1402 *Macromolecules* **1993**, *26*, 1402-1406

Anionic Polymerization of Acrylic Monomers. 10. ^{13}C and ^{7}Li NMR Studies on the Monomeric Model of Living Poly(methyl methacrylate)

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Received June 19, 1992; Revised Manuscript Received November 16, 1992

ABSTRACT: A monomeric model structurally comparable to the active end of a living poly(methyl methacrylate) (PMMA), i.e., a methyl α-lithioisobutyrate (MIBLi)/THF solution, was studied by both ^{7}Li and ^{13}C NMR. It has been shown that two different coordination aggregates exist in a MIBLi/THF solution. That situation corresponds to a slow exchange process between tetramer and dimer, i.e.

$$(MIBLi)_4 + 2nS \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2(MIBLiS_n)_2 \quad (S = THF)$$

the later being favored by a decrease in temperature or concentration. Such an equilibrium is characterized with $\Delta H = -2.1$ kcal/mol and $\Delta S = -13.7$ cal/mol·K by means of ^{7}Li NMR. Again, ^{13}C NMR results obtained suggest that a MIBLi/THF solution displays a charge-delocalized character, which is different from a O–Li-bonded structure in solid state established by crystal analyses of several similar ester enolates.

Introduction

A sizable body of literature has resulted from investigations of active species and mechanisms in anionic polymerization of methacrylic ester monomers by a variety of techniques;[1-6] still several significant questions remain unanswered. They concern the type and structure of ion pairs, their dynamic behavior (how fast and by which mechanism ion-pair exchange occurs), and their related roles in anionic polymerization.

The nature of the active species in the anionic polymerization of nonpolar monomers, e.g., styrene, has been disclosed in depth on the basis of spectroscopic, conductometric, and kinetic investigations.[7] Up to now, however, ion pairs in anionic polymerization of (meth)acrylic esters have largely not been studied by direct methods, mainly because they do not display spectra (e.g., UV–visible) that are useful in terms of the interpretation of the ion-pairing structure. To data indirect information on the structure of ion pairs has originally come from NMR investigation on the stereochemistry of partially deuterated polyacrylates[1a] and largely from kinetic studies.[3-5] An "intramolecular solvation" model has been proposed by these authors. More recent kinetic experiments,[5c] as well as ^{13}C NMR[2b] and conductivity[5c] measurements, however, did not corroborate this, especially in polar solvents. Clearly, additional data are required to better describe the nature of that complicated active species.

Again, it has been reported from this laboratory that a perfectly "living" polymerization of methyl methacrylate (MMA) and *tert*-butyl acrylate (tBuA) could be obtained by using a classical initiator in the presence of simple inorganic salts.[8,9] In order to characterize more precisely the structure of such a complexed species (a most interesting initiator and modified propagating ion pair) and accordingly elucidate the resulting living character, it seemed of great importance to first investigate in detail the structure of uncomplexed ion pairs.

It is well-known that the NMR spectroscopy is one of the most useful tools used in the characterization of the ion-pairing behavior in anionic polymerization. Several NMR techniques have been successfully applied to establish the importance of kinetic and thermodynamic factors responsible for living character and stereoselectivity in the anionic polymerization of monomers, such as styrene,[10] dienes,[11] and 2-vinylpyridine.[12] As for anionic polymerization of alkyl (meth)acrylates, which is accompanied by considerable side reactions, it is very difficult to obtain the suitable living oligomers. NMR investigations were hardly carried out on real systems except for ^{13}C NMR results of model compounds corresponding to methacrylate anions as reported by Bywater.[2]

As a prelude to our systematic studies of ion pairs and related complexes with different kinds of ligands in anionic polymerization of (meth)acrylic esters by means of NMR spectroscopy, we report here on the utility of both ^{13}C and ^{7}Li NMR for the characterization and quantitative estimation of differing ions pairs (and aggregates) of methyl α-lithioisobutyrate (MIBLi; 1) in THF, structurally corresponding to the active chain end of poly(methyl methacrylate).

$$(CH_3)_2C(Li)COOCH_3$$

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Experimental Section

Methyl isobutyrate from Aldrich was purified and dried by distillation from CaH_2 (two times). It was then stored under a nitrogen atmosphere. *N*-Lithiodiisopropylamide (97%) was a commercial product from Aldrich and was used as received. THF and THF-d_8 also from Aldrich were refluxed over benzophenone sodium ketyl and distilled immediately prior to use. Hexane, toluene, and benzene-d_6 were refluxed over CaH_2 and distilled over StLi living oligomer just before use.

