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# Study of the Propagation Center in the Anionic Polymerization of (Meth)acrylic Monomers: NMR Study of Di-*tert*-butyl 2-Lithio-2,4,4′-trimethylglutarate and Living Poly(*tert*-butyl methacrylate) Oligomers in THF/Toluene Mixtures

**C. Zune,[†] P. Dubois,[†,⊥] J. Grandjean,[‡] J. Kriz,[§] J. Dybal,[§] L. Lochmann,[§] M. Janata,[§] P. Vlcek,[§] and R. Jérôme*,[†]**

*Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6, 4000 Liège, Belgium; Laboratoire de Chimie Fine aux Interfaces, University of Liège, Sart-Tilman, B6, 4000 Liège, Belgium; and Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 16202 Prague 6, Czech Republic*

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ABSTRACT: Solvation influences both the stereoregularity and molecular weight distribution (MWD) of poly(*tert*-butyl methacrylate) (PtBMA) prepared by anionic polymerization of tBMA with a lithium counterion in THF/toluene mixed solvents at −78 °C. As a probe of the structural changes of the propagating species, multinuclear $^{7}$Li, $^{1}$H, and $^{13}$C NMR analysis of di-*tert*-butyl 2-lithio-2,4,4′-trimethylglutarate (a model dimer, **A**) and of short-length living PtBMA chains is reported and discussed. Whatever the system, the main structure of the lithium ester enolate in THF/toluene mixtures is similar to that one reported in THF. In the case of **A** and for toluene contents exceeding 50% v/v, partly organized pseudophases can additionally be detected in the $^{7}$Li NMR spectra, but they do not provide well-developed $^{1}$H and $^{13}$C NMR signals. The chemical shifts of $^{1}$H and $^{13}$C signals of **A** support the dimeric form of this model. An equilibrium between dimeric and nonaggregated living PtBMA chains has been previously proposed to dominate in pure THF. However, marked self-termination of low-molecular weight living oligomers prepared in THF/toluene mixtures can be observed at 263 K, in contrast to the stability observed in pure THF up to 298 K. Another contrasting feature is the broadening of the molecular weight distribution which can be explained by an aggregation process that stabilizes oligomers at the early stage of the anionic polymerization as supported by SEC-RI and SEC-UV eluograms.

## Introduction

Whereas the anionic polymerization of most methacrylates is living in tetrahydrofuran (THF) at −78 °C when a highly delocalized and sterically hindered organolithium initiator is used,[1] the anionic polymerization of methyl methacrylate (MMA) and *tert*-butyl methacrylate (tBMA) is poorly controlled in toluene/THF mixed solvents (while keeping other conditions unchanged) as shown by broad and even multimodal molecular weight distributions (MWD's).[2,3] However, the anionic polymerization of tBMA leads to narrow and unimodal MWD polymer in pure toluene at −78 °C in the presence of a lithium counterion.[1,2] The unexpected behavior of tBMA[2] and MMA[3] in THF/toluene mixtures has recently been explained by multiple equilibria between nonassociated and associated ion pairs.[2,3] The increase of the final MWD under these experimental conditions has also been tentatively explained by either a radical change in the structure of the propagating species (THF-solvated and nonsolvated active species)[1] or by oligomers propagating more slowly than the living chains.[3] Since no clear information on the structure of the PtBMA propagating chains in THF/toluene mixtures has been reported yet, the main purpose of this study is to analyze short length living PtBMA chains as polymeric models by multinuclear ($^{13}$C and $^{7}$Li) NMR, in addition to a more detailed $^{1}$H, $^{13}$C, and $^{7}$Li NMR study of di-*tert*-butyl 2-lithio-2,4,4′−trimethylglutarate (**A**), which is a model for the very stage of polymerization. These data will be discussed and compared to results reported in pure THF.[4] This structural analysis will be completed by kinetic data and size exclusion chromatography (SEC) of the crude products formed at the early stage of polymerization.

