A Capping Method for Nitrogen Anion Initiated Living Anionic Polymerization for Synthesizing Alkyl Methacrylate Macromonomers

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ABSTRACT: Lithium alkylamides are important functional initiators for anionic polymerization of methacrylates, but only sterically hindered ones can initiate a successful living polymerization. A capping method is reported here to modify nitrogen anion initiators (capping reaction) for living anionic polymerization of alkyl methacrylates. Dimethylacrylamide (DMA) and *tert*-butyl methacrylate (^{t}BMA) were found to be effective capping agents for lithium diallylamide. After capped with DMA or ^{t}BMA, the initiator efficiency of lithium diallylamide was increased from 0.1 to 0.9 for various monomers. Monosubstituted lithium alkylamides (vinyloxypropylamide and allylamide) could not directly initiate the polymerization of methacrylates due to severe reaction with the carbonyl groups in the monomers. After capped with DMA, the initiators polymerized methacrylates with initiator efficiency about 0.4−0.6, depending on the monomer type. ^{t}BMA was not suitable as capping agent for the monosubstituted lithium amides. Using these capped initiators, we subsequently synthesized block copolymers. ^{1}H NMR demonstrated that all the polymers prepared had terminal unsaturated groups from the initiators.

Introduction

Living anionic polymerization is very versatile for the synthesis of well-defined polymers with precisely controlled molecular structure and molecular weight[1,2] as well as functionalities.[3,4] Typical initiators for anionic polymerization are carbon anion compounds such as butyllithium. Recently, nitrogen anions were also used for anionic polymerization of methacrylates.[6−8] The nitrogen anion initiators are of particular interest because the resulting polymers are terminally amino-functionalized, which provides building blocks for functional ionomers after quaternization with alkyl halide or acid.[9,10] Another important application of nitrogen anion initiated polymerization is the synthesis of macromonomers,[11] since nitrogen anions are active enough to initiate the polymerization of various methacrylates, but do not react with some unsaturated groups such as allyl, vinyloxy, and styrenic groups at low temperature.[11] However, similar to the carbon anion initiators, the limitation to nitrogen anion initiators is that only sterically hindered initiators can successfully initiate living anionic polymerization of methacrylates.[8] For example, lithium diisopropylamide initiated a living polymerization of MMA with 94% initiator efficiency, while the less bulky initiator, lithium diethylamide, had only 26% initiator efficency,[8] and lithium monoalkylamide could not initiate methacrylate polymerization because of serious reaction of the nitrogen anion with carbonyl groups.[11] This strict requirement limits the application of nitrogen anion initiators.

In this paper, we report a general capping method with dimethylacrylamide (DMA) or *tert*-butyl methacrylate (^{t}BMA) for nitrogen anion initiators to improve their efficiency. After capping, the efficiency of less bulky lithium amide initiators such as lithium diallylamide was increased from 0.1 to 0.9, and that of lithium monoalkylamide was increased from 0 to 0.6. Macromonomers were subsequently prepared and characterized.

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Experimental Section

Reagents and Solvents. Methyl methacrylate (MMA), 2-dimethylaminoethyl methacrylate (DMAEMA), dimethylacrylamide (DMA) and *tert*-butyl methacrylate (^{t}BMA) from Aldrich were stirred over CaH_2 for 24 h, distilled from CaH_2, washed with triethylaluminum and redistilled again under a reduced pressure. LiCl (99.9%) from Aldrich was dried at 130 °C and then dried again at 100 °C under vacuum just before use. THF was refluxed over potassium under nitrogen atmosphere. Diallyamine (DA), allylamine (AA), and 3-aminopropyl vinyl ether (VPE) were stirred and distilled over CaH_2. A solution of *sec*-butyllithium in hexane (1.3 M) (^{s}BuLi) was purchased from Aldrich and its concentration was titrated by a standard method.