The methyl α-lithioisobutyrate (MIBLi) was prepared under pure nitrogen from equimolar amounts of methyl isobutyrate and *N*-lithiodiisopropylamide in hexane at −78 °C as reported previously.[13] The resulting white MIBLi solid was dissolved in the desired volume of solvent at −78 °C and then directly filtered under nitrogen into NMR tubes which were sealed under vacuum.

The ^{1}H, ^{13}C, and ^{7}Li NMR spectra were obtained with a Bruker AM 400 superconducting magnet system operating in the FT

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0024-9297/93/2226-1402$04.00/0

Table I
^{13}C NMR Chemical Shifts (ppm)[a] of 0.5 M Carbanion 1 in THF

	C(O)		C_α			OCH_3		$(CH_3)_2$	
T, °C	set 1	set 3	set 1	set 2	set 3	set 1	set 2	set 1 & set 2	set 3
25[b]	176.8			34.3		51.3		19.2	
−80[c]	160.8	159.0	73.9	72.3	65.8	57.5	56.7	18.7, 18.2	18.6
−80	160.5	158.9	73.5	71.8	65.4	57.0	56.0	18.3, 18.0	18.9
−60	160.5	158.9	73.4	72.2	65.4	56.9	56.2	18.4, 18.0	18.9
−40	160.5		72.8	72.5		56.7		18.4, 17.9	
20	160.6		72.7			56.7		18.3, 17.7	

[a] Relative to the high-field signal of THF-d_8, 25.3 ppm. [b] Corresponding parent ester, i.e., methyl isobutyrate, $(CH_3)_2CHCOOCH_3$. [c] In the THF-d_8/toluene (10/90, v/v) mixture.

mode at 400, 100.6, and 155.5 MHz, respectively, using a deuterium lock. The ^{13}C spectral assignments were aided by an off-resonance technique, and all chemical shifts were referenced to high-field resonance of THF-d_8, whose chemical shift was separately determined to be 25.3 ppm relative to $(CH_3)_4Si$. Lithium-7 NMR spectra were referenced to a 0.2 M LiCl solution in THF.

Results and Discussion

As previously described, methyl α-lithioisobutyrate (MIBLi) was generated by reacting the *N*-lithiodiisopropylamide with methyl isobutyrate.[13] Several of those metalated esters were hydrolyzed with water at low temperature. The ^{1}H and ^{13}C NMR spectra of the hydrolysis products were found to be identical to the one of the corresponding parent ester, indicating that pure model compounds were prepared. The salt solution in THF was then investigated by using ^{13}C and ^{7}Li NMR.

Carbon-13 NMR Data of MIBLi in THF: Evidence for the Coexistence of Two Types of Delocalized Species. Carbon-13 NMR chemical shifts of the carbanion should reflect its structure in solution; i.e., any substantial change in the structure of an ion pair and aggregate will cause a change in the electron distribution on the carbanion, particularly at the α-carbon. The ^{13}C NMR spectra of 0.5 M MIBLi were recorded in THF between −80 and +20 °C (Table I) and show complex spectral changes. On the basis of ^{13}C NMR studies, Bywater had previously observed only one species for MIBLi in THF even at −60 °C.[2a] In contrast, it is obvious from the present results that three sets of 100.6-MHz ^{13}C NMR signals for MIBLi in THF were detected below −60 °C (Figure 1), indicative of the presence of more than one species.

Although MIBLi is virtually insoluble in aromatic hydrocarbons, its solubility in a toluene/THF mixture (90/10, v/v) was sufficient to record useful ^{13}C NMR spectra. It was found that the overall pattern of such spectra of 0.5 M MIBLi solutions was similar to the one in pure THF, except for a little difference in chemical shifts (Table I). This might imply no significant effects on the structure and equilibrium of different species by introduction of significant amounts of toluene into THF.

