Macromolecules **1994,** *27,* 2249–2255

Studies of Dilithium Initiators. 5. ^{7}Li NMR Analysis of Ionic Species

A. L. Gatzke and D. Patrick Green*

Advanced Polymeric Systems Laboratory, Central Research and Development, The Dow Chemical Company, Midland, Michigan 48674

Received November 12, 1993; Revised Manuscript Received February 10, 1994●

ABSTRACT: Lithium-7 NMR spectroscopy was used to study the dilithium initiator (DLI) (1,3-phenylenebis(3-methyl-1-[methylphenyl]pentylidene))dilithium (1). In hydrocarbon solution, 1 was found to exist predominantly as polyaggregated species, and all the aggregates exchanged rapidly on the NMR time scale at temperatures above 0 °C. Addition of an equivalent per lithium of the tridentate ligand *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) to 1 quantitatively converted the various polyaggregates to a single new species which was assigned to be monomeric 1 with each lithium complexed by one PMDETA ligand. The early stages of isoprene polymerization initiated by both the monolithium initiator (MLI) (1,1-diphenyl-3-methylpentylidene)lithium (2) and 1 were monitored by ^{7}Li NMR. Several different poly(isoprenyllithium) aggregates were visible in polyisoprene solutions initiated with 2, one of which exchanged much more rapidly with dimeric 2 than the others. Initiation with DLI 1 results in formation of a third type of species along with the two poly(isoprenyllithium) aggregates. This third species contains initiator living ends and is believed to be a mixed aggregate of both isoprenyllithium and initiator. Initiation by both 1 and 2 proceeds more rapidly than subsequent propagation. Under seeding reaction conditions, PMDETA has no obvious effect on the early stages of isoprene polymerization initiated by either 1 or 2.

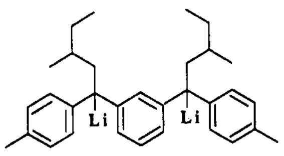
Introduction

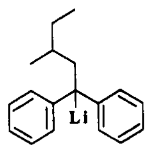
Preceding reports in this series[1] on dilithium initiator (DLI) 1,3-phenylenebis(3-methyl-1-[methylphenyl]pentylidene)dilithium (1) have demonstrated its effectiveness as initiator for anionic polymerization and utility in the preparation of triblock copolymers of styrene–butadiene–styrene (SBS) and styrene–isoprene–styrene (SIS). While diene polymerization initiated with 1 in pure hydrocarbon solution produced broad, bimodal molecular weight distributions, addition of small amounts of donor solvents improved the reactivity of 1 and enabled narrow, monomodal molecular weight distributions to be obtained.[1c,2] The most effective donor additive was the triamine chelator *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) which allowed for control of both the molecular weight and backbone microstructure of the polymer.[1a]

It is known that in nonpolar and weakly polar solvents, aggregation phenomena play an important role in determining the reactivity of organolithium reagents. Previous kinetic studies of diene polymerization initiated with monolithium[3] and dilithium[4] initiators in hydrocarbon media have concluded that rate behavior is directly influenced by changes in aggregation state. Hence, understanding the solution structure of lithium reagents is important for effectively rationalizing and predicting their reactivity. Herein we report results of ^{7}Li NMR spectroscopic studies of 1 in hydrocarbon solution. Aggregation equilibria of 1 were examined along with the growth of living ends in the early stages of isoprene polymerization. The effect of PMDETA on both the aggregation state of 1 and the polymerization of isoprene was studied. For comparison, similar studies of the monolithium initiator (1,1-diphenyl-3-methylpentylidene)lithium (2) were performed.

Experimental Methods

General Procedures. All glassware was dried in a 110 °C oven for at least 4 h and flushed with nitrogen for at least 10 min. All reactions and sample preparations were performed using Schlenk-type equipment and standard high-vacuum techniques. All lithium reagent concentrations were determined by Gilman's double-titration method.[9] ^{1}H and ^{7}Li NMR spectra were obtained on a Varian VXR-4000 spectrometer operating at 300 and 116.59 MHz, respectively. Lithium-7 spectra were recorded over a spectral width of 2000 Hz (16K data points) using a 7-μs pulse width (100–500 transients) and were referenced to external 0.30 M LiCl/methanol standard (0.0 ppm) at −80 °C.


1


2

Solvents and Materials. Diphenylethylene (DPE) was purchased from Aldrich Chemical Co. Isoprene, purchased from Goodyear Tire and Rubber Co., was purified by passing through a column of activated alumina followed by vacuum distillation from dibutylmagnesium. Hexane and toluene were purchased from Fisher Scientific Co. and purified by passing through a column of activated alumina. PMDETA was obtained from Alfa Products and distilled from calcium hydride. *sec*-Butyllithium (*sec*-BuLi) was purchased from Lithium Corporation of America. 1,3-Bis[1-(methylphenyl)ethylene]benzene (MPEB) and solutions of DLI 1 and MLI 2 were prepared according to literature procedures.[1a]

General Procedure for Preparation of Samples for Lithium NMR. A 5-mm NMR tube was dried, fitted on a high-vacuum line and flushed with nitrogen, and evacuated four times while heating gently with a propane torch. The desired sample solution was added through a septum to an NMR tube using a syringe equipped with a 12-in. needle. The sample was frozen in liquid nitrogen, reevacuated, and sealed under vacuum using a propane torch.

