Trialkylsilyl-Protected Functional Initiators for Stereospecific Anionic Polymerization of Methacrylates

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Summary: Anionic polymerizations of methyl methacrylate with trialkylsilyl-protected lithium benzylamides were conducted in the presence of aluminum compounds such as *n*-Bu_3Al. When the Me_3Si-protected amide was used, the carbonyl attack took place to some extent to form a methacrylamide derivative with slightly lower initiator efficiency (~0.9). In the case of *i*-Pr_3Si-protected amide, the carbonyl addition was completely suppressed. The obtained polymers had narrow molecular weight distribution and carried benzylamino end-group, as revealed by NMR analysis, which is readily accessible for further chemical transformations such as acylation with acryloyl chloride and debenzylation with H_2/Pd-C. Difuntional initiators with protected groups were also examined.

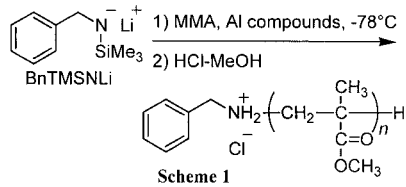
Keywords: anionic polymerization; initiators

Introduction

End-functional polymers have attracted much attention since they can be used for constructing more elaborated polymer chain architectures. Anionic initiators which comprise a functional group or its precursor have been utilized to obtain end-functional polymers [1]. However, living anionic polymerizations of acrylic monomers often require careful selection of initiators to suppress several types of side reactions in initiation process such as carbonyl addition, which have limited the utility of the functional anionic initiators for the acrylate polymerization.

Lithium *N*-benzyltrimethylsilylamide (BnTMSNLi) has been reported to undergo conjugate addition to methyl crotonate exclusively [2]. The present work aims at obtaining end-functional poly(meth)acrylates by exploring the possibility of utilizing BnTMSNLi as a functional initiator in combination with aluminum Lewis acids which are known as effective additives for stereospecific living polymerization of (meth)acrylates (**Scheme 1**).

The polymer obtained carries benzylamino group at the initiating chain-end [3], which can be removed by the treatment with H_2/Pd-C to form a PMMA with primary amine



Scheme 1

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function at the chain end. Several other trialkylsilyl-protected lithium benzylamides and their difunctional derivatives were also synthesized, and the effect of the trialkylsilyl groups on the polymerization mechanism was minutely investigated.

Experimental

N-benzyltrimethylsilylamine and other trialkylsilyl-protected benzylamines (BnR_3SiNH) were synthesized from benzylamine and R_3SiCl (R_3Si; *tert*-butyldimethylsilyl=TBS, triisopropylsilyl=TIPS). Trialkylsilyl-protected lithium amides (BnR_3SiNLi) were prepared from BnR_3SiNH and *n*-BuLi. The procedures for BnTMSNLi were described previously [3]. BnTBSNLi and BnTIPSNLi were prepared and analyzed similarly.

Polymerizations were carried out in glass ampoules filled with dried nitrogen. Dried toluene and aluminum compounds were added and then cooled to polymerization tempertures. The monomer and the lithium amides were added in this order to initiate the polymerization. The reactions were terminated by adding MeOH containing aqueous HCl.

NMR spectra were measured in $CDCl_3$ at 55°C, CD_3CN at 75°C or dimethylsulfoxide (DMSO)-d_6 at 110°C. *M*n of PMMAs was determined by ^1H NMR spectroscopic end-group analysis, by using benzylmethylene proton signal (4.2ppm) of the initiator fragments and methoxy methyl proton signal (3.7ppm). *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 (7.5mm *i.d.* × 300mm) using THF as an eluent at 40°C with standard PMMA (Shodex) calibration.

Results and discussion

Polymerization with BnTMSNLi Polymerization of MMA with BnTMSNLi in combination with *n*-Bu_3Al, bis(2,6-di-*tert*-butylphenoxy)methylaluminum [$MeAl(ODBP)_2$] or bis-(2,6-di-*tert*-butylphenoxy)ethylaluminum [$EtAl(ODBP)_2$] (1/3) was conducted in toluene at −78°C (**Table 1**). The polymerization with BnTMSNLi alone gave PMMA in a quantitative yield but with broad MWD in low initiator efficiency. Polymerizations with BnTMSNLi / $MeAl(ODBP)_2$ (runs 5, 6) and BnTMSNLi / $EtAl(ODBP)_2$ (runs 7, 8) afforded PMMAs with controlled molecular weights and narrow MWDs. In the case of BnTMSNLi / *n*-Bu_3Al, however, addition order of the reagents affected the polymerization greatly (runs 3, 4). The initiator efficiency was considerably low and the obtained polymer had rather broad MWD when MMA was added to the premixed solution of BnTMSNLi and *n*-Bu_3Al (run 3).

