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Effect of Chelation of the Lithium Cation on the Anionic Polymerization of Methyl Methacrylate Using Organolithium Initiators[†]

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ABSTRACT: Benzyllithium (BzLi) and 1,1-diphenylhexyllithium (DPHLi) were used to inititate the anionic polymerization of methyl methacrylate (MMA) in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) in THF at −78 and −40 °C. PMMAs with predetermined molecular weights and narrow polydispersities could be obtained with benzyllithium initiator at −78 °C in THF in the absence of TMEDA. Interestingly, even at −40 °C, DPHLi in conjunction with TMEDA was able to provide PMMAs with control on molecular weight and polydispersity values of less than 1.2. The results are explained on the basis of the solvation of the Li^+ cation by TMEDA resulting in the stabilization of the propagating enolate anion.

Introduction

A major challenge in the living anionic polymerization of alkyl methacrylates is the suppression of side reactions occurring during initiation with classical initiators and the intramolecular solvation of the lithium counterion during the propagation step. Considerable effort has been expended in achieving living anionic polymerization of methyl methacrylate (MMA).[1−12] It has been shown that living anionic polymerization of MMA can be obtained by either using a sterically hindered stabilized carbanion such as 1,1-diphenylhexyllithium (DPHLi) or modifying the reactivity of the propagating enolate by added adjuvants such as alkoxides, crown ethers, alkali metal halides, etc. While DPHLi can successfully initiate MMA polymerization at −78 °C in tetrahydrofuran (THF), it has been shown[2] to be a poor initiator at −40 °C. The use of additives with organolithium initiators offers the advantage of controlled MMA polymerization at elevated temperatures.[5,7−9] Thus, a combination of organolithium initiator in conjunction with aluminum alkyls or dibenzo-18-crown-6 yields monodisperse poly(methyl methacrylate) (PMMA) with controlled molecular weight at 0 °C in toluene. However, when LiCl is used as an additive, it does not influence the termination reactions[10] and hence MMA has to be polymerized only at −78 °C for obtaining control.

We, therefore, reasoned that the intramolecular solvation of Li^+ during propagation could be suppressed by chelating the cation with *N,N,N′,N′*,-tetramethylethylenediamine (TMEDA). Extensive literature is available on the anionic polymerization of nonpolar hydrocarbon monomers[13−16] using TMEDA as an additive. However, its utility in the anionic polymerization of MMA has been far less studied. Matsuzaki *et al.*[17] employed TMEDA in conjunction with *n*-butyllithium (*n*-BuLi) for MMA polymerization in toluene at 0 °C and obtained only a 4% yield of PMMA. The objective of their work was only to investigate the effect of polar additives on the tacticity and yield of PMMA. The results are not surprising considering the fact that *n*-BuLi is not a good anionic initiator for MMA. Under the conditions employed, reaction of *n*-BuLi with toluene in the presence of TMEDA would lead to formation of only an insignificant amount of benzyllithium.

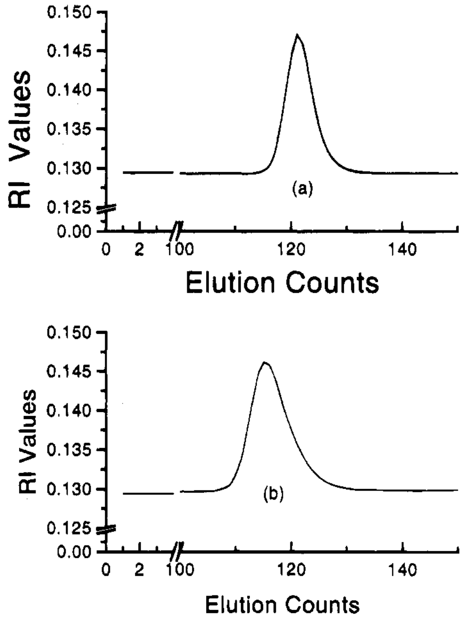

Figure 1. SEC traces for PMMAs prepared with (a) BzLi initiator without TMEDA, M_n = 19 200, M_w/M_n = 1.12 and (b) DPHLi with TMEDA (1:4 molar ratio) at −40 °C, M_n = 36 200, M_w/M_n = 1.21.