The spectra are clearly ascribed to pure MIBLi for the following reasons. First, ^{13}C NMR spectra obtained from several preparations are fully reproducible. Second, the ^{1}H and ^{13}C NMR spectra show the absence of any *N*-lithiodiisopropylamide (LDA), thus ruling out the possible coordination between MIBLi and LDA impurities. Finally, the hydrolysis products of MIBLi showed the exclusive presence of methyl isobutyrate by ^{1}H and ^{13}C NMR, ruling out the presence of products from side reactions of the carbanion.

In the first set of resonances (set 1), i.e., δ 160.5/73.5/57.0/18.3, 18.0 (in ppm, at −80 °C) for $C(O)/C_\alpha/OCH_3/(CH_3)_2$, respectively, the fact that the roughly equal absorptions at 18.3 and 18.0 ppm do not vary with temperature from −80 °C to at least +20 °C indicates that they present nonequivalent methyls consistent with a pronounced double-bond character of the C_α–C(O) bond (Figure 1). Moreover, it can be seen from data in Table I that the C_α signal moves to a much lower field versus the parent ester (39 ppm). Conversely, the corresponding ester group carbonyl signal (C(O)) shifts upfield about 16 ppm. from its original position. These results are consistent with previous observations.[2a] Furthermore, it is also obvious that the ^{13}C chemical shift of α-carbon is considerably upfield of the normal values for sp^2-hybridized carbon. Recognizing the relationship between chemical shifts and charge distributions, these shifts might indicate some charge delocalization.

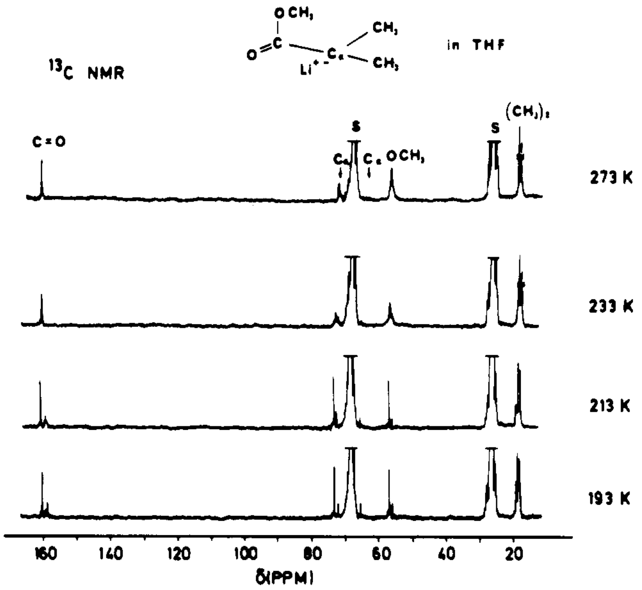
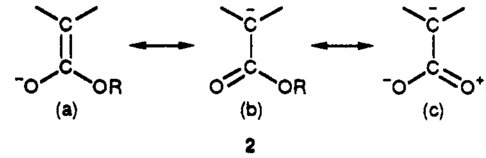


Figure 1. ^{13}C NMR spectra of MIBLi in THF (0.5 M) at different temperatures, relative to the high-field signal of THF-d_8 at 25.3 ppm. Signals S are the THF and THF-d_8 resonances.

The observation of set 2 signals, i.e., δ 71.8/56.0 (in ppm, at −80 °C) for C_α/OCH_3, respectively, also parallels Bywater's observation.[2] As suggested by him, two resonances for the $(O)CH_3$ and C(Li) atoms (in set 1 plus set 2) are due to a predominant structure of the type "$RC(O^-)=O^+CH_3$" in MIBLi. Such an explanation is possible but not plausible as shown by the corresponding canonical structure (2 c). In that respect, the C–OR bond



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of the ester also has a partial double-bond character,[14a] which would also produce restricted rotation around the

C(O)–OR bond resulting in two sets of nonequivalent resonances at the C_α and OCH_3 groups. It is noteworthy from Figure 1 that these two signals average to a broad line with a ^{13}C chemical shift close to that of the downfield one as temperature is increased: It seems likely that the barrier to rotation around $C(O)–OCH_3$ is low compared to a normal double bond (but high compared to a single bond!).