● Abstract published in *Advance ACS Abstracts,* March 15, 1994.

0024-9297/94/2227-2249$04.50/0

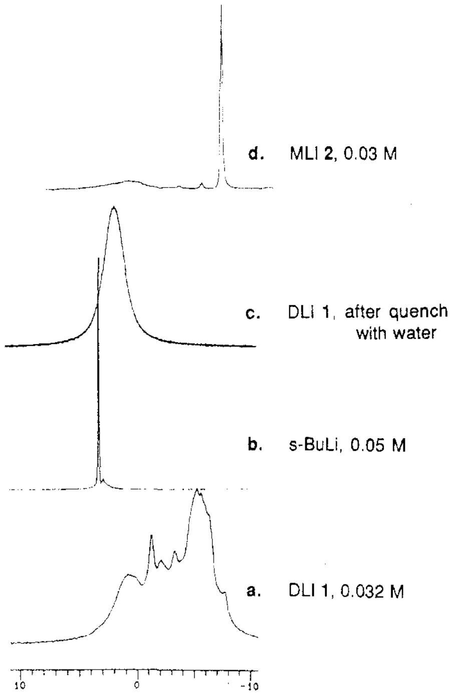


Figure 1. ^{7}Li NMR spectra at −80 °C: (a) DLI 1, 0.032 M in hexane; (b) *sec*-BuLi, 0.05 M in hexane; (c) DLI 1 after completely decomposed from exposure to moisture; (d) MLI 2, 0.03 M in toluene.

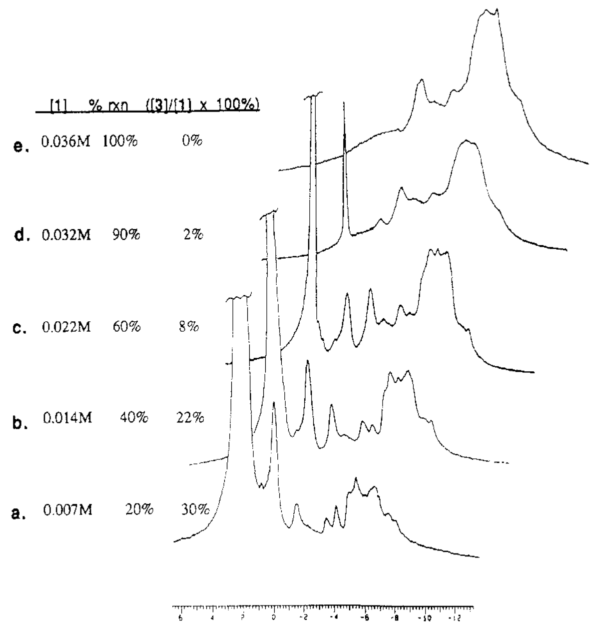


Figure 2. ^{7}Li NMR spectra at −90 °C of MPEB (0.036 M) and *sec*-BuLi (0.072 M) in hexane. The sample was heated at 40–50 °C between spectra.

Results and Discussion

General Comments on the Experimental Approach. Solutions of 1 and 2 were prepared *in situ* through the reaction of *sec*-BuLi with MPEB and DPE, respectively. The progress of the reactions was monitored by GC as described in an earlier report.[1a] Stock solutions of 1 and 2 were prepared the same day as needed to minimize the amount of decomposition impurities. Since 2 is nearly insoluble in hexane, it was prepared in toluene. Sample solutions were typically prepared on a 25-mL scale, and ~0.8 mL of solution was transferred to a 5-mm NMR tube which was subsequently sealed under vacuum. While all efforts were made to avoid solution contamination, small amounts of decomposition always occurred as evident in the NMR spectra. We did not conduct experiments at concentrations typical of polymerization (<0.001 M) because the amount of decomposition was too significant (>25%) relative to the amount of lithium reagent. Instead, we worked at the more concentrated "seeding" reaction conditions (0.05–0.01 M), where "seeding" refers to the technique of polymerizing a small fraction of monomer with the initiator in significantly less solvent.[1a,10]

^{7}Li is easily observed and very sensitive at natural abundance (95%, $I = {}^3/_2$). There are two main sources of broadening in lithium NMR spectra: dynamic exchange (T_2) and quadrupolar relaxation (T_1). Quadrupolar relaxation is caused by interaction of the nuclear quadrupole moment with electric field gradients in the molecule. Although sharp lines can occur in cases where a symmetrical environment about lithium exists, this is rarely the case. We generally obtained spectra at low temperature to minimize T_2 broadening. However, the rate of quadrupolar relaxation, which increases with decreasing temperature, was always quite high, and relatively broad signals were obtained. No scalar couplings ($^1J_{\text{Li-C}}$) could be measured in any of the ^{7}Li NMR spectra obtained.

Lithium-7 NMR of Monolithium Initiator 2. We first examined 0.03 M MLI 2 in toluene by low-temperature ^{7}Li NMR. The spectrum, pictured in Figure 1d, contained a sharp peak at −7.4 ppm as the dominant signal, which was assigned as dimeric 2.[5] Additionally, there were a few minor resonances including a broad peak at 3 to −1 ppm which was attributed to decomposition products such as LiOH and other lithium salts. Support for this latter assignment exists in the fact that its relative intensity increased as [2] decreased. Variable-concentration spectra were obtained over a concentration range of 0.005–0.06 M and appeared the same except for the relative intensity of the broad signal assigned to lithium salts. Variable-temperature ^{7}Li NMR spectra of 0.03 M 2 in toluene were obtained (not shown). As the temperature was increased from −85 to +30 °C, the signal at −7.5 ppm remained sharp while the other peaks assigned to lithium salts broadened significantly. This suggested that, on the NMR time, lithium interchange between 2 and the lithium salts is slow at temperatures as high as 30 °C.