Therefore, we undertook a study of the anionic polymerization of MMA using DPHLi and benzyllithium (BzLi) in THF using TMEDA as an additive. The benzyl anion was chosen for this study because, unlike the styryl anion, it lacks the methyl group on the carbon atom, making it a more suitable candidate for initiating MMA anionically. Moreover, this anion has been far less investigated. Hatada *et al.*[18] employed BzLi as an initiator for the anionic polymerization of MMA at −78 °C in THF with a view to study the effect of organolithium initiators on the tacticity of PMMA. High polydispersity of 1.84 was obtained. Yield data were not reported.

Experimental Section

MMA (Aldrich) was stirred over CaH_2 for 24 h, distilled under vacuum, and stored under a nitrogen atmosphere. Just prior to polymerization, the required amount of MMA was

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Table 1. Influence of TMEDA on the BzLi-Initiated Anionic Polymerization at −78 °C in THF

10^4[BzLi] (mol)	[M] (mol)	[ligand]:[I] molar ratio	% yield[a]	$10^{-3}M_{n,calc}$[b]	$10^{-3}M_{n,SEC}$	M_w/M_n	$M_{n,SEC}/M_{n,calc}$
1.40	0.0280	0	97	19.45	19.20	1.12	0.99
0.76	0.0280	0	100	36.80	40.40	1.13	1.10
1.40	0.0280	1	100	20.05	20.90	1.11	1.04
0.38	0.0541	3	98	173.70	174.40	1.11	1.00
0.69	0.0280	3	100	40.63	42.00	1.11	1.03

[a] As precipitated from *n*-hexane. [b] $M_{n,calc} = \{[M]/[I]\} \times$ yield factor.

Table 2. Effect of TMEDA on the DPHLi-Initiated Anionic Polymerization in THF at −78 °C

10^4[I] (mol)	[M] (mol)	[ligand]:[I] molar ratio	% yield[a]	$10^{-3}M_{n,calc}$	$10^{-3}M_{n,SEC}$	M_w/M_n	$M_{n,SEC}/M_{n,calc}$
0.886	0.0280	0	100	31.60	28.7	1.18	0.91
0.886	0.0280	4	100	31.60	30.9	1.18	0.98

[a] As precipitated from methanol.

Table 3. Effect of TMEDA on the DPHLi-Initiated Anionic Polymerization in THF at −40 °C

10^4[I] (mol)	[M] (mol)	[ligand]:[I] molar ratio	% yield[a]	$10^{-3}M_{n,calc}$[b]	$10^{-3}M_{n,SEC}$	M_w/M_n	$M_{n,SEC}/M_{n,calc}$
1.47	0.0419	0	68	19.5	15.70	1.20	0.81
0.80	0.0280	0	68	23.8	36.60	1.22	1.54
0.88	0.0280	1	100	31.9	31.80	1.19	1.00
1.47	0.0367	3	100	25.0	25.65	1.16	1.03
1.54	0.0374	3	100	24.3	27.80	1.14	1.14
0.80	0.0280	4	100	35.0	36.20	1.21	1.03
0.80	0.0300	6	100	37.5	40.40	1.21	1.06

[a] As precipitated in methanol. [b] $M_{n,calc} = \{[M]/[I]\} \times$ yield factor.