Preparation of Initiator and Polymerization. A typical polymerization procedure was as follows: To a glass reactor previously treated with chlorotrimethylsilane and flame dried, 0.0685 g of LiCl was added, heated at 100 °C under vacuum, and purged with nitrogen 5 circles. Then 30 mL of THF and 0.0511 g of diallylamine were charged to the reactor. The reactor was cooled to −78 °C by dry ice. A solution of butyllithium (0.41 mL, 1.3 M) was dropwise added with stirring. After 30 min, 0.10 g dimethylacrylamide (DMA) in 1 mL of THF was introduced and stirred at −78 °C for 1 h. Then 3.38 mL MMA was introduced to the reactor. After 2 h, the polymerization was terminated by adding 0.2 mL of methanol. The aliquot was poured into 200 mL of a petroleum ether mixture. The precipitate was separated and dried in a vacuum at 30 °C for 24 h. A yield of 3.14 g of PMMA was obtained.

Isolation of the Reaction Products of Lithium 3-Vinyloxypropylamide with MMA. In a 100 mL flask, 0.20 g of 3-vinyloxypropylamine and 0.248 g of LiCl in 50 mL of THF was reacted with 1.52 mL of butyllithium solution (1.3 mol/L) at −78 °C, as described above. After 30 min of stirring, 0.20 g of MMA was added to the solution. The solution was further stirred for 30 min, 50 μL of water was then injected into the solution, and the mixture was stirred for 2 min. The volatile in the flask was removed at room temperature under vacuum and collected. The remnant left in the flask was dissolved in 2 mL of $CDCl_3$, and the resulting solution was subjected to ^{1}H NMR: 6.6 (broad, 1H, N*H*), 6.35 (q, 1H, =C*H*-O−), 5.64 and 5.24 (2H, CH_2=C(CH_3)), 4.18, 4.09, 3.98 and 3.94 (2H, CH_2=

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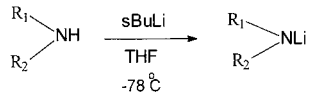
Scheme 1. Preparation of Alkylamide by the Reaction of Alkylamine with sBuLi



Allylamine: R_1 = H, R_2= CH_2=CH-CH_2- (LiAA)

Diallylamine: $R_1 = R_2$= CH_2=CH-CH_2- (LiDA)

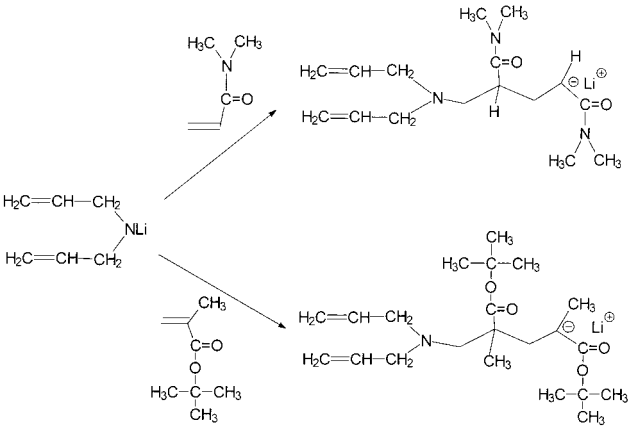
3-Vinyloxypropylamine: R_1=H, R_2= CH_2=CH-O-$CH_2CH_2CH_2$- (LiVPA)

Table 1. Methyl or *tert*-Butyl Methacrylate Polymerization Initiated by Lithium Diallylamide in the Presence of Lithium Chloride[a]

run	monomer	capping agent	convn (%)	M_n (calcd)	M_n (GPC)	initiator efficiency	M_w/M_n
1	MMA		92	3000	25 770	0.11	1.16
2	^{t}BMA		99	4100	4400	0.97	1.06
3	^{t}BMA		99	7110	7900	0.90	1.06
4	MMA	DMA	99	3000	3900	0.78	1.04
5	MMA	DMA	99	6000	6080	0.98	1.05
6	MMA	DMA	99	8000	8500	0.94	1.06
7	MMA	^{t}BMA	99	4100	4900	0.84	1.05
8	MMA	^{t}BMA	99	10 000	11 500	0.89	1.11
9	MMA	^{t}BMA	98	12 000	13 300	0.90	1.12
10	DMAEMA	^{t}BMA	99	4700	4900	0.96	1.03
11	DMAEMA	DMA	99	4200	4440	0.95	1.04

[a] [LiDA] = 0.017 mol/L in THF; LiCl/LiDA = 3; −78 °C.