Lithium-7 NMR of DLI 1. Pictured in Figure 1a is a ^{7}Li NMR spectrum of 0.03 M DLI 1 in hexane obtained at −80 °C. In contrast to 2, 1 exists as a complex mixture of aggregated species which exhibit chemical shifts over a range of 10 ppm. As in the spectra of 2, spectra of 1 contain a broad, downfield signal that stretches from +4 to −1 ppm which has been associated with lithium salt impurities. Solutions of both 1 and 2 which were allowed to completely decompose from exposure to moisture exhibited *only* this broad resonance (e.g., Figure 1c).

A hexane solution of 2:1 *sec*-BuLi/MPEB was prepared, and the formation of 1 was monitored by ^{7}Li NMR. The sample was heated at 40–50 °C for increasing amounts of time between each spectrum obtained to hasten the reaction between *sec*-BuLi and MPEB. The spectra, presented in Figure 2, show the conversion of *sec*-BuLi to 1. *sec*-Butyllithium appears as a sharp singlet at 4 ppm. (See Figure 1b for *sec*-BuLi alone in hexane.) Previous kinetic studies[1,7] have shown that the monolithium adduct 3, which results from the addition of one *sec*-BuLi to MPEB, accumulates only to a small degree during the reaction since *sec*-BuLi adds more rapidly to 3 than it does to MPEB.[8] Percent reaction was estimated by integration of the lithium signals. Using the kinetic data reported by Tung et al.,[1a] we estimated the amount of 3 and 1 present in each solution from the percent reaction (Figure 2). The relative intensity of the sharp signal at

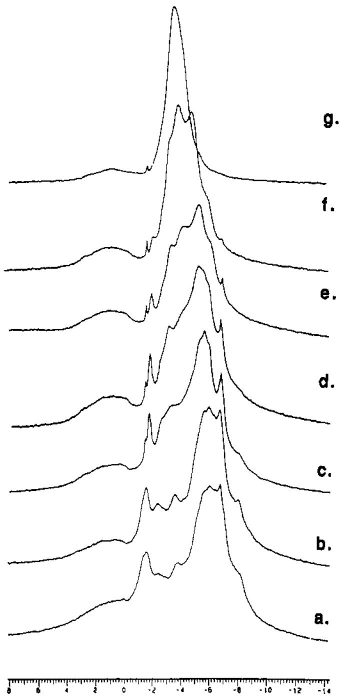
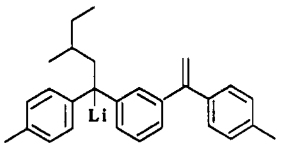


Figure 3. Variable-temperature ^{7}Li NMR spectra of 1 (0.028 M in hexane).

–0.2 ppm was consistent for 3, since it decreased as the reaction proceeded and disappeared entirely upon completion of reaction. Figure 2a shows that 1 exists primarily as dimeric and polyaggregated species even at low concentrations (0.007 M).



3

Pictured in Figure 3 are variable-temperature ^{7}Li NMR spectra of 0.028 M DLI 1 in hexane. The signals of the various aggregates of 1, which were decoalesced and fairly resolved at low temperature, broadened together as temperature increased. Figure 3g shows one broad signal for 1 aggregates at 20 °C, which is indicative that fast intraggregate exchange occurs on the NMR time scale. The lithium salt impurities exchange slowly with 1 since separate signals for each are visible.

Effect of PMDETA on Aggregation. The effect of the tridentate chelator PMDETA on the aggregation of both 1 and 2 in hydrocarbon solution was examined by low-temperature ^{7}Li NMR. It is well documented that PMDETA promotes deaggregation of organolithium compounds and often induces formation of monomeric species.[6] It was therefore no surprise to see that PMDETA had dramatic affects on the aggregation states of both 1 and 2. Pictured in Figure 4 are ^{7}Li NMR spectra obtained at –90 °C of 0.01 M MLI 2 in toluene solutions that contained increasing amounts of PMDETA. With 0.2 equiv of PMDETA present, two new signals appeared which were both downfield of dimeric 2. The strong downfield shifts of these signals is indicative of nitrogen-coordinated lithium species.[6b] With 1 equiv of PMDETA added, the furthest downfield peak at –0.6 ppm grew in quantitatively at the expense of the other signals of 2. The signal at –0.6 ppm has been assigned to monomeric species 4, where lithium is tricoordinated by the three nitrogens of PMDETA. The addition of a second equivalent of PMDETA had no further effect, which supports the formation of a 1:1 complex of PMDETA and 2. The resonance at –4.0 ppm which appeared in spectra with <1 equiv of PMDETA present (Figure 4b,c) has a chemical shift approximately equidistant from unsolvated 2 and monomeric species 4. It was speculated that this signal is associated with dimeric species 5 where one PMDETA is shared by both lithiums. The equilibrium constant for the formation of 5 cannot be high since both monomeric 4 (δ –0.6) and unsolvated dimer (δ –7.4) exist along with it.