## Experimental Methods

**Solvents and Materials.** Solvents (THF, toluene, THF-$d_8$, and toluene-$d_8$) were purified as reported elsewhere[2]. sBuLi (from Aldrich, 1.4 M in hexane) was diluted in hexane, and the concentration was measured by the double Gilman titration method.[5] 1,1-Diphenylethylene (DPE) was purchased from Aldrich Chemical Co., dried over nBuLi, and distilled under reduced pressure just before use. tBMA was purchased from BASF and dried over $CaH_2$ before being distilled under reduced pressure and stored under an inert atmosphere at −20 °C. Just before polymerization, a 10% $Et_3Al$/DIBAL (diisobutylaluminum hydride) solution in toluene was added to tBMA until a persistent yellow color was observed, and the monomer was then distilled under reduced pressure.

Di-*tert*-butyl 2-lithio-2,4,4′-trimethylglutarate was prepared by the addition of tBMA to *tert*-butyl 2-lithioisobutyrate by the method reported elsewhere.[6] After recrystallization and drying, the product was dissolved in tetrahydrofuran-$d_8$/toluene-$d_8$ solvent mixture under purified argon at room temperature, transferred into a previously cooled NMR tube, and sealed off under nitrogen.

Di-*tert*-butyl 2,4,4′-trimethylglutarate was prepared by hydrolysis of di-*tert*-butyl 2-lithio-2,4,4′-trimethylglutarate, purified by distillation, and analyzed by GC (99.9% purity).[6]

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[†] CERM, University of Liège.

[‡] Laboratoire de Chimie Fine aux Interfaces, University of Liège

[§] Academy of Sciences of the Czech Republic

[⊥] Present address: Service des Matériaux Polymères et Composites, University of Mons-Hainaut, Place du Parc 20, 7000 Mons, Belgium.

* Author for correspondence.

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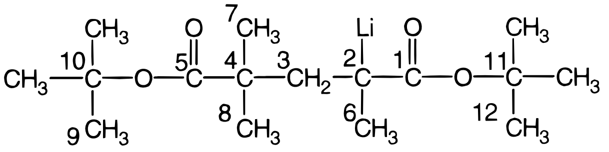
**Scheme 1. Structure of Di-*tert*-butyl 2-Lithio-2,4,4′-trimethylglutarate (A)**



**A**

**Polymerization.** Polymerization was carried out in a previously flame-dried glass reactor connected to a NMR tube under a dry nitrogen atmosphere. Liquids were transferred by previously flame-dried syringes and/or stainless steel capillaries. The initiator, i.e., diphenylhexyllithium (DPHLi), was prepared in THF by the monoaddition of sBuLi to 1,1-diphenylethylene. The purified monomer was then added to the initiator solution cooled to −78 °C. For kinetic measurements, the polymerization was quenched by acidic methanol after various times (15 s to 5 min), and the monomer conversion was determined by weighing the polymer precipitated in cold hexane and dried. For NMR measurements, a desired volume of the polymerization mixture was transferred into a NMR tube which was rapidly sealed off under nitrogen. The rest of the solution was quenched by methanol and the polymer characterized by size exclusion chromatography (SEC). For $^{13}$C NMR analysis of [PtBMA$^-$,Li$^+$], tBMA ($3.1 \times 10^{-3}$ mol) was first polymerized by DPHLi ($1.75 \times 10^{-4}$ mol) in THF/toluene mixed solvent at −78 °C followed 20 min later by the addition of labeled $^{13}$C tBMA ($2.4 \times 10^{-4}$ mol). The monomer enriched in $^{13}$C at the carbonyl site was prepared according to a seven-step synthesis, starting from acetic acid-*1*-$^{13}$*C* as detailed elsewhere.[7]