Scheme 2. Capping Reaction of LiDA with DMA or ^{t}BMA



CH−O−), 3.72 (t, 2H, −O−CH_2), 3.35 (q, 2H, CH_2NH), 1.9 ppm (m, 5H, $CH_2CH_2CH_2$ and =C(CH_3)). To the collected volatile was added 0.2 g of CaH_2 powder, and it was stirred for 5 h. The solvent (THF) was removed under vacuum. Deuterium oxide (D_2O) was slowly added to the remaining solid. The mixture was centrifuged, and the clear D_2O solution was subjected to ^{1}H NMR: 3.10 ppm (CH_3O).

Characterization. Nuclear Magnetic Resonance (NMR) Spectroscopy. Proton (^{1}H) NMR spectra were recorded on a Bruker ARX-200 spectrometer at 200 MHz. ^{1}H NMR chemical shifts in $CDCl_3$ were reported downfield from 0.00 ppm using residual $CHCl_3$ signal at 7.23 ppm as an internal reference. When D_2O was used as solvent, the residual H_2O signal at 4.63 ppm was used as reference.

Molecular Weight Measurements. Number and weight-average molecular weights (M_n and M_w, respectively) were determined by gel permeation chromatography (GPC) using THF−2% (v/v) triethylamine as eluent at 25 °C with an RI detector. Narrow polystyrene standards (Polysciences) were used to generate a calibration curve (Varian MicroPak column G1000, 3000, 7000 HXL). Data were recorded and processed using the Windows-based Millenium 2.0 software package.

Results and Discussion

1. Diallylamine−BuLi System for Alkyl Methacrylate Polymerization. The lithium alkylamide was prepared in situ by reaction of alkylamine with butyllithium (Scheme 1). It was confirmed that butyllithium reacted with alkylamine by abstracting proton from NH or NH_2 to produce lithium amide, but it did not attack the unsaturated moieties in the initiator at −78 °C.[11]

The MMA polymerization with the resulting lithium diallylamide (LiDA) was investigated first, and the results are shown in Table 1. LiDA did initiate MMA polymerization at −78 °C with a 92% conversion and the produced polymer had a polydispersity as low as 1.16 (Table 1, entry 1). However, the molecular weight of PMMA was much higher than the calculated value. The initiator efficiency (M_n(calcd)/M_n(GPC)) was only 0.1. Changing experimental conditions such as increasing lithium chloride concentration and decreasing the initiator and monomer concentrations did not improve the initiator efficiency. It was suggested that low bulky lithium alkylamide, e.g., lithium diethylamide, associated in solution and therefore only part of the initiators, initiated the polymerization.[8] To help one to understand the cause of the low initiator efficiency of LiDA in MMA polymerization, ^{t}BMA was also polymerized under the same conditions (Table 1, entries 2 and 3). The polymerization of ^{t}BMA with LiDA proceeded completely, yielding polymers with precisely controlled molecular weight (initiator efficiency higher than 0.9) and narrow molecular weight distribution. This indicates that in the presence of LiCl, LiDA quantitatively initiated ^{t}BMA, which means that LiDA did not associate in the solution, and therefore, the low initiator efficiency of LiDA in MMA polymerization was not caused by association of LiDA. The disassociation nature of LiDA made it possible to be further modified. On the other hand, the low polydispersity of PMMA prepared with LiDA (Table 1, entry 1) suggests that the propagating anion did not experience termination or chain transfer reaction once the chain growth was started. The low initiator efficiency of LiDA in MMA polymerization was therefore attributed to the reaction of nitrogen anion attacking the carbonyl groups of the monomer and polymer, rather than due to their association.

Increasing the steric hindrance of the initiator substituents could minimize such side reaction. For example, ^{s}BuLi at −78 °C could not initiate MMA polymerization,[12,13] while diphenylhexyllithium was an efficient initiator for various alkyl methacrylates.[14] Dimethyl-