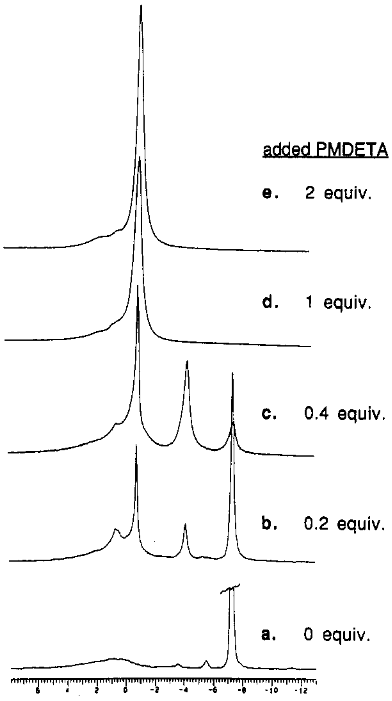
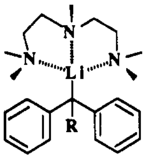
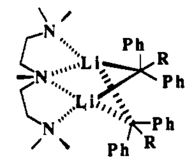


Figure 4. ^{7}Li NMR spectra at –90 °C of 2 (0.01 M in toluene) with increasing amounts of PMDETA.



4

R = CH_2-(s-butyl)



5

Addition of PMDETA to 1 in hexane was monitored by ^{7}Li NMR, and the spectra are presented in Figure 5. The presence of 0.2 equiv/lithium of triamine caused considerable deaggregation of the DLI polyaggregates and formation of two new signals at –0.4 and –3.8 ppm. With 0.4 equiv/Li of triamine, the spectrum (Figure 5c) appeared remarkably like that of 2 with 0.2 equiv of PMDETA: the polyaggregates of 1 were reduced to <10%, and sharp signals of dimeric 1 existed along with two new species. The three signals of 1 at –1.3, –2.2, and –3.4 ppm were not visibly affected by the first additions of PMDETA. This suggests that these aggregates are relatively weak Lewis acids since they do not effectively compete for the triamine. With 1 equiv/Li of PMDETA present, 1 was quantitatively converted to a single new species with a chemical shift (δ –0.6) nearly identical to that of 4 and has been assigned to monomeric DLI 1, where each lithium is complexed by one PMDETA ligand. The intermediate complex which grew only slightly at –3.8 ppm is believed to be a dimer of 1 where one triamine ligand is shared by two lithiums, analogous to 5. This latter species was only present in

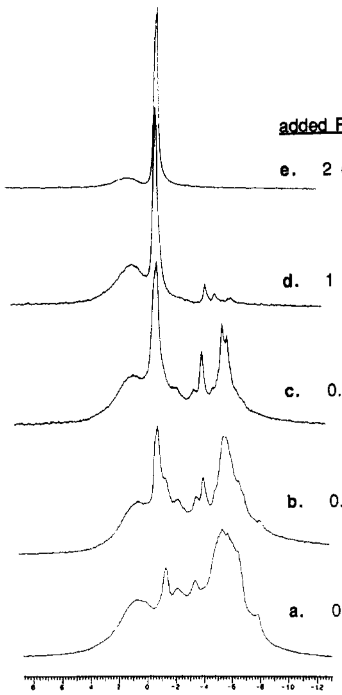


Figure 5. ^{7}Li NMR spectra at -80 °C of 1 (0.032 M in hexane) with increasing amounts of PMDETA.

Table 1. ^{1}H NMR Data of Isolated Products from Toluene Solutions of 2 Which Had Been Seeded with Isoprene Followed by MeOH Quench

Li spectrum	initial [2] (M)	isoprene added (equiv)	DP	% 3,4-polyisoprene	% protonated initiator ends
Figure 6b	0.045	0.5	0.7	8	45
Figure 6c	0.045	1.0	1.1	8	9
Figure 6d	0.045	2.0	2.0	9	1
Figure 6e	0.045	6.0	6.2	10	<1
Figure 8b	0.01	0.5	0.7	10	37
Figure 8c	0.01	1.0	1.2	12	6
Figure 8d	0.01	2.0	2.2	10	1
Figure 8e	0.01	6.0	6.4	10	<1

small amounts relative to monomeric DLI 1, even when [PMDETA] < [1]. Apparently, PMDETA prefers to complex one lithium even with excess unsolvated 1 present in solution.

Addition of Isoprene to MLI 2 in Toluene. Small amounts of isoprene (0–6 equiv/living end) were added to toluene solutions of 2 at 45–50 °C and allowed to react for 10–15 min. During this time, the color of the solutions changed from the distinct maroon of 2 to the lighter orange of isoprenyllithium, the degree of which depended on the amount of isoprene added. Samples of these solutions were sealed in NMR tubes to be analyzed by low-temperature ^{7}Li NMR, and the remaining portions were quenched with MeOH. The products of the latter solutions were isolated and analyzed by ^{1}H NMR to determine the amount of 2 that remained in each solution before quench (from the relative integration of the benzyl proton), the degree of polymerization (DP), and the percent of 3,4-polyisoprene. These data are listed in Table 1. The DP's were very close to that anticipated from the amount of isoprene added; slight errors in addition probably account for the differences. The amount of 3,4-polyisoprene was consistently around 10%. Initiation was rapid relative to propagation since little unreacted 2 remained after the addition of 1 equiv or more of isoprene.