Table 4. Effect of DPHLi-Initiated Anionic Polymerization in THF at −23 °C

10^4[I] (mol)	[M] (mol)	[ligand]:[I] molar ratio	% yield[a]	$10^{-3}M_{n,calc}$	$10^{-3}M_{n,SEC}$	M_w/M_n	$M_{n,SEC}/M_{n,calc}$
0.88	0.0280	0	68	32.0	38.7	1.44	1.21
0.88	0.0280	3	100	32.0	57.6	1.54	1.80

[a] As precipitated in methanol.

transferred into a distillation unit, treated with triisobutylaluminum solution drop by drop until a persistent yellowish green color developed,[19] and distilled under reduced pressure.

TMEDA obtained from Sisco, Bombay, was distilled over NaOH. It was redistilled over CaH_2 and stored over dry molecular sieves under a nitrogen atmosphere. THF was purified by refluxing over a deep purple sodium−benzophenone complex. It was collected under nitrogen and redistilled over oligo(styryllithium) just before polymerization.

1. Preparation of the 1:1 Adduct of *n*-Butyllithium and 1,1-Diphenylethylene (DPE). The required amount of *n*-BuLi was reacted with a little excess of DPE at −40 °C in THF, and the solution was allowed to gradually attain room temperature. A deep red color developed immediately in THF, indicating the formation of the 1,1-diphenylhexyl anion (DPHLi).

2. Preparation of the Benzyllithium (BzLi) Initiator. Tribenzyltin chloride, used in the synthesis of benzyllithium, was prepared according to a previously reported procedure using tin powder and benzyl chloride in water.[20] After Soxhlet extraction with acetone to remove excess metallic tin from the crude tribenzyltin chloride, it was recrystallized from ethyl acetate (mp 140−143 °C) and used for initiator formation. Benzyllithium was prepared by a metal displacement reaction using tribenzyltin chloride and lithium metal in THF at room temperature[21] for 12 h. The greenish brown benzyllithium in THF was used immediately for polymerization.

Polymerization Procedure. Polymerization was carried out in a flame-dried 250 mL round bottom flask under a nitrogen atmosphere. The solvent, initiator, TMEDA, and monomer were transferred using cannula and syringe techniques. Required amounts of THF and TMEDA were transferred into the flask, and the initiator solution was added drop by drop until a persistent red color was observed. Usually, 0.2−0.4 mL of 0.08 M initiator solution was required for 100 mL of solvent to quench the impurities in the system. Subsequently, the required amount of initiator was added and the temperature of the flask was brought to −78 or −40 °C (with a dry ice−acetone or dry ice−acetonitrile bath). Freshly distilled MMA was then added to the initiator solution. Reaction was terminated after 15 min with distilled methanol, and a portion of the reaction mixture was precipitated in methanol while the rest was precipitated in *n*-hexane. The polymer samples were dried under vacuum at 80 °C for 4 h.

Polymer Characterization. The molecular weight distribution of the polymers was determined by size exclusion chromatography in THF at 30 °C on a Waters 150C chromatograph equipped with five μ-Styragel columns (10^5, 10^4, 10^3, 500, and 100 Å) and a refractive index detector. The number-average molecular weight (M_n) and polydispersity ratio (M_w/M_n) were calculated from size exclusion eluograms on the basis of a poly(methyl methacrylate) calibration.

Results and Discussion

Benzyllithium Initiator. Results of BzLi-initiated MMA polymerizations are summarized in Table 1. It is seen that at −78 °C BzLi alone is able to bring about controlled polymerization of MMA. These results are contrary to the earlier observations.[18] The difference in the results observed between our work and that reported by Hatada *et al.*[18] seems to arise because of the abnormally high concentration of the monomer (10 wt %) and the unusually high polymerization time (3 h) employed by them. Thus, under appropriate conditions, BzLi can quantitatively initiate the anionic polymerization of MMA to yield monodisperse PMMAs (Figure 1a) of a predetermined molecular weight similar to DPHLi. It is, however, interesting to note that (α-methylstyryl)lithium (α-MeStLi) under similar conditions does not initiate MMA polymerization in a controlled manner.[11] The subtle difference in reactivity between these two initiating systems is possibly due to the presence of one methyl group in α-MeStLi. It is also known that in the absence of any additive styryllithium is not a good initiator for MMA, due to its ability to attack the carbonyl group of MMA.[12] This is due to the higher reactivity of styryllithium and (α-methylstyryl)-

lithium anions. Comparatively, benzyllithium is less reactive (absence of alkyl groups with +I effect) and therefore carbonyl attack is minimized significantly.