In addition to the results described above, a striking change also takes place in the ^{13}C NMR spectra below −60 °C when considering a third set of signals (set 3), i.e., 158.9/65.4/18.9, ? (in ppm, −80 °C) for $C(O)/C_\alpha/(CH_3)_2$ atoms, respectively. Within a given spectrum at the same temperature the area ratios for each of set 3/(set 2 + set 1) are roughly equal, but they vary with temperature (Figure 1), and temperature variation is reversible. It seems most likely that two forms, which are in equilibrium at low temperature, set 1 + set 2 and set 3, exist in a MIBLi/THF solution.

The formation of two different types of ion pairs differing in the degrees of (cation) solvation seems implausible. First, a solvent-separated enolate structure of MIBLi in THF is very improbable because of very strong O–Li interaction. Second, a solvent separation between the carbanion and the Li ion might be feasible but implausible since there is no evidence from related polymerization kinetics for such a process. Finally, it is also evident from the present ^{13}C NMR results that the exchange of anions between different ion pairs is slow on the NMR time scale, i.e., τ(anion) > 1.0 s. This is atypical for simple ion pairs of differing states of solvation, since the exchange processes of this type are generally observed to be very fast, say, τ(anion) ~ 10^{-8} s.[14b–d]

However, there are convincing evidences from IR and VPO measurements of several ester enolate THF solutions that there are aggregates present.[13,15] Indeed, the fact that the ^{13}C chemical shift differences of 7 and 1.6 ppm for C_α and C(O), respectively, between two forms of MIBLi in THF might suggest that both have different degrees of aggregation because a change in the degree of aggregation generally produces larger enolate shifts.[14e–g] Jackman et al. have observed 1.6 and 4.6 ppm differences at C-1 and C-2 between the dimer and tetramer of lithioisobutyrophenone in dimethoxyethane.[14e] House and co-workers have observed similar results for the enolate of phenylacetone.[14f] Thus, the NMR changes in Figure 1 might likewise be due to the equilibrium between different aggregates, which is also more consistent with the aforementioned slow interconversion process.

Lithium-7 NMR Spectra: Quantitative Estimation of Different Aggregates in a MIBLi/THF Solution. NMR studies on organolithium species, using mostly ^1H and ^7Li nuclei, have in recent years quantitatively revealed many details of their coordinative aggregation. For MIBLi, in particular, the ^7Li NMR method is potentially much more useful than ^1H since no hydrogen atom is directly bounded to the metalated carbon. The 155.5-MHz ^7Li NMR spectra of this salt at different temperatures are shown in Figure 2. Below about −70 °C, two peaks, named A and B, are well separated by 0.19 ppm, at −0.52 ppm (A) and −0.71 ppm (B), respectively (relative to 0.2 M LiCl solution in THF at 298 K). The resonance intensity of peak B decreases as the temperature is increased, and this species finally disappears at 223 K. For species A, its intensity is correspondingly increased, and it still resonates at a similar chemical shift even at 273 K. These results clearly indicate an equilibrium between two species with slow exchange on the NMR time scale at low temperature.

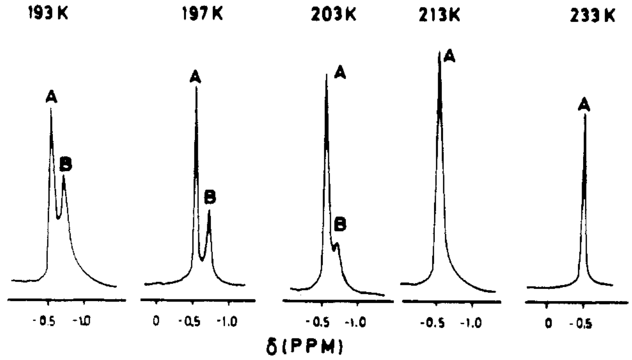


Figure 2. ^7Li NMR of MIBLi in THF (0.2 M) at different temperatures.

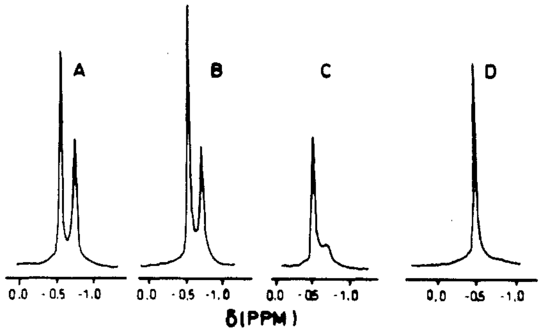


Figure 3. ^7Li NMR of MIBLi in THF at −76 °C at different concentrations: (A) 0.133 M; (B) 0.20 M; (C) 0.40 M; (D) 2.0 M.

