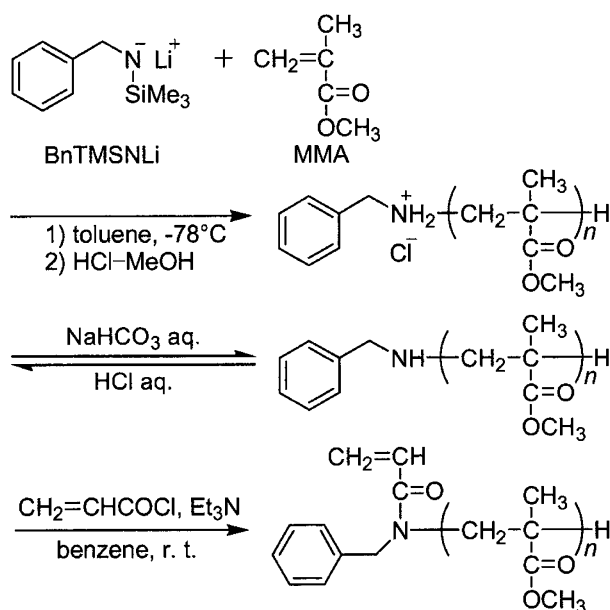


R = CH$_3$ : MeAl(ODBP)$_2$
C$_2$H$_5$: EtAl(ODBP)$_2$
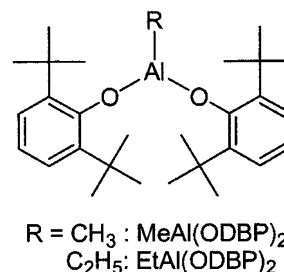
**Equation 1.**

diphenylethylenediamine monolithium amide in THF afforded PMMA having secondary amino group at the initiating chain-end, though initiator efficiency and MWD of the polymer were not fully discussed.[23] After introducing terminal carboxylic acid unit through the reaction with succinic anhydride, they carried out end-cyclization of the hetero-telechelic PMMA to obtain cyclic PMMA.

Lithium bis(trimethylsilyl)amide (TMS$_2$NLi) has been known as a strong base with low nucleophilicity, and used as a mild lithiation reagent.[24] Despite of its low nucleophilicity, Nagasaki *et al.* reported that TMS$_2$NLi could initiate anionic polymerization of MMA.[25] They declared that the polymerization provides a PMMA having a primary amino end-group after acid treatment. However, the polymer obtained had broad MWD and the initiator efficiency was low (*ca.* 0.07), probably owing to the inherently low nucleophilicity of TMS$_2$NLi. Antoun *et al.*[20] and Couper *et al.*[22] used TMS$_2$NLi in combination with several additives such as LiCl for polymerization of MMA. The initiator efficiency was still low (< 0.1), and MWD of the obtained polymers were relatively broad. As described above, we have found that several aluminum compounds are effective for the stereocontrol in methacrylate polymerizations. Thus, we have examined anionic polymerization of methacry-

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**Scheme 1.**

lates with TMS$_2$NLi/tributylaluminum ($n$-Bu$_3$Al) or TMS$_2$NLi/MeAl(ODBP)$_2$ in toluene.[26] The initiator efficiency was improved as compared to the polymerization with TMS$_2$NLi alone. In the case of TMS$_2$NLi/$n$-Bu$_3$Al, however, the initiating chain-end of the polymer was $n$-butyl group instead of amino group to be derived from TMS$_2$N-fragment, probably due to ate complex formation from TMS$_2$NLi and $n$-Bu$_3$Al, which initiated the polymerization by releasing $n$-butyl group.

On the other hands, Yamamoto and co-workers have reported that lithium $N$-benzyltrimethylsilylamide (BnTMSNLi) reacted with methyl crotonate to generate a conjugate-addition product exclusively, while other lithium amides including LDA and TMS$_2$NLi produced carbonyl-addition and $\gamma$-hydrogen-abstraction product in addition to the conjugate-addition product.[27]

The present work aims at obtaining stereoregular end-functional polymethacrylates by exploring the possibility of utilizing BnTMSNLi as a functional initiator in combination with $n$-Bu$_3$Al, MeAl(ODBP)$_2$, or EtAl(ODBP)$_2$ for the polymerization of methacrylates.