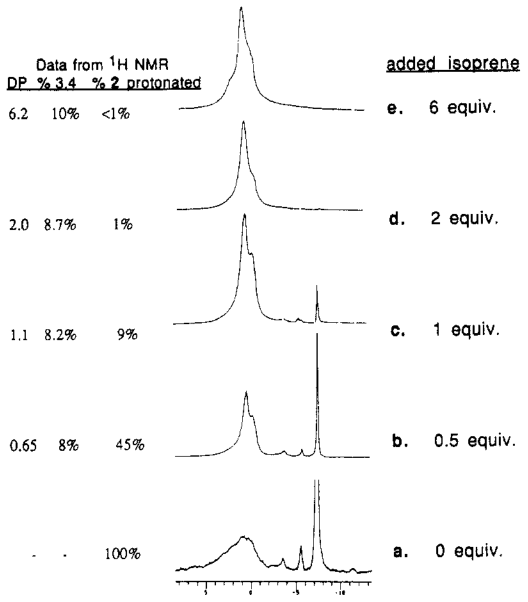


Figure 6. ^{7}Li NMR spectra at -85 °C of 2 (0.045 M in toluene) after reaction with 0–6 equiv of isoprene.

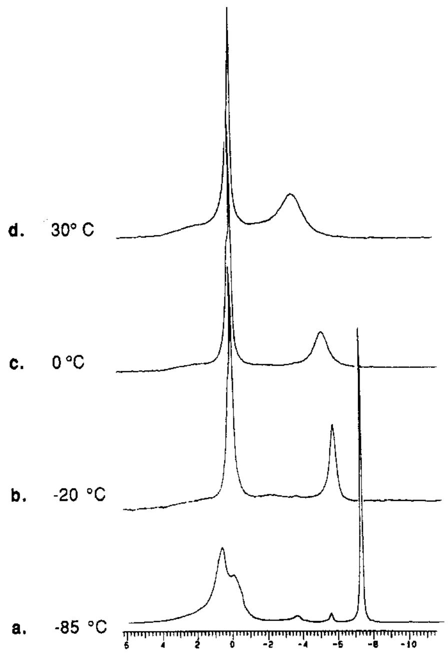


Figure 7. Variable-temperature ^{7}Li NMR spectra of 2 (0.045 M in toluene) with 0.5 equiv of isoprene.

Presented in Figure 6 are ^{7}Li NMR spectra obtained of 0.045 M solutions of 2 which had been seeded with increasing amounts of isoprene as described above. The addition of isoprene to 2 resulted in the formation of at least two new peaks at 1.0 and 0.2 ppm. These signals are similar in nature to those observed by Sigwalt and coworkers for tetrameric poly(isoprenyllithium) species.[4c] The amount of dimer which remained in some of the lithium spectra was slightly less than what the ^{1}H NMR analyses had indicated. These small differences most likely represent the amount of 2 that terminated during the preparation of the samples for ^{7}Li NMR. However, the possibility cannot be ruled out that a new, mixed aggregate exists which contains both 2 and poly(isoprenyllithium). If such an aggregate does form, its propensity to do so must be very low since homodimer of 2 still exists with >90% of 2 converted to isoprenyllithium species.

Variable-temperature spectra were obtained of 2 with 0.5 equiv of isoprene added and are pictured in Figure 7. As the temperature was increased, the signal of dimeric 2 (δ -7.4) broadened and began to coalesce with a downfield signal. Since variable-temperature spectra of 2 itself show no such behavior, the exchange probably involves some

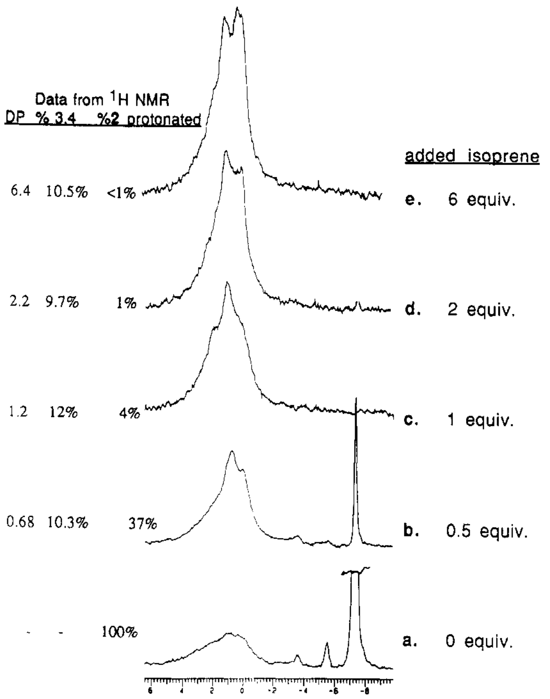


Figure 8. ^{7}Li NMR spectra at −85 °C of 2 (0.01 M in toluene) after reaction with 0–6 equiv of isoprene.