**NMR Measurements.** $^1$H, $^{13}$C, and $^7$Li NMR spectra of the model dimer **A** were measured at 300.1, 75.5, and 116.6 MHz, respectively, with a Bruker DPX 300 spectrometer. The NMR spectra of the oligomers were recorded with a ARX Bruker 400 MHz spectrometer ($^{13}$C and $^7$Li NMR spectra were measured at 100.13 and 155.5 MHz, respectively). A 0.1 mol/L LiCl solution in tetrahydrofuran (THF) was used as external standard at 298 K for $^7$Li NMR spectra. $T_1$ and $T_2$ were measured by the conventional inversion−recovery method and the Carl−Purcell B techniques.[10] All pulse sequences and other experimental methods used were reported elsewhere.[8−10] The resonance peaks were fitted to a Lorentzian curve by a simplex algorithm. The dynamic evaluations were performed in the same way as in a previous study.[8]

**Size exclusion chromatography** (SEC) was carried out in THF at 30 °C with a Hewlett-Packard 1037A apparatus equipped with a refractive index detector. Molecular weight and polydispersity ($M_w/M_n$) were calculated on the basis of a polystyrene calibration (Waters polystyrene standards, from $M_n$ = 600 to 300 000). A set of 500, 100, and 50 Å Polymer Laboratories columns and a Waters 484 UV detector were used for the analysis of the low molecular weight oligomers.

## Results

**$^7$Li, $^1$H, and $^{13}$C NMR Study of Solvent Effects on a Model Dimer, Di-*tert*-butyl 2-Lithio-2,4,4′-trimethylglutarate (A).** In THF and THF/toluene mixtures, the solubility of **A** (Scheme 1) is very poor, particularly at the low temperatures required by the stability of this dimer.[11] The tendency of **A** to form oversaturated solution by rapid cooling has been used to increase the sensitivity. Measurements that require 4−5 h at 253 K can actually be performed before the solute crystallizes.

Relevant parts of the $^1$H and $^{13}$C NMR spectra of **A** (0.08 M) in THF-$d_8$/toluene-$d_8$ mixtures at 253 K are shown in Figures 1 and 2, respectively. The $^1$H and $^{13}$C signals discussed below correspond to the superscripts in Scheme 1 and have been assigned as follows. Protons have been correlated with the directly attached carbons (C-3, C-6, C-7, C-8, C-9, C-12) by $^1$H−$^{13}$C COSY (HETCOR) (Figure 1 in Supporting Information) and with the nonprotonated carbons (C-2, C-4, C-10, C-11) by 2D COLOC (Figure 2 in Supporting Information) and 1D SSLR INEPT[10] (Figure 3 in Supporting Information). The latter method has been used for solutions of a higher toluene content, in which **A** starts to crystallize after 4 h. So, connectivities have been found for the following proton−carbon pairs: 6−2, 12−11, 10−9, (7 + 8)−4, (7 + 8)−5. C9 and C12 have been distinguished from each other because of the similarity of the chemical shifts for the carbon signals 9 and 12 and for the corresponding carbons in *tert*-butyl 2-lithioisobutyrate.[10c] To fasten the record of the $^{13}$C NMR spectra, a long-range DEPT sequence has been used. (Signal 6 is then missing as result of the corresponding coupling constant.) No marked change is observed in the $^{13}$C spectra of **A** (Figure 2) when the toluene content is increased up to 98%. However, some differences are noted when the $^{13}$C NMR spectrum of **A** in pure THF is compared to a spectrum previously reported by Kriz et al.[11] In this work, only one set of signals is observed instead of two sets in the former spectrum, attributed to nonaggregated species **(A)$_1$** and to dimeric aggregates **(A)$_2$**.[11] On this basis, only the dimeric aggregates **(A)$_2$** would be observed in the spectrum of Figure 2. The origin for this difference has to be found in the sample history (e.g., temperature and dissolution rate of **A** in THF) and, more likely, in the presence of some impurities. In this work, the sample has been heated for a short time at ca. 40 °C, and a second set of signals has appeared upon cooling to −20 °C. Under even short heating, **A** is expected to decay with release of lithium *tert*-butoxide, which is known to interact with **A** and thus to promote the **A$_2$** deaggregation.[11] Actually, small signals characteristic of lithium *tert*-butoxide can be found not only after short heating in this work but also in the previously published spectra.[11] However, whatever the spectra, no signal for the known cyclic ketone byproduct has been observed, in contrast to what happens after longer periods of decay.[11] Since the purity of the solution seems to be extremely important, all the samples have been prepared very carefully, so that only one set of signals typical of the dimer aggregate **(A$_2$)** has been observed for all fresh THF solutions. Some traces of hydrolyzed product (di-*tert*-butyl 2,4,4′-trimethylglutarate) have been detected in some spectra of **A**, but the amount was negligible compared to the lithiated product.