## EXPERIMENTAL

### Materials

MMA (Nacalai Tesque) and acryloyl chloride (Aldrich Co. Ltd) were purified by fractional distillation under reduced nitrogen pressure, dried over calcium dihydride (CaH$_2$) and vacuum-distilled just before use. Triethylamine (Nacalai Tesque) was distilled under nitrogen, dried over CaH$_2$, and vacuum-distilled. Toluene, benzene and heptane were purified in the usual manner, mixed with a small amount of $n$-BuLi (Nacalai Tesque), and distilled under high vacuum.

$N$-Benzyltrimethylsilylamine (BnTMSNH) was prepared, according to the literature[28] with a slightly modification, from benzylamine (Tokyo Chemical Industry) and trimethylsilyl chloride (1 equiv.) (Nacalai Tesque) in diethyl ether in the presence of CaH$_2$ then fractionally distilled and dried over Molecular Sieves 4A. BnTMSNLi was prepared from BnTMSNH and $n$-BuLi (1 equiv.) in hexane at 0°C.[29] The solvent was removed under vacuum to leave a white solid, and the product was recrystallized several times by dissolving it in heptane and cooling to −20°C. After most of the heptane was removed by a syringe and the residual heptane was evaporated under vacuum to dryness, the solid residue was dissolved in toluene giving a clear red solution. The concentration of this solution was determined by $^1$H NMR in toluene-$d_8$ at 35°C in combination with density measurements.

2,6-Di-*tert*-butylphenol was fractionally distilled and used as a heptane solution. Trimethylaluminum (Me$_3$Al) (Aldrich Co. Ltd) and triethylaluminum (Et$_3$Al) (Kishida Chemical) were used as received.

MeAl(ODBP)$_2$ and EtAl(ODBP)$_2$ were prepared according to the literatures[11, 12, 30, 31] from Me$_3$Al or Et$_3$Al and 2,6-di-*tert*-butylphenol (2 equiv.) in toluene at 0°C. Recrystallization procedures were similar to the case of BnTMSNLi and used as toluene solutions.

### Polymerization

Polymerizations were carried out in glass ampoules filled with dried nitrogen passed through Molecular Sieves 4A cooled at −78°C. Dried toluene and alkylaluminum were added to the glass ampoules, which were then cooled to polymerization temperature. Polymerization was initiated either by adding monomer after BnTMSNLi or by adding BnTMSNLi after monomer. The reactions were terminated by adding methanol containing aqueous HCl at the polymerization temperature. The reaction mixtures were poured into hexane, and the precipitates were collected by filtration, and then washed with hexane and 3 N HCl several times. The recovered polymers were dried under vacuum at 60°C.

### Acrylation Reaction

PMMA [number average molecular weight ($M_n$) = 2800, $M_w/M_n$ = 1.07, 100 mg (0.036 mmol)], obtained by the anionic polymerization with BnTMSNLi/$n$-Bu$_3$Al, was dissolved in 3 mL dry benzene, and then acryloyl chloride (1.11 mmol) and triethylamine (3.0 mmol) were added in order at ambient temperature. After 20 h, the reaction mixture was poured into hexane. The precipitate collected by filtration was dissolved in chloroform and shaken with

**Table I.** Polymerization of MMA with BnTMSNLi/aluminum compounds in toluene at $-78\,°C$ for 24 h[a]

| run | Al compound | $M_n$ | | | $M_w^{[d]}/M_n$ | Tacticity/%[e] | | |
|-----|-------------|-------|------|-------|-----------------|----------------|------|------|
| | | SEC[d] | NMR[e] | Calcd. | | mm | mr | rr |
| 1[b] | none | 4200 | 4800 | | 6.37 | 79.6 | 16.4 | 4.0 |
| 2[c] | | 4400 | 4800 | | 9.10 | 81.5 | 15.6 | 2.9 |
| 3[b] | $n$-Bu$_3$Al | 6700 | 8600 | | 1.42 | 4.1 | 18.3 | 77.6 |
| 4[c] | | 2800 | 2800 | 2600 | 1.07 | 6.0 | 13.1 | 80.9 |
| 5[b] | MeAl(ODBP)$_2$ | 3100 | 3300 | | 1.21 | 13.3 | 64.7 | 22.0 |
| 6[c] | | 3000 | 3100 | | 1.21 | 13.8 | 65.8 | 20.4 |
| 7[b] | EtAl(ODBP)$_2$ | 2700 | 2800 | | 1.09 | 6.0 | 13.8 | 80.2 |
| 8[c] | | 2900 | 2900 | | 1.10 | 5.3 | 14.6 | 80.1 |

[a]Toluene 10 mL, BnTMSNLi 0.4 mmol, Al/Li = 3, MMA 10 mmol, yield 100%. [b]Addition order; aluminum compounds, BnTMSNLi, MMA. [c]Addition order; aluminum compounds, MMA, BnTMSNLi. [d]Determined by SEC in THF (PMMA standards). [e]Determined by 400 MHz $^1$H NMR (CDCl$_3$, 55 °C).