Scheme 3. Reaction of LiVPA with MMA

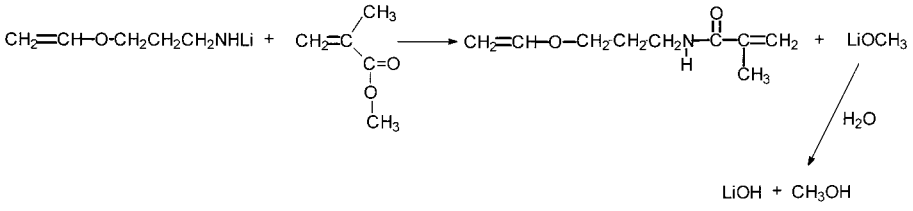


Table 2. Polymerizations of Alkyl Methacrylates Initiated by Primary Amine/*sec*-Butyllithium in the Presence of Lithium Chloride

entry	amine	capping agent	monomer	convn (%)	M_n (calcd)	M_n (GPC)	initiator efficiency	M_w/M_n
1	VPE		MMA	0				
2	VPE		DMAEMA	0				
3	AA		MMA	0				
4	VPE	BMA	MMA	99	3200	37 800	0.08	1.18
5	VPE	DMA	MMA	99	1500	5000	0.30	1.07
6	VPE	DMA	MMA	99	3200	8300	0.39	1.13
7	VPE	DMA/^{t}BMA	MMA	99	3300	6400	0.51	1.16
8	VPE	DMA/^{t}BMA	MMA	100	6300	13 200	0.48	1.23
9	VPE	DMA	BMA	98	4500	8300	0.54	1.12
10	VPE	DMA	BMA	99	7300	11 400	0.65	1.19
11	VPE	DMA	DMAEMA	98	2555	4700	0.54	1.14
12	VPE	DMA	DMAEMA	98	4900	8600	0.57	1.11
13	VPE	DMA	DMAEMA	99	9700	16 800	0.57	1.22
14	AA	DMA	DMAEMA	99	4900	8000	0.61	1.13

[a] [initiator] = 0.017 mol/L in THF; LiCl/LiVPA or LiAA = 3; −78 °C.

Table 3. Block Copolymerization of DMAEMA with MMA and ^{t}BMA[a]

entry	initiator	M1	M1/initiator	convn (%)	M_n	M_w/M_n	M2	M2/initiator	convn (%)	M_n	M_w/M_n
1	LiDA	DMAEMA	20	99	4000	1.03	MMA	20	99	6100	1.06
2	LiDA	DMAEMA	40	98	7200	1.08	MMA	40	100	11 600	1.07
3	LiDA	DMAEMA	30	98	4900	1.07	^{t}BMA	30	100	10 400	1.07
4	LiVPA	DMAEMA	30	98	8700	1.15	MMA	30	100	17 900	1.23
5	LiVPA	DMAEMA	30	98	8700	1.16	^{t}BMA	30	100	19 100	1.21

[a] [initiator] = 0.017 mol/L in THF; LiCl/LiDA or LiVPA = 3; −78 °C.

acrylamide (DMA) could be polymerized by carbon anion and its polymer was stable with carbon anion at −78 °C,[15] and *tert*-butyl methacrylate (^{t}BMA) had little side reaction with LiDA (Table 1, entries 2 and 3). These two chemicals were therefore used to modify LiDA (capping reaction) for the MMA polymerization. Lithium diallylamide was allowed to react with 2-fold (molar) DMA or ^{t}BMA prior to the monomer addition (Scheme 2).

In contrast to the very low initiator efficiency of uncapped LiDA, DMA- or ^{t}BMA-capped LiDA had initiator efficiencies higher than 0.9 in the polymerizations of MMA and dimethylaminoethyl methacrylate (DMAEMA) (Table 1, entries 4−11). The molecular weight was precisely controlled by the monomer/LiDA ratio. The polydispersities of PMMA were lower than 1.1. These results indicate that the modified anionic centers by DMA or ^{t}BMA efficiently initiated the MMA or DMAEMA polymerization by greatly suppressing the reaction with carbonyl groups.

2. Primary Amine−BuLi Initiated Polymerization. Primary amines (allylamine and 3-vinyloxypropylamine) were also used to prepare polymers with terminal unsaturated groups. Similar to the preparation of lithium diallylamide, lithium monoalkylamides (lithium 3-vinyloxypropylamide (LiVPA) and lithium allylamide (LiAA)) were also prepared by reacting corresponding primary amines with BuLi (Scheme 1). The polymerization results of different monomers by these initiators are shown in Table 2.