In agreement with $^{13}$C spectrum, the $^1$H NMR spectrum of **A** in pure THF showed only one set of signals characteristic of the dimeric aggregate (**A$_2$**). Figure 1 shows that the toluene content has a much stronger effect on the $^1$H chemical shifts than on the $^{13}$C ones. For example, the chemical shifts changed by 0.6 ppm for H6 and by 0.3 ppm for H9, H8, and H7 when pure THF is replaced by a 10/90 v/v THF/toluene mixture. The pronounced difference in the behavior of H6 and the other protons indicates that more than a simple isotropic solvent shift (well-known for aromatic solvents and checked by us for the same solvent mixtures with the protonated analogue of **A**) is operative consistently with a slight shift of the Li-binding group toward the ester−enolate structure. The same tendency results from the careful examination of the $^{13}$C spectra, which may indicate a tighter binding in the **(A)$_2$** dimer.

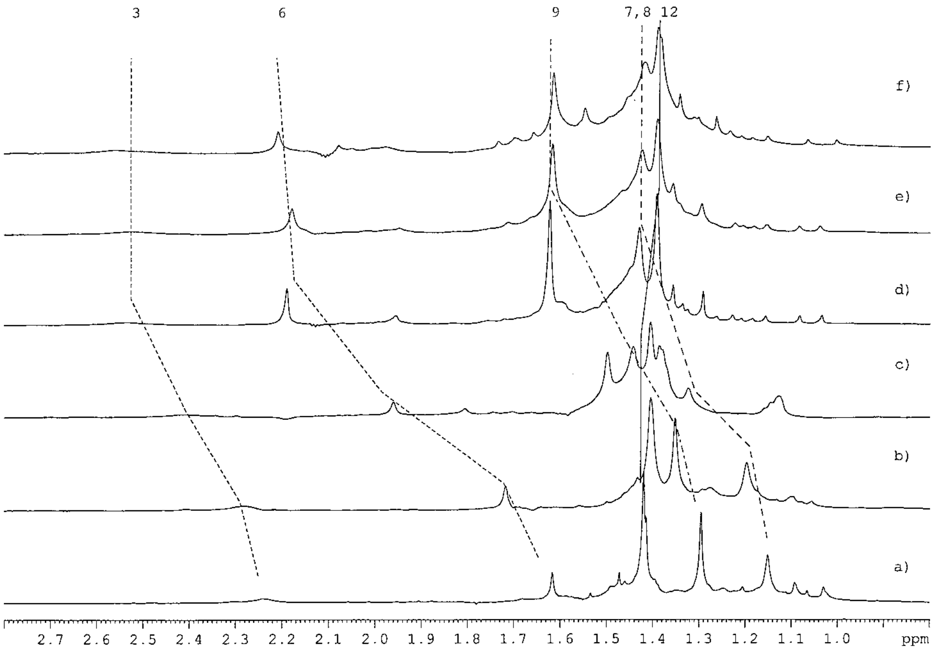


**Figure 1.** The 300.1 MHz $^1$H NMR spectra of **A** at 253 K in THF-$d_8$/toluene-$d_8$ (v/v %) at 0.08 M: (a) 100/0, (b) 80/20, (c) 40/60, (d) 20/80, (e) 10/90, (f) 2/98.