3 N HCl, and then the chloroform was evaporated to dryness.

*Measurements*

$^1$H NMR spectra were measured in chloroform-*d* at 55 °C on a JEOL JNM400 spectrometer operated at 400 MHz. Tacticities of PMMAs were determined from $\alpha$-methyl hydrogen signals. $M_n$ was determined by $^1$H NMR spectroscopic end-group analysis, by using benzylmethylene proton signal (4.2 ppm) of the initiator fragments and methoxy methyl proton signal (3.7 ppm). $M_n$ and molecular weight distribution (MWD) were also determined by size exclusion chromatography (SEC) using a JASCO TRI ROTAR-V chromatograph equipped with Polymer Laboratories SEC columns MIXED-C × 2 (7.5 mm i.d. × 300 mm) using THF as an eluent at 40 °C. SEC chromatograms were calibrated against standard PMMA samples (Shodex).

## RESULTS AND DISCUSSION

Polymerization of MMA with BnTMSNLi in combination with $n$-Bu$_3$Al, MeAl(ODBP)$_2$ or EtAl(ODBP)$_2$ (1/3) was conducted in toluene at $-78°C$ and the results were summarized in Table I. In the first series of experiments, the reagents were added to toluene in the following order; aluminum compounds, BnTMSNLi, and monomer, as reported for the polymerization with $t$-BuLi/aluminum compounds.[7–18] The polymerization with BnTMSNLi alone gave PMMA in a good yield but with broad MWD in low initiator efficiency (run 1). In contrast, the polymerizations with BnTMSNLi/MeAl(ODBP)$_2$ (run 5) and BnTMSNLi/EtAl(ODBP)$_2$ (run 7) afforded PMMAs which had controlled molecular weights and narrow MWDs. In the case of BnTMSNLi/$n$-Bu$_3$Al, however, $M_n$ was fairy larger than the expected one and

the MWD was relatively broad (run 3). We anticipated that BnTMSNLi formed a complex with $n$-Bu$_3$Al such as ate complex and lost nucleophilic addition reactivity, while MeAl(ODBP)$_2$ and EtAl(ODBP)$_2$ were too bulky to form such complexes at least at $-78\,°C$. To avoid such kind of complex formation prior to the initiation reaction, we attempted to change the addition order of the reagents as aluminum compounds, monomer and BnTMSNLi so that the initiation reaction takes place before the complex formation. The polymerizations with BnTMSNLi alone and with BnTMSNLi/MeAl(ODBP)$_2$ or BnTMSNLi/EtAl(ODBP)$_2$ were not affected significantly by the change of the addition order (runs 2, 6, 8). On the contrary, the addition order exerted great influence on the polymerization with BnTMSNLi/$n$-Bu$_3$Al (run 4). The initiator efficiency was so much improved that the $M_n$ value became close to the calculated one and the MWD was narrower. These results support above-mentioned anticipation that BnTMSNLi forms the complex with $n$-Bu$_3$Al but not with MeAl(ODBP)$_2$ or EtAl(ODBP)$_2$.