Polymerization of MMA at −40 °C using benzyllithium as initiator did not give controlled polymerization in both the presence and absence of TMEDA. Apparently, the reactivity of the benzylic anion is sufficiently high at −40 °C that such peripheral solvation of Li$^+$ with TMEDA doses not exert any influence.

1,1-Diphenylhexyllithium Initiator. Anderson *et al.*[1] have reported the usefulness of DPHLi as an initiator for MMA polymerization at −78 °C in THF. In our studies DPHLi initiator also gave good control of the molecular weight and molecular weight distribution even in the absence of TMEDA at −78 °C (Table 2).

At −40 °C and in the absence of TMEDA, molecular weight control is lost.[2] Teyssie *et al.*[3] demonstrated that additives such as lithium chloride help in obtaining better control at −78 °C. However, control on polymerization of MMA cannot be achieved at −40 °C even in the presence of alkali metal halide. It has been shown[10] that the addition of LiCl does not help in eliminating the termination reaction at −40 °C.

In the absence of any additive at −40 °C, polymer yield was only ~70% and the polydispersity of the resultant PMMA increased to 1.24 (Table 3). As much as 30% polymer was isolated as methanol soluble oligomer possessing molecular weights less than M_n = 5000. This indicates that 30% of the active species are deactivated due to the termination reaction occurring during the initial stages of the polymerization at −40 °C.

Various molar ratios of DPHLi:TMEDA were used in the study. The presence of a chelating agent such as TMEDA dramatically changes the course of the reaction. Table 3 shows the typical data of the polymerization of MMA in the presence of TMEDA at −40 °C. It can be seen that the presence of TMEDA in an equimolar amount with respect to the initiator DPHLi results in quantitative conversion with good control of molecular weight. The molecular weight distributions (MWD) of the resultant PMMA are narrow (MWD 1.16−1.2) and free from oligomer contamination. Increasing the molar concentration of TMEDA does not significantly influence the molecular weight control or the polydispersity of the PMMA (Figure 1b).

Thus, chelation of the Li$^+$ cation is a convenient method to gain control of the anionic polymerization of MMA using DPHLi as initiator. Apparently, the termination reaction is suppressed by the chelating agent at −40 °C due to peripheral solvation. However, at −23 °C (dry ice and CCl_4) the control is lost (Table 4). Experiments done at −23 °C, in both the presence and absence of TMEDA, are characterized by broad MWDs and low conversions. The molar ratio of initiator to TMEDA does not seem to have any significant influence on the molecular weight and its distribution.

The effect of TMEDA chelation on the initiation and propagation steps is not clear at present. A detailed kinetic study of this system reveals that the apparent rate constant of MMA polymerization is considerably decreased in the presence of TMEDA.[22] Depending on the monomer studied, either an increase or a decrease in the polymerization rate has been reported in the presence of TMEDA.[14,16] Helary and Fontanille[16] observed that coordination of lithium polystyrene by TMEDA, depending upon the active center concentration, decreased or increased the overall polymerization rate. In the present study, the TMEDA to initiator molar ratio did not have any effect on either the molecular weight or its distribution. Stabilization of the propagating enolate by the formation of chelated complex with TMEDA would result in a decrease of termination or transfer reaction. This in turn suppresses the coordination of the lithium atom to the carbonyl group in the antepenultimate unit, resulting in quantitative yields of PMMA with good control on the molecular weight and its distribution at −40 °C.

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