^{13}C NMR experiments of the initiator solution revealed that complex formation between BnTMSNLi and *n*-Bu_3Al caused the lower initiator efficiency as well as broader MWD.

Figure 1 shows ^1H NMR spectra of PMMA with α-benzylamino-group in hydrochloride form, neutralized α-benzylamino-PMMA, and α-(*N*-acryloylbenzylamino)-PMMA. Conversions of the end-group transformation were quantitative in all the cases. Treatment of the former two PMMAs with H_2/Pd-C produced PMMAs with primary amine terminus. The initiators were also effective for the polymerization of other methacrylates and acrylates. In the polymerization of allyl methacrylate, BnTMSNLi with $MeAl(ODBP)_2$ and

Table 1. Polymerization of MMA with BnTMSNLi / aluminum Lewis acids in toluene at -78°C for 24hr.[a]

run	aluminum Lewis acid	*M*n[b] SEC[e]	*M*n[b] NMR[f]	*M*w[e] / *M*n
1[c]	none	4200	4800	6.37
2[d]		4400	4800	9.10
3[c]	*n*-Bu_3Al	6700	8600	1.42
4[d]		2800	2800	1.07
5[c]	$MeAl(ODBP)_2$	3100	3300	1.21
6[d]		3000	3100	1.21
7[c]	$EtAl(ODBP)_2$	2700	2800	1.09
8[d]		2900	2900	1.10

[a] Toluene 10ml, BnTMSNLi 0.4mmol, Al/Li = 3, MMA 10mmol, yield 100%. [b] Expected *M*n is 2600. [c] Addition order; toluene, aluminum Lewis acid, BnTMSNLi, MMA. [d] Addition order; toluene, aluminum Lewis acid, MMA, BnTMSNLi. [e] Determined by SEC in THF (PMMA standards). [f] Determined by ^1H NMR ($CDCl_3$, 55°C).

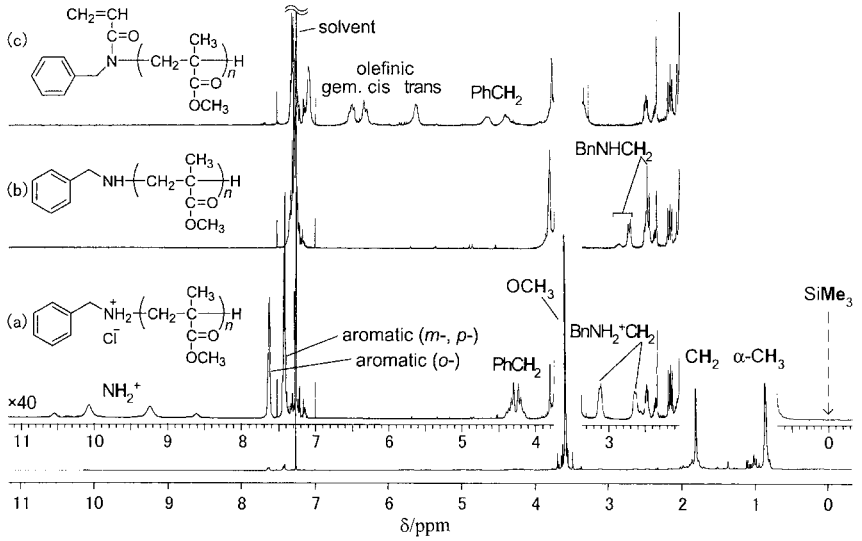


Figure 1. 400MHz 1H NMR spectra of PMMA ($CDCl_3$, 55°C). (a) α-benzylamino-PMMA HCl salt
(b) α-benzylamino-PMMA (c) α-(N-acryloylbenzylamino)-PMMA.

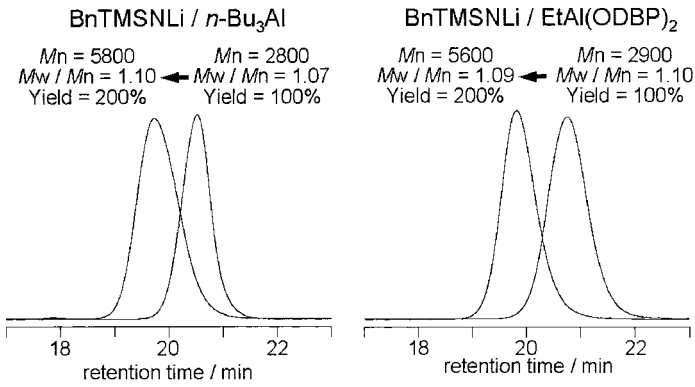


Figure 2. Livingness of polymerization of MMA with BnTMSNI in combination with n-Bu_3Al or $EtAl(ODBP)_2$ in toluene at −78°C.