Figure 1a illustrates $^1$H NMR spectrum of PMMA prepared with BnTMSNLi/$n$-Bu$_3$Al (Table I, run 4). Since the polymerization was terminated with HCl–MeOH, it is expected that the trimethylsilyl group in the initiator fragment is easily eliminated and hydrochloride salt of PMMA with benzylamino end-group is produced. In fact, the PMMA did not show trimethylsilyl group signal around 0 ppm, and exhibited ammonium proton signals at lower magnetic field. Aromatic and benzyl methylene proton signals, which derived from the initiator fragment, were observed around 7.6, 7.4, and 4.2 ppm, respectively. Moreover, the spectrum showed methylene proton signals of the first monomer unit, which attached to the amino end-group. $M_n$ estimated from integral in-
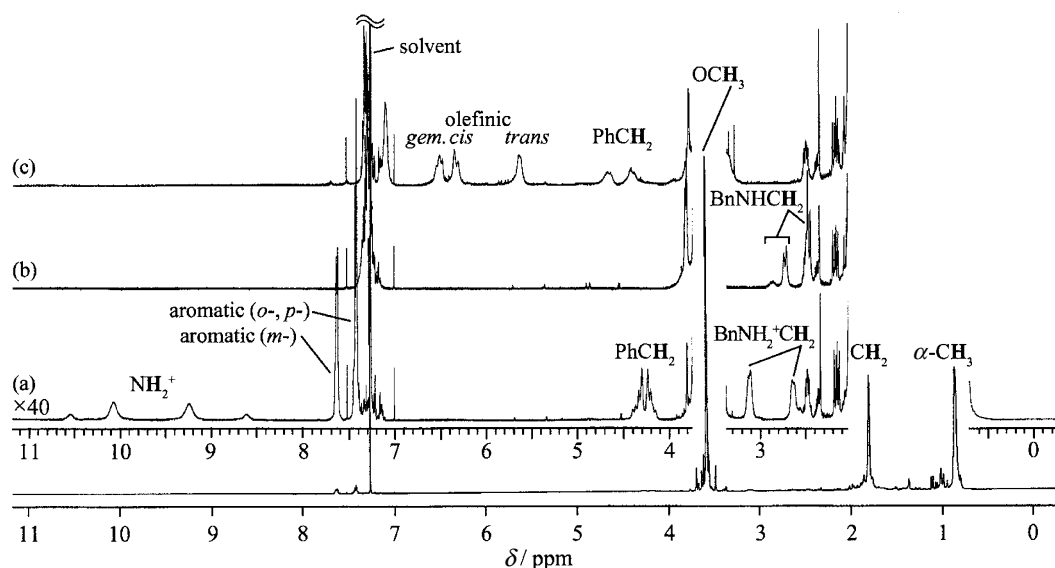
**Figure 1.** $^1$H NMR spectra of PMMA (CDCl$_3$, 55 °C). (a) $\alpha$-Benzylamino-PMMA hydrochloride salt, (b) $\alpha$-benzylamino-PMMA, (c) $\alpha$-($N$-acryloylbenzylamino)-PMMA.

tensity ratio of benzyl and methoxy proton signals was close to the expected value, suggesting high initiator efficiency (> 0.9). The fact that the $M_n$ estimated by $^1$H NMR end-group assay also agreed with the value determined by SEC analysis indicates that each polymer molecule has one benzyl amino group. The polymers obtained by BnTMSNLi/MeAl(ODBP)$_2$ or BnTMSNLi/EtAl(ODBP)$_2$ gave similar spectra. Tacticities of the produced polymers were isotactic rich ($mm \approx 80\%$) in the case of BnTMSNLi alone. Heterotactic rich polymers ($mr \approx 65\%$) were obtained with BnTMSNLi/MeAl(ODBP)$_2$, and syndiotactic rich ones ($rr \approx 80\%$) with BnTMSNLi/$n$-Bu$_3$Al and BnTMSNLi/EtAl(ODBP)$_2$. The polymerization of MMA with $t$-BuLi/$n$-Bu$_3$Al gives the polymer with higher $rr$ content ($rr > 90\%$).[7,8] Syndiotacticity of the polymers obtained in the present work was estimated relatively low, partly due to the overlap signals of monomer units at and near chain ends.

In order to confirm the existence of the amino end-group, a chloroform solution of the polymer was shaken with aqueous NaHCO$_3$ to convert the ammonium salt to free amine. In the $^1$H NMR spectrum of the polymer after treatment with NaHCO$_3$ (Figure 1b), ammonium proton signals around 10 ppm disappeared and methylene proton signals at 3.1 and 2.6 ppm shifted to higher field. Aromatic proton signals around 7.6 and 7.4 ppm shifted to overlap CHCl$_3$ signal, and benzyl methylene proton signal at 4.2 ppm was assumed to shift to overlap methoxy signal. When this polymer was treated with aqueous HCl, the $^1$H NMR spectrum became identical to that in Figure 1a, which indicates the reversible protonation of amino group.

To further confirm the presence of the amino group

and its feasibility of further derivatization, the PMMA was reacted with acryloyl chloride to convert the end group to $N$-acryloylbenzylamino group. Figure 1c illustrates the spectrum of the obtained polymer, which demonstrates the existence of acrylamide group. $M_n$ calculated from integrations of methoxy and olefinic protons was 2800, which is consistent with the value of the starting polymer. Thus, it is proved that the reaction was quantitative, and that the amino end-group had high reactivity enough for quantitative conversion.

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