When lithium monoalkylamide (LiVPA or LiAA) was directly used, no polymer was obtained in either MMA or DMAEMA polymerization (Table 2, entries 1−3). The reaction mechanism of lithium monoalkylamide with methacrylate was examined by a 1:1 (molar) reaction of LiVPA and MMA (see Experimental Section). 3-Vinyloxypropyl methacrylamide and methanol were isolated from the reaction solution of LiVPA and MMA. This indicates that the monoalkylamide reacted with the carbonyl groups (Scheme 3) instead of initiating the monomer because of its low bulkiness of the substituents and high nucleophilicity of the nitrogen anions. Similar results were observed that ^{n}Bu- *or* ^{s}BuLi could not initiate MMA polymerizations.[12,13] Therefore, DMA and ^{t}BMA were also used to cap these monosubstituted

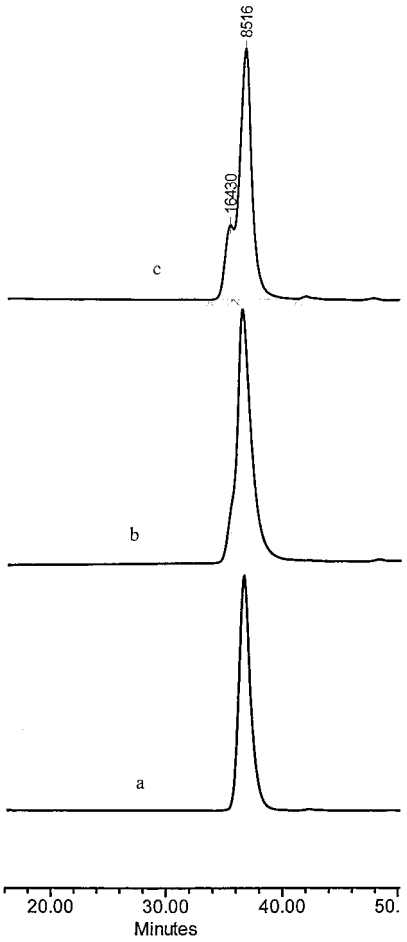
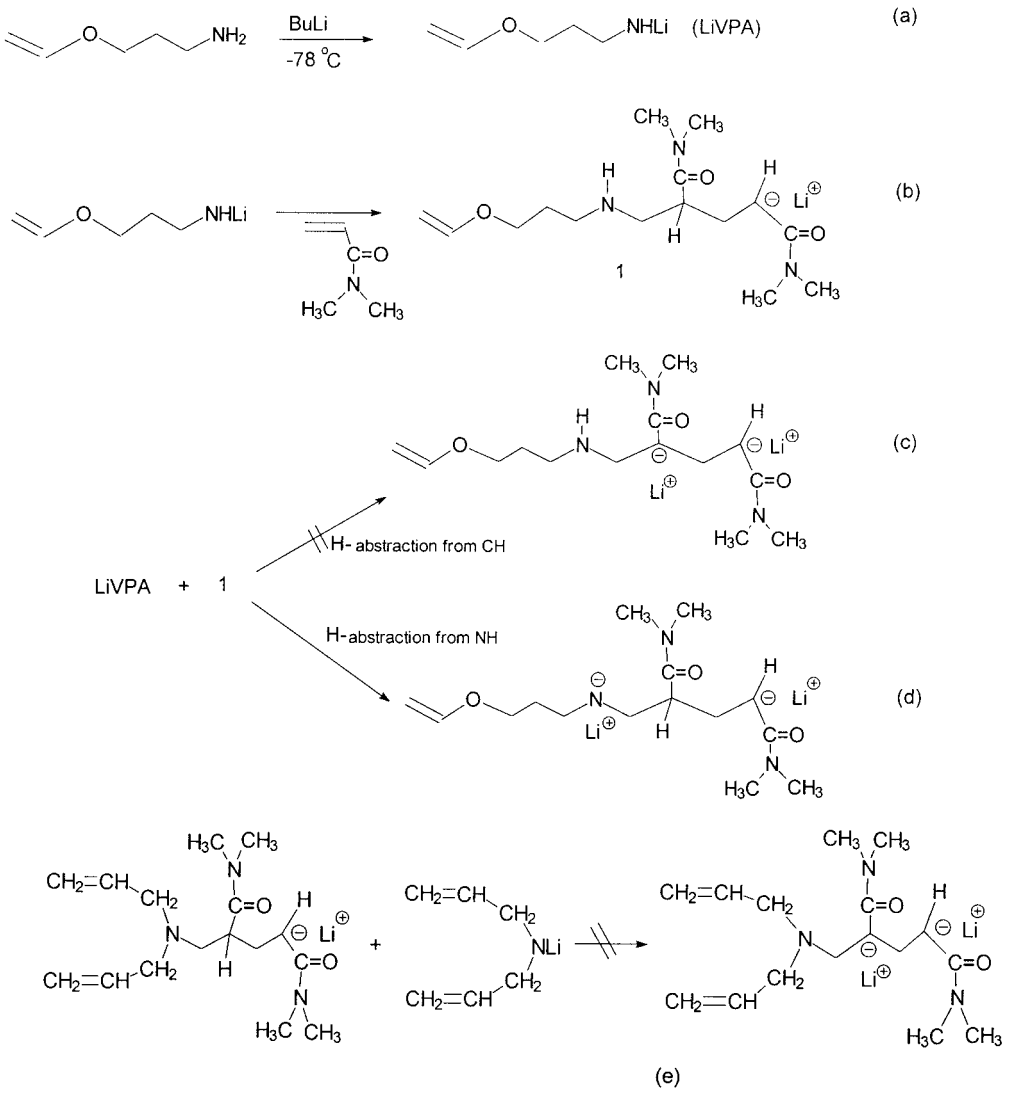