Table 2. ^{1}H NMR Data of Isolated Products from Toluene Solutions of DFI 1 Which Had Been Seeded with Isoprene Followed by MeOH Quench

Li spectrum	initial [1] (M)	isoprene added/Li (equiv)	DP/Li	% 3,4-poly-isoprene	% protonated initiator ends
Figure 9b	0.01	0.5	0.66	15	44
Figure 9c	0.01	1.0	0.97	17	7
Figure 9d	0.01	2.0	1.8	18	1
Figure 9e	0.01	6.0	5.9	17	<1

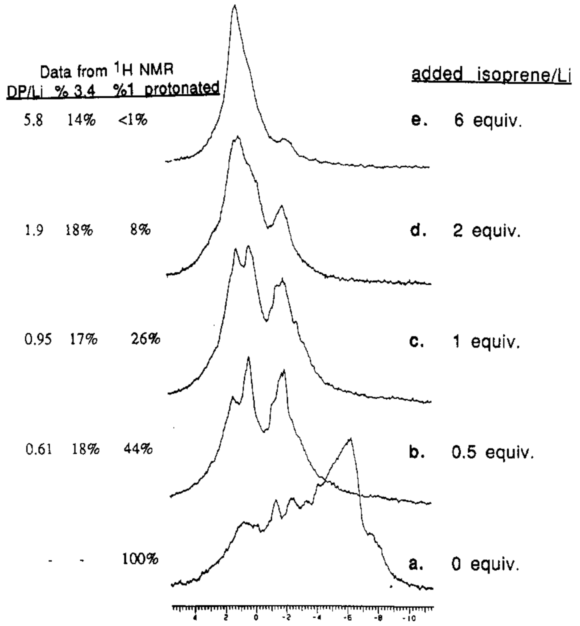


Figure 9. ^{7}Li NMR spectra at −90 °C of 1 (0.01 M in toluene) after reaction with 0–6 equiv/Li of isoprene.

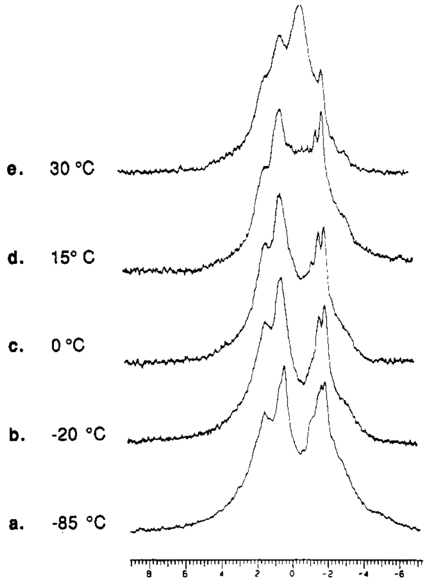


Figure 10. Variable-temperature ^{7}Li NMR spectra of 1 (0.01 M in toluene) after reaction with 0.5 equiv/Li of isoprene.

poly(isoprenyllithium) species. Additionally, the peak at 0.5 ppm sharpened as the temperature increased, which suggests that a poly(isoprenyllithium) species exchanges more rapidly with 2 than it does with the other poly(isoprenyllithium) aggregates.

A similar set of ^{7}Li NMR spectra were obtained of 0.01 M solutions of 2 which contain added isoprene and are pictured in Figure 8. ^{1}H NMR analysis of these solutions was also performed, the data from which are included in Table 1.

Addition of Isoprene to DLI 1 in Toluene. Similar seeding reactions were performed to prepare low molecular weight polyisoprene in toluene using 1 as initiator. After the reactions were complete, portions of each were sealed in NMR tubes and analyzed by ^{7}Li NMR. The remaining solutions were terminated with MeOH and analyzed by ^{1}H NMR. The ^{1}H NMR data, presented in Table 2, were similar to those obtained with 2 as initiator. The DP/Li obtained through proton integration correlated well with the amount of isoprene added, and the 3,4-polyisoprene content varied between 14 and 18%. The percent of DLI living ends that remained after reaction with isoprene was also determined for each solution through integration of the benzylic protons.

Lithium-7 NMR spectra of 0.01 M solutions of 1 with increasing amounts of polyisoprene added are presented in Figure 9. The spectrum of 1 in toluene (Figure 9a) appears much like that of 1 in hexane. With ~0.5 equiv of isoprene added (DP/Li = 0.6), three new peaks appeared while the signals of 1 nearly disappeared. The ^{1}H NMR spectrum of the corresponding "quenched" solution indicated that 44% of the living ends of 1 remained in solution. Whether the living initiator was one- or two-ended was not determined. However, the fact that neither polyaggregates nor dimers of 1 were visible with >40% of the living ends present in solution was surprising. The initiator living end must associate with isoprenyllithium to form a mixed aggregate. The signals between −1 and −3 ppm have therefore been attributed to mixed aggregates of poly(isoprenyllithium) and initiator living ends. Intermolecular and/or intramolecular aggregation may occur. The two furthest downfield signals were assigned to poly(isoprenyllithium) species, since they have chemical shifts (δ 1.6, 0.5) similar to those of poly(isoprenyllithium) species obtained from MLI 2.