Table II
Concentration in Methyl α-Lithioisobutyrate (MIBLi) of Species A (−0.52 ppm) and B (−0.71 ppm) as a Function of the Total Concentration and Temperature

T, K	[MIBLi], M	[A], M	[B], M
197	0.05	0.019	0.031
197	0.133	0.066	0.067
197	0.20	0.108	0.092
197	0.40	0.274	0.126
208	0.20	0.119	0.081
204	0.20	0.117	0.083
202	0.20	0.113	0.087
199	0.20	0.111	0.089
197	0.20	0.108	0.092
193	0.20	0.105	0.095

The relative amount of the two kinds of species exhibits a significant dependence on the total concentration in MIBLi (Figure 3). Thus, a solution which was 0.133 M in MIBLi contained 49.6% of the species A, while a 0.40 M solution contained 68.5% of the same form. At very high concentration, say, a 2.0 M solution, only the more aggregated species could be clearly detected. This concentration dependence is indicative of different degrees of association of two forms of MIBLi. Species A, whose relative amount increases with increasing concentration, must be more aggregated than species B.

Use of peak area ratios in the ^7Li NMR spectra of these samples, together with the quantities of MIBLi and THF used, provided the concentrations of the two forms A and B at different total concentrations and temperatures (Table II). The plot of log[A] versus log[B] for this system at 197 K has a slope of 1.83 with a correlation coefficient of 0.99. This result indicates that one species, A, is a dimer of the other, B, but does not tell whether the equilibrium involves monomer–dimer, dimer–tetramer, etc. As it has been well established up to now that MIBLi has a degree of aggregation of about 3.5 at 298 K over the concentration range of 0.07–0.34 M in THF by vapor phase osmometry,[15]

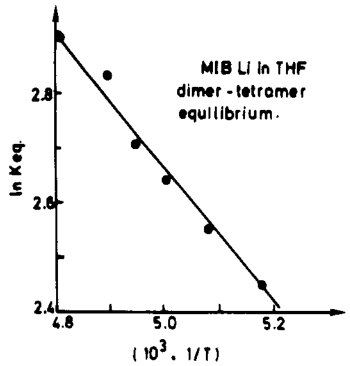


Figure 4. van't Hoff plot for MIBLi tetramer–dimer equilibrium in THF (tetramer direction).

Table III
^{7}Li NMR Data for the Line Widths[a] of Tetrameric (A) and Dimeric (B) Methyl α-Lithioisobutyrate (MIBLi) (0.2 M) in THF

T, K	dimer (B)	tetramer (A)
193	21.3	12.7
197	12.5	5.8
199	12.1	5.5
202	24.7	9.6
208	39.3	13.4

[a] At half-height ($\Delta\nu_{1/2}$, Hz).

we interpret our results in terms of a tetramer–dimer equilibrium.

From the data in Table I, we can evaluate the equilibrium constants $K = k_1/k_{-1}$

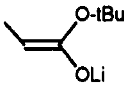
$$(\mathrm{MIBLi})_4 + 2_n\mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2(\mathrm{MIBLiS}_n)_2 \quad (\mathrm{S} = \mathrm{THF}) \tag{1}$$

for that tetramer–dimer equilibrium. Using equilibrium data at different temperatures also provides the thermodynamic parameters for this equilibrium, as $\Delta H = -2.1$ kcal/mol and $\Delta S = -13.7$ cal/mol·K (see Figure 4).

The dissociation enthalpy is rather small, and negative, close to those of −2.06 kcal reported by Seebach and −1.4 kcal by Fraenkel for the dissociation of butyllithium tetramer to dimer[16] and neopentyllithium dimer to monomer[17] in THF, respectively, as obtained from ^{13}C NMR data. On the other hand, a similar tendency has also been found by Jackman et al. in NMR spectroscopic studies on a large number of lithium phenolates in weekly polar aprotic solvents, such as THF, pyridine, etc.[18] It is generally found that dissociation of organolithium species to smaller aggregates in coordinating solvents is accompanied by increased coordination (solvation) to lithium and thus is favored at lower temperature.[16–18] The exothermicity of extra coordination to lithium might overcome energies associated with the possible bridged C–Li–C or O–Li–O bonds which are then cleaved.[17] The present results could therefore suggest that the dissociating behavior of MIBLi in THF is similar to the one generally observed for solvated organolithium compounds. The fact that the entropy change for the dissociation is negative might reasonably be interpreted in terms of steric restriction due to extra solvent molecules in the solvated dimer, relative to the tetramer.[19]