Figure 1. GPC traces: (a) PMMA (Table 1, entry 6); (b) PMMA (Table 2, entry 6); (c) polyDMAEMA (Table 2, entry 12).

Scheme 4. Deprotonation during Capping Reaction



lithium amides for polymerization (Table 2, entries 4−14). Though ^{t}BMA was a good capping agent for lithium diallylamide, it could not completely cap LiVPA. The ^{t}BMA-capped LiVPA had an initiator efficiency of about 0.08 (Table 2, entry 4). This indicates that monosubstituted lithium amide also reacted with the carbonyl group in ^{t}BMA. ^{t}BMA is therefore not a good capping agent for monosubstituted lithium amides. In contrast, capped with DMA, LiVPA had initiator efficiencies of about 0.3−0.4 for MMA polymerization and 0.5−0.6 for ^{t}BMA and DMAEMA polymerization. The initiator efficiency of LiVPA for MMA polymerization could be further improved by capping LiVPA with DMA first and then with ^{t}BMA (Table 2, entries 7 and 8). DMA-capped lithium allylamide had an initiator efficiency of 0.6 in the DMAEMA polymerization. These results demonstrated that when capped with DMA, the monosubstituted lithium alkylamide effectively initiated alkyl methacrylate polymerization, which greatly diversifies the application of nitrogen anion initiated anionic polymerization. The initiator efficiency of DMA-capped monosubstituted lithium alkylamide is comparable to those of oxygen anion initiated DMAEMA polymerization.[16]

The molecular weight distributions of the polymers prepared by DMA-capped LiVPA and LiAA were about 1.1, slightly broader than those by lithium diallylamide.

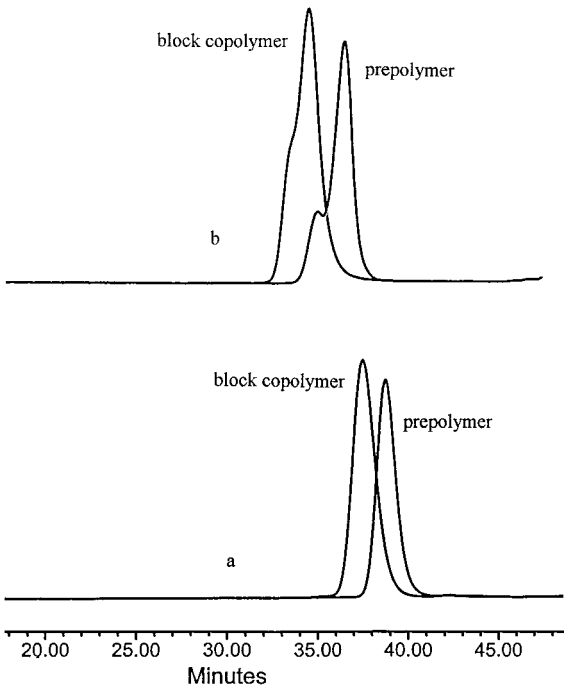


Figure 2. GPC traces of prepolymers and block copolymers: (a) Table 3, entry 1; (b) Table 3, entry 4.