Variable-temperature ^{7}Li NMR spectra of this same sample (polyisoprene initiated with 1; DP/Li = 0.6) were obtained to determine at what temperature the various lithium species exchanged with one another. Surprisingly, few changes occurred until −20 °C (see Figure 10). Apparently, both the homoaggregates and mixed aggregates of poly(isoprenyllithium) have a greater barrier for interconversion than aggregates of 1 itself. Even at 15 °C,

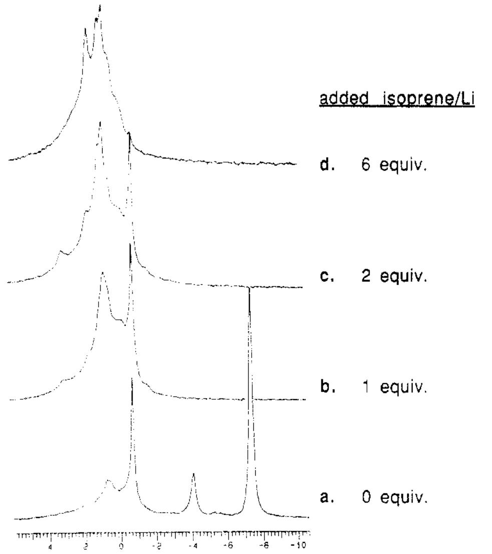


Figure 11. ^{7}Li NMR spectra at −90 °C of **2** (0.03 M in toluene with 0.2 equiv of PMDETA/Li) after reaction with 0–6 equiv of isoprene.

exchange processes were relatively slow on the NMR time scale. Although not obvious in the low-temperature spectrum, the high-temperature spectra clearly show two distinct, relatively sharp signals at δ −1.6 and −1.9 which exist as part of the peak assigned to mixed aggregates of **1** and poly(isoprenyllithium). These two signals remained sharp even at 30 °C while the other peaks broadened significantly due to rapid exchange. Since slower exchange is suggestive of greater stability, the mixed aggregate may exhibit lower reactivity.

Lithium-7 NMR spectra of solutions of **1** with 1, 2, and 6 equiv/Li of isoprene added (Figure 9c–e) indicated that poly(isoprenyllithium) aggregates grew at the expense of the DFI/poly(isoprenyllithium) mixed aggregate(s). With 6 equiv of isoprene present, essentially all initiator living ends had reacted. The signal at δ 1.6 became dominant once several isoprene units were added. While nearly all MLI **2** had initiated upon addition of 1 equiv of isoprene, DLI **1** required over 2 equiv of isoprene/Li for complete initiation. This suggests that, at these concentrations, the ratio of initiation:propagation rates is lower for **1** than **2** and may reflect the ability of **1** to form intramolecular aggregates.

Effect of PMDETA on Isoprene Polymerization. In an attempt to monitor by ^{7}Li NMR the effect of PMDETA on isoprene polymerization, seeding reactions were run at 45–50 °C using initiator solutions that contained 0.2 equiv of triamine/Li. The subsequent product mixtures were analyzed by ^{7}Li NMR. Figure 11 contains ^{7}Li NMR spectra obtained at −90 °C of polyisoprene solutions (0–6 equiv of isoprene) which were initiated with **2**/PMDETA. Spectrum 11a is of **2** with 0.2 equiv of triamine and contains signals of dimeric **2** (δ −7.4) and PMDETA solvated species **4** (δ −0.6) and **5** (δ −4.0). Spectra of solutions in which isoprene had been added contain new signals downfield near those observed earlier for isoprenyllithium species. Monomeric complex **4** was the only MLI aggregate visible once isoprene was added, and its concentration decreased to nearly zero with 6 equiv of isoprene present.

To correctly compare the above spectra with poly(isoprenyllithium) solutions which were initiated *without* triamine, several isoprene polymerization reactions initiated with **2** were run in toluene, and PMDETA was added *after* the reaction was complete. Lithium-7 NMR spectra were obtained by polyisoprene solutions initiated with **2**/PMDETA and analogous solutions in which triamine had been added *after* polymerization (see Figure 13). The two sets of spectra appear nearly identical to one another, which suggests PMDETA has little effect on the products obtained from isoprene polymerization initiated with **2**.

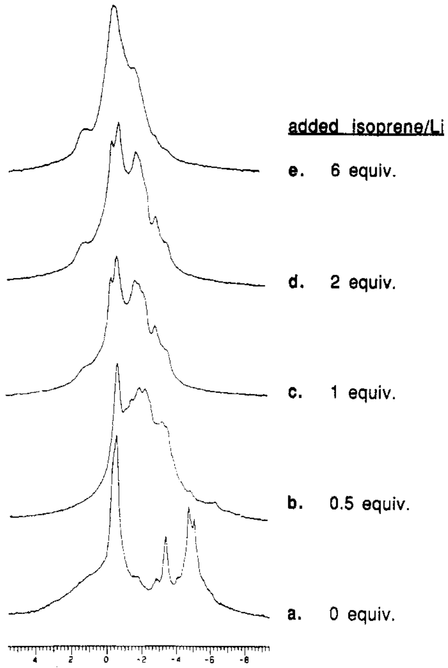


Figure 12. ^{7}Li NMR spectra at −90 °C of **1** (0.033 M in toluene with 0.2 equiv of PMDETA/Li) after reaction with 0–6 equiv of isoprene.