The difference in the ^{7}Li nuclear quadrupolar-induced relaxation times, as indicated by different line widths, is also striking. It could be observed from Table III that half line widths of the dimer are consistently larger than those of the tetramer, which might result from either the different electric field gradient around the Li nucleus or the different molecular correlation times. A difference in molecular correlation times is an improbable source of line-width difference, as models show that both aggregates have approximately the same largest dimension and that the dimer is the smaller overall (with consequently a shorter correlation time leading to narrower signals).[19] Thus, a likely explanation is that the electric field gradient around the Li nucleus is greater in the dimer. Again, as the temperature is raised to 199 K both lines narrow and then broaden. This is most likely because there is no significant exchange between lithium of two aggregates at very low temperature and that exchange becomes important upon increasing temperature.[19]

The crystal structure analyses have been carried out for lithium enolates of *tert*-butyl propionate (**3**), *tert*-butyl 2-methylpropionate (**4**), and methyl 3,3-dimethylbutanoate (**5**), structurally similar to MIBLi (**1**).[20]



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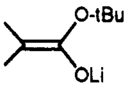

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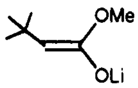

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From a detailed analysis of crystallographic data for **3**–**5** crystals obtained from a THF/TMEDA mixture (**3** and **4**) and THF (**5**), it has been revealed that dimeric aggregates $(\mathbf{3})_2$·2TMEDA and $(\mathbf{4})_2$·2TMEDA are based on $\mathrm{Li_2O_2}$ four-membered rings (with one TMEDA per Li), whereas a $\mathrm{Li_4O_4}$ cubic type geometry occurs in the tetrameric $(\mathbf{5})_4$·4THF (with one THF per Li). Although the crystal structures often may be reasonably good approximations of the nature of many organolithium compounds in solution, it is essential that dissolving a crystal often leads to a new solvated structure. The organolithium compounds in THF solution may generally well have more than one THF per Li instead of the one found in the solid state.

In addition, we note some other differences here. The change in chemical shift of the metalated carbon (C_α) in MIBLi with respect to the parent ester, i.e., methyl isobutyrate, possibly results from two different trends, one caused by the hybridization change from sp^3 to sp^2 and another due to more electron density delocalized to that C_α position. Generally, the former leads to about a 100 ppm downfield shift and the latter to about 160–200 ppm/electron in ^{13}C NMR spectra.[21] Although it is not possible to estimate quantitatively the negative charge delocalized to an α-carbon atom due to lack of suitable reference compounds having pure sp^2 carbons for MIBLi, the 39 ppm downfield shift of the α-carbon versus the parent ester does suggest that the negative charge in the present system is not totally concentrated at the oxygen atom but also delocalized to other atoms, typically the α-carbon.

In conclusion, an aggregation equilibrium between tetramer and dimer in a methyl α-lithioisobutyrate/THF solution structurally corresponding to the active end of a living PMMA is now well established thanks to the use of ^{13}C and ^{7}Li NMR. It seemed that the multinuclear NMR investigation of model compounds does provide some unique valuable indications about the nature of active species of anionic polymerization of alkyl (meth)acrylate, in particular, since it is quite difficult to obtain very direct information concerning the ion-pairing behaviors in such anionic polymerization systems by other direct methods. The effects of various factors, such as solvent, cation size, ester substituent, and different types of ligands, etc., on the structure and equilibrium of ion pairs (and aggregates) are currently investigated. Attempts to correlate the established ion-pairing behaviors with the polymerization process characteristics are also being developed. They will be the topics of a series of forthcoming papers.

Acknowledgment. NMR data were obtained through the facilities of the CREMAN center at the University of Liège. We express our sincere appreciation to Mr. A. Bouillez and Mrs. C. Henrard-Schouille for their skillful technical assistance and our gratitude to the Service de la Programmation de la Politique Scientifique and to FNRS (Brussels, Belgium) for general financial support.

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