$EtAl(ODBP)_2$ gave heterotactic and syndiotactic polymers, respectively. In the case of n-butyl acrylate, BnTMSNLi / $EtAl(ODBP)_2$ produced a syndiotactic polymer with narrow MWD.

In order to examine whether BnTMSNLi / aluminum Lewis acids systems are living or not, a second portion of MMA (1 eq. to the first portion) was added to a solution of the polymerization mixture after the first portion of MMA had been completely consumed. In both cases of BnTMSNLi / n-Bu_3Al and BnTMSNLi / $EtAl(ODBP)_2$, obtained polymers had nearly doubled Mn with narrow MWD, proving the livingness of these systems (**Figure 2**).

Effects of R_3Si-group on polymerization of MMA with BnR_3SiNLi Other trialkylsilyl-protected lithium amides such as BnTBSNLi and BnTIPSNLi were also synthesized and used as initiator in combination with aluminum Lewis acids for MMA polymerizations (**Table 2**). All the initiating systems afforded PMMAs in quantitative yields, and the values of Mn and MWDs of the obtained polymers were not so different from the ones obtained with BnTMSNLi. However, the addition order of the reagents did not affect the polymerization in the cases of BnTBSNLi/n-Bu_3Al and BnTIPSNLi / n-Bu_3Al systems but in the case of BnTMSNLi/n-Bu_3Al, as described previously. The results suggest that the less reactive *ate*-complex formation does not occur between n-Bu_3Al and BnTBSNLi or BnTIPSNLi at least −78°C, probably due to larger steric hindrance of TBS- and TIPS-groups than TMS-group.

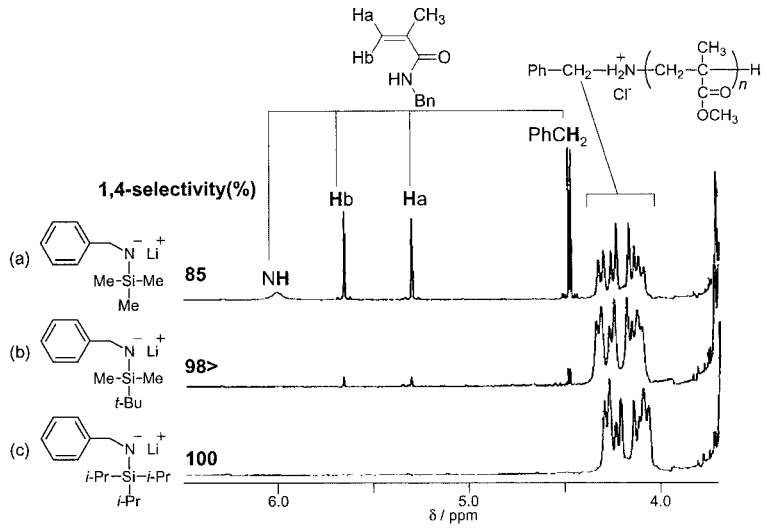
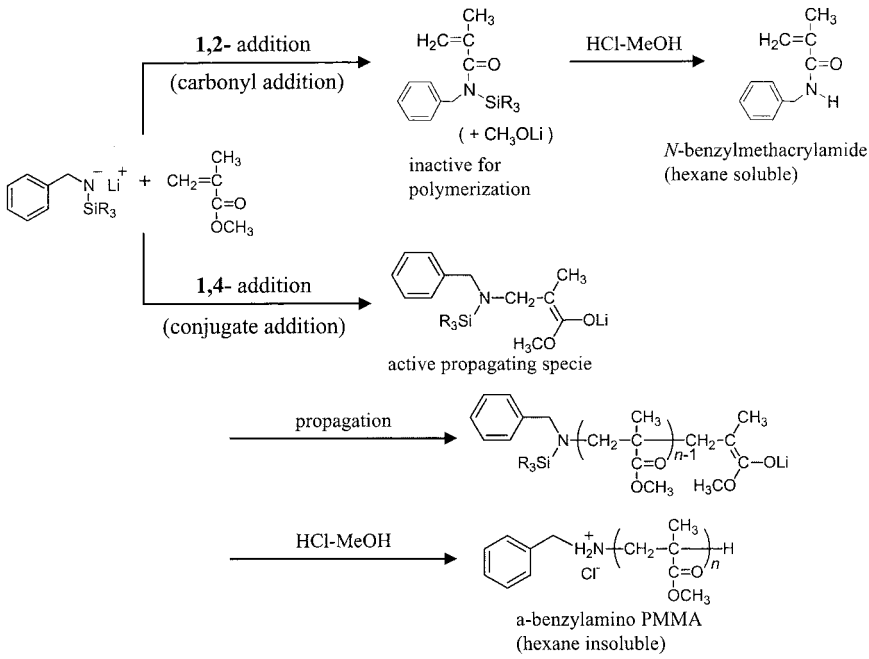