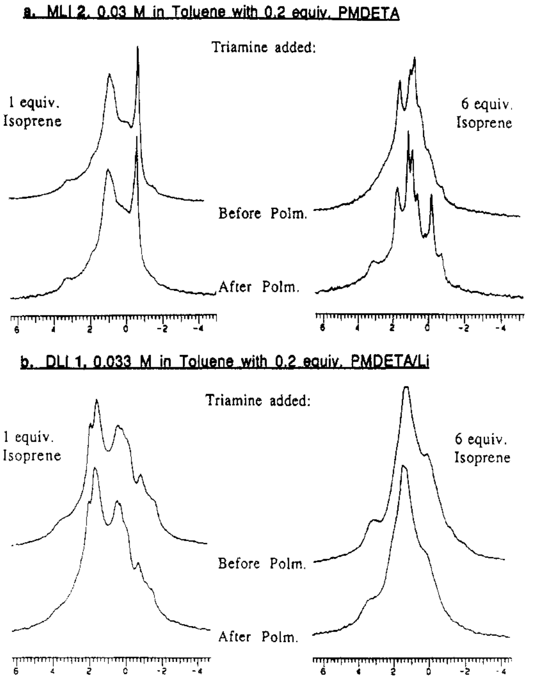


Figure 13. ^{7}Li NMR spectra at −90 °C in toluene after reaction with 1 and 6 equiv of isoprene/Li: (a) **2** (0.03 M); (b) **1** (0.033 M). PMDETA (0.2 equiv/Li) was added either before or after reaction as indicated.

Identical seeding reactions were performed as described above using DLI **1**. Figure 12 shows ^{7}Li NMR spectra obtained for solutions of polyisoprene initiated with **1**/0.2 equiv of PMDETA. Figure 13 shows comparative spectra of these polyisoprene solutions where PMDETA had been added either before or after polymerization. As with MLI **2**, the two sets of spectra are nearly identical (see Figure 13). This led us to conclude that, under seeding reaction conditions, PMDETA has no obvious effect on the products generated during early stages of isoprene polymerization initiated by either 1 or 2.

Conclusions

Direct observation of 1 by ^{7}Li NMR spectroscopy showed it to exist as a complex mixture of polyaggregated species which exchange rapidly on the NMR time scale at temperatures above 0 °C. This is in contrast to 2, which exists predominantly as a dimer in hydrocarbon solution. Addition of the tridentate ligand PMDETA to both 1 and 2 quantitatively converted each to a single, new species believed to be monomers with each lithium complexed by one PMDETA ligand.

^{7}Li NMR spectra of polyisoprene solutions initiated by 1 and 2 show at least two different poly(isoprenyllithium) aggregates. Spectra of the solutions initiated with 1 contain an additional resonance which was assigned to a mixed aggregate of poly(isoprenyllithium) and DLI initiator living ends. This latter species could be cyclic involving intramolecular aggregation and undergoes exchange reactions relatively slowly.

Under seeding reaction conditions, initiation of isoprene polymerization by both 1 and 2 proceeded more rapidly than subsequent propagation. PMDETA had no obvious effect on the products obtained in the early stages of isoprene polymerization initiated by either 1 or 2.

References and Notes

(1) (a) Tung, L. H.; Lo, G. Y.-S. Paper 1 in this series, submitted to *Macromolecules.* (b) Tung, L. H.; Lo, G. Y.-S.; Bredeweg, C. J.; Gatzke, A. L. Paper 2 in this series, submitted to *Macromolecules.* (c) Tung, L. H.; Lo, G. Y.-S.; Gatzke, A. L.; Otterbacher, E. W. Paper 3 in this series, submitted to *Macromolecules.* (d) Tung, L. H.; Lo, G. Y.-S. Paper 4 in this series, submitted to *Macromolecules.*

(2) (a) Lo, G. Y.-S.; Otterbacher, E. W.; Bezoari, M. D.; Walther, B. W. U.S. Patent 4,960,842, 1990. (b) Tung, L. H.; Lo, G. Y.-S.; Beyer, D. E. U.S. Patents 4,172,100 (1979), 4,172,190 (1979), and 4,196,154 (1980). (c) Tung, L. H.; Lo, G. Y.-S.; Griggs, J. A. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1551.

(3) (a) Szwarc, M. *Adv. Polym. Sci.* **1983**, *49*, 1. (b) Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 34. (c) Van Beylen, M.; Bywater, S.; Smets, G.; Szwarc, M.; Worsfold, D. J. *Adv. Polym. Sci.* **1985**, *86*, 89.

(4) (a) Morton, M.; Fetters, L. J.; Pett, R. A.; Meier, J. F. *Macromolecules* **1970**, *3*, 327; *Polym. Lett.* **1972**, *10*, 561. (b) El Madani, A.; Favier, J.-C.; Hémery, P.; Sigwalt, P. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 329. (c) El Madani, A.; Belleney, J.; Favier, J.-C.; Hémery, P.; Sigwalt, P. *Polym. Int.* **1993**, *31*, 169.

(5) 2 has benzyllithium character. It has been reported that benzyllithium exists predominantly as a dimer in hydrocarbon solution. Brown, T. L. *Acc. Chem. Res.* **1968**, *1*, 23.

(6) (a) Fraenkel, G.; Henrichs, M.; Hewitt, M.; Su, B. M. *J. Am. Chem. Soc.* **1984**, *106*, 255. (b) Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371. (c) Fraenkel, G.; Winchester, W. R. *J. Am. Chem. Soc.* **1988**, *110*, 8720.

(7) McGrath, J. E.; Broske, A. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26* (1), 237.

(8) This phenomenon can be explained through complex induced proximity effects. Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 1.

(9) Gilman, H.; Haubein, A. H. *J. Am. Chem. Soc.* **1944**, *66*, 1515.

(10) Szwarc, M.; Van Beylen, M.; Van Hoyweghen, D. *Macromolecules* **1987**, *20*, 445.