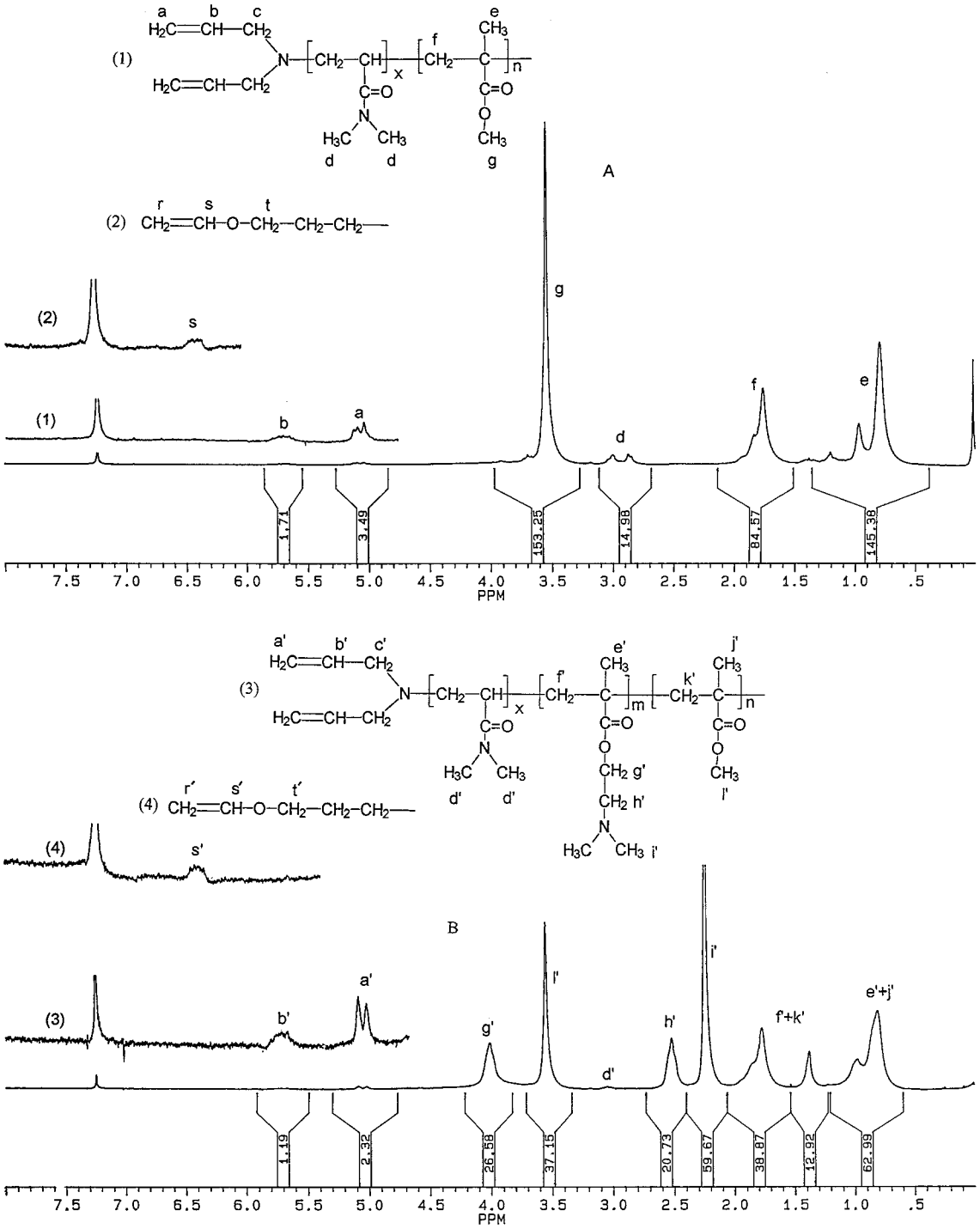


Figure 3. ^{1}H NMR spectra of PMMA (A) and polyDMAEMA−PMMA block copolymer (B). Key: (A) PMMA, (1), Table 1, entry 5; (2), Table 2, entry 6; (B) polyDMAEMA-*b*-PMMA (3), Table 3, entry 1; (4) Table 3, entry 4.