Figure 3. 500MHz ^{1}H NMR spectra of PMMAs prepared with (a) BnTMSNLi/Bu_3Al and (b) BnTBSNLi/*n*-BU_3AL and (c) BnTIPSNLi/*n*-Bu_3Al ($CDCl_3$, 55°C).

Though almost no difference was found in the polymers obtained with these lithium amides, the ^{1}H NMR spectra of the crude polymerization mixtures with BnTMSNLi / *n*-Bu_3Al, recovered without precipitation, indicate several characteristic signals even in olefinic region (**Figure 3**), which were not seen in the spectra of the polymers precipitated in hexane. From the analyses of the hexane-soluble part of the crude mixture by ^{1}H NMR, ^{13}C NMR and mass spectrometry, the signals were assigned to *N*-benzylmethacrylamide, which should be produced by carbonyl addition of the lithium amide to MMA. In the initiation process, BnTMSNLi attacked to the carbonyl function of MMA to form *N*-trimethylsilyl-*N*-benzylmethacrylamide with release of lithium methoxide. *N,N*-disubstituted methacrylamide derivatives are known to lack in anionic polymerization ability, except for methacryloyl aziridine [4]. In fact, MALDI-TOF mass analysis of the ologomers indicated no methacrylamide units in the chain. Thus, this silyl-protected methacrylamide was left intact during the polymerization, and converted to *N*-benzylmethacrylamide by desilylation with HCl-MeOH addition (**Scheme 2**).

Based on the above-mentioned results, quantitative analyses of the benzylamino chain-end of the polymer and the methacrylamide in the crude polymerization products were made by ^{1}H NMR to estimate the ratios of normal initiation (conjugate addition or 1,4-addition) and side reaction (carbonyl addition or 1,2-addition) in the initiation step of the polymerization.

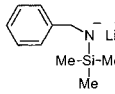
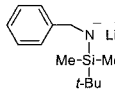
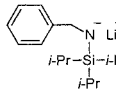


Scheme 2. 1,2- and 1,4- addition in the initiation reaction of MMA by R_3Si-protected lithium benzylamide.

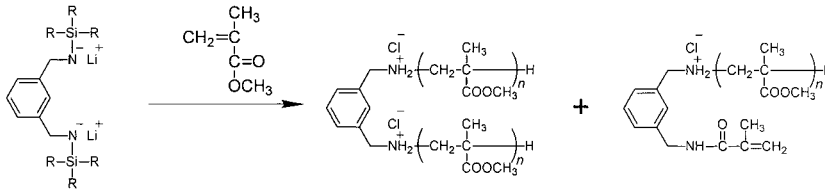
Partial ^1H NMR spectra of crude polymerization mixtures obtained with other BnR_3SiNLi / *n*-Bu_3Al are also shown in **Figure 3**. Obviously, the ratios of 1,4-addition increased with bulkier silyl group in lithium amides used, and BnTIPSNLi protected with the largest TIPS group perfectly suppresses the generation of the methacrylamide. This indicates that bulky silyl group effectively prevents 1,2-addition. The existence of aluminum Lewis acids causes almost no changes in 1,4-selctivity in the polymerization reaction. The addition orders of the reagents also did not affect the selectivity. These facts indicate that the selectivity in initiation reaction mainly depends on the structure (bulkiness) of the lithium amides. The methacrylamide formation does not cause a serious problem for end-functional polymer synthesis. However, we have recently found that polymerizations of MMA by difunctional lithium amide initiators with similar structures as BnR_3SiNLi were directly affected by the R_3Si-protecting groups; 1,2-addition resulted in the formation of PMMA with a methacrylamide function whose molecular weight is a half of the expected one, and thus the initiator with TIPS protecting groups was inevitable [5] (**Scheme 3**).

With the amide carrying TIPS protecting groups, the formation of PMMA with a methacrylamide function was completely suppressed.

Table 2. Polymerization of MMA with BnR_3SiNLi / aluminum Lewis acids at −78°C in toluene for 24hr[a].

BnR_3SiNLi	Aluminum Lewis acids	*Mn* SEC[c]	*Mn* ^{1}H NMR[d]	*Mn* Calcd.	*Mw*[c] *Mn*
 BnTMSNLi	none	2800	3000	2600	15.66
	n-Bu_3Al	2700	2800		1.08
	n-Bu_3Al[b]	6700	8600		1.42
	$EtAl(ODBP)_2$	2700	2800		1.09
 BnTBSNLi	none	2700	2700	2600	6.11
	n-Bu_3Al	2700	2700		1.08
	n-Bu_3Al[b]	2700	2700		1.08
	$EtAl(ODBP)_2$	2700	2600		1.11
 BnTIPSNLi	none	3300	3100	2600	8.35
	n-Bu_3Al	2800	2800		1.11
	n-Bu_3Al[b]	2900	2900		1.09
	$EtAl(ODBP)_2$	2700	2600		1.15

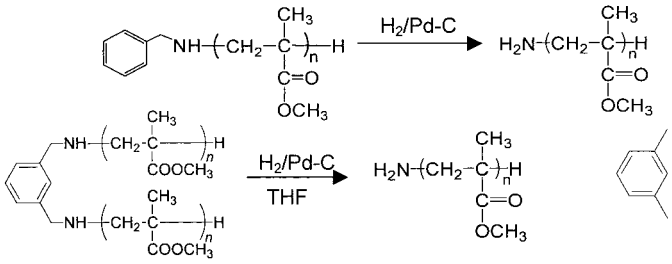
a MMA 10 mmol, BnR_3SiNLi 0.4 mmol, Al 1.2 mmol, toluene 10 ml.
Addition order; toluene, Al, MMA, BnR_3SiNLi. Yields are quantitative.
b Addition order; toluene, Al, BnR_3SiNLi, MMA.
c Determined by SEC(PMMA standards).
d Determined by 500 MHz ^{1}H NMR($CDCl_3$, 55°C).



Scheme 3. Polymerization of MMA with difunctional lithium amide.

The benzylamino group at the chain end can be eliminated by the reaction with H_2/Pd-C as well known. Typically, the reaction of the PMMA is conducted in THF or dichloromethane at room temperature by bubbling H_2 gas in the presence of Pd-C. By applying this chemistry to the PMMA prepared with the TIPS-protected difunctional initiator, the chain lengths of the two PMMA chains emanating from the central xylylene unit were examined by SEC analysis of the product (**Scheme 4**). The chromatogram of

the hydrogenation product exhibited a narrow MWD and a half *Mn* of the original PMMA, confirming that the both lithium amide sites of the initiator effectively initiated the polymerization to grow the PMMA chains of the almost identical chain length (**Figure 4**).



Scheme 4. Debenzylation reaction and its application to a PMMA formed with a difunctional initiator.

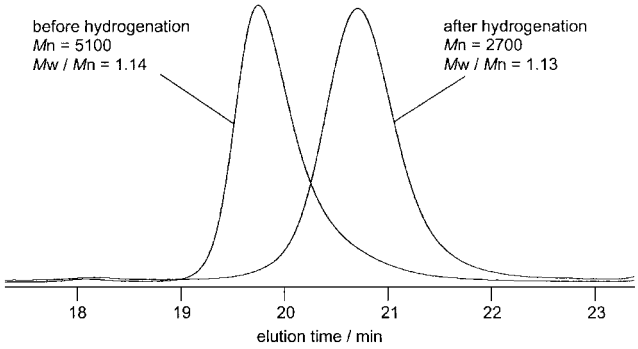


Figure 4. SEC chromatograms of the PMMA prepared with the difunctional initiator and its hydrogenation product.

Conclusion

Silyl-protected lithium amides are uniquely effect anionic initiators for the polymerization of acrylic monomers to provide end-functional polymers with benzylamino functions. Moreover, the benzylamino groups are easily eliminated by hydrogenation with Pd-C to give primary amino-functional polymers. As a consequence, the initiators may be categorized as doubly protected lithium amide compounds. We are currently extending the possibility of the living polymerization systems to obtain a heterotelechelic PMMA with amino group at one end and carboxyl function at the other.

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