Figure 1 shows the GPC traces of PMMA and polyDMAEMA prepared by capped LiDA or LiVPA. PMMA and polyDMAEMA obtained from capped LiDA had narrow unimodal distribution, while the products prepared by DMA-capped LiVPA or LiAA were bimodal. The high-molecule weight peak had doubled molecular weight. Its intensity depended on the method of capping agent addition. If DMA was added dropwise, the peak became significant or even dominant. However, it could be greatly suppressed if the capping agent was added quickly.

The bimodal GPC traces of the polymers prepared by capped LiVPA or LiAA may be caused by the presence of bifunctional initiator species formed by deprotonation (Scheme 4). LiVPA reacted with DMA and generated a secondary amine (NH) group (Scheme 4b). The later added LiVPA abstracted proton from the secondary amine and created bifunctional initiator (Scheme 4d). LiVPA could not abstract the methine proton of the DMA unit (Scheme 4c), since DMA-capped lithium diallylamide produced polymers without shoulder peak (Figure 1), suggesting the absence of the reaction in Scheme 4e. The bifunctional initiator species produced polymers having doubled molecular weight.

3. Synthesis of Amphiphilic Diblock Macromonomers. PolyDMAEMA is a water-soluble polymer. The

block copolymer of DMAEMA with MMA or ^{t}BMA is amphiphilic. For example, PDMAEMA−PMMA block copolymer can form micelles in deionized water.[17,18] A macromonomer of the block copolymer, namely AB block-macromonomer, can be a useful precursor for targeted products by copolymerization. Taking advantage of the living polymerization initiated by capped initiators, the block copolymers of DMAEMA with MMA or ^{t}BMA bearing terminal unsaturated groups have been synthesized, as shown in Table 3.

LiDA or LiVPA capped with ^{t}BMA or DMA first initiated DMAEMA polymerization to give a living prepolymer. A second monomer was then introduced to produce block copolymer. For capped-LiDA initiated block polymerization, the molecular weights for both blocks were precisely controlled with low polydispersities. The GPC traces of the block copolymer were unimodal showing no sign of dead prepolymer (Figure 2 a). This suggests that the living DMAEMA prepolymer chains quantitatively initiated the second monomer. Similarly, DMA-capped LiVPA initiated DMAEMA and then MMA or ^{t}BMA to produce block copolymers. The molecular weight of the polymers with DMA-capped LiVPA as initiator had molecular weights higher than predicted for both blocks, similar to the results of the homopolymerization. The polydispersity for the block copolymer was about 1.2. The GPC traces of the block copolymer (Figure 2b) had a small shoulder peak at high molecular region, which was derived from a bifunctional initiator, similar to the homopolymer.

4. Characterization of the Polymer Structure. The macromonomer structures of the prepared homopolymers and block polymers using these functional initiators were characterized by ^{1}H NMR (Figure 3). For all MMA homocopolymers and block copolymers prepared from LiDA, the allyl group (CH_2═CH−CH_2−) signals appeared at 5.7 (═CH) and 5.05 ppm (CH_2═). For the polymers obtained from LiVPA, the vinyl signal (═CH−O−) was at 6.4 ppm. Other prepared polymers had similar results. The molecular weights calculated from the NMR spectra agreed with the GPC results. These results confirm that the polymers initiated by lithium diallylamide or vinyloxypropylamide, allylamide had terminal unsaturated groups. The vinyl group is readily copolymerizable with other vinyl monomers. The diallyl group is also a good copolymerizable unit after the diallylamino group is quaternized.[11,19]

Conclusion

A novel capping method was proposed for nitrogen anion initiated polymerization of alkyl methacrylates. For lithium diallylamide, both DMA and ^{t}BMA can be used as capping agent. But monosubstituted lithium amides require the use of DMA as capping agent. After capping, disubstituted lithium amide had initiator efficiencies up to 0.9 for all the monomers studied in this work, while DMA-capped monosubstituted lithium amide had initiator efficiencies of about 0.4−0.6, depending on monomer type. This capping method greatly diversifies the application of nitrogen initiators.

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