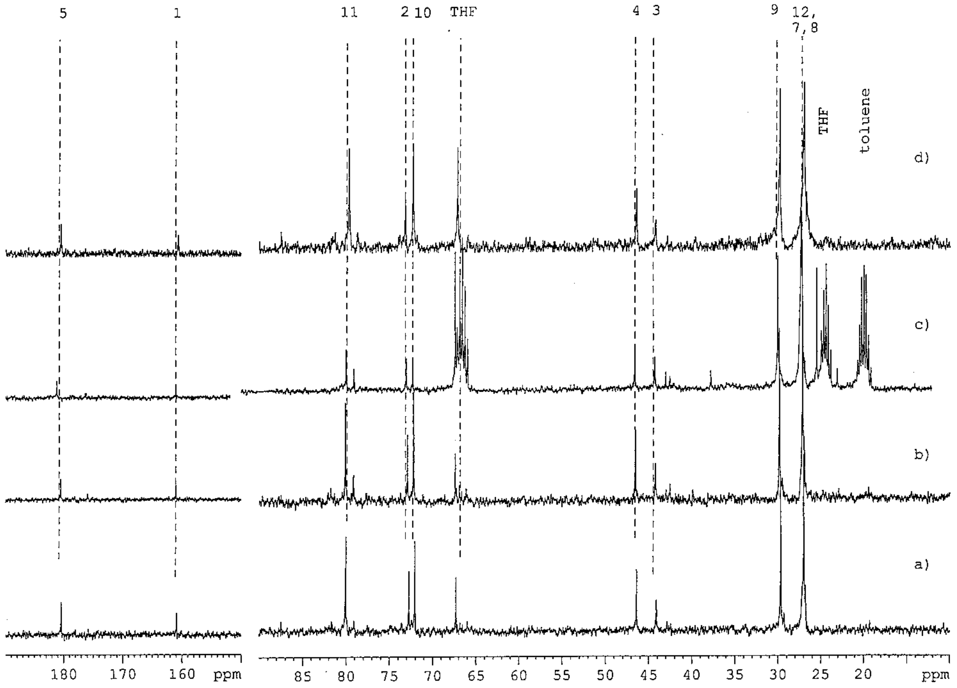


**Figure 2.** The 75.5 MHz $^{13}$C DEPT-LR NMR spectra of **A** at 253 K in THF-$d_8$/toluene-$d_8$ (v/v %) at 0.08 M: (a) 100/0, (b) 80/20, (c) 40/60, (d) 20/80.

Nevertheless, for all the THF/toluene compositions, only one major set of signals is observed; i.e., no important change in the aggregation occurs. Some other minor peaks can be detected (cf. Figure 1), however, which are more likely due to other states of **(A)$_2$** (solvation, conformation, association). Some of these peaks have been assigned to the protonated form (hydrolyzed product), but in relatively low concentrations.

Both $^1$H and $^{13}$C spectra thus indicate that the toluene content of the THF/toluene mixed solvents has no substantial effect on the structure or aggregation state of **A**. To confirm this conclusion, $^1$H $T_1$ relaxation times have been measured for all the solutions at 253 K. As shown in Table 1, $T_1$ for nearly all protons decreases upon increasing the toluene content, but possibly in relation to an increased solution viscosity (and thus longer correlation and cross-correlation times). Since no profound changes in the structure of **A** are found, it is

**Table 1. $^1$H Relaxation Times $T_1$ (s) of Di-*tert*-butyl 2-Lithio-2,4,4′-trimethylglutarate (A, 0.08 M) in Various THF/Toluene Mixed Solvents at 253 K**

| | $T_1$ relax. times (ms) (THF/toluene content (v/v %)) | | | |
|---|---|---|---|---|
| proton no. | 10/90 | 20/80 | 40/60 | 80/20 |
| H3 | 0.17 | 0.19 | 0.2 | 0.2 |
| H6 | 0.41 | 0.43 | 0.44 | 0.47 |
| H7,8 | 0.19 | 0.2 | 0.2 | 0.18 |
| H9 | 0.3 | 0.35 | 0.32 | 0.34 |
| H12 | 0.25 | 0.27 | 0.32 | 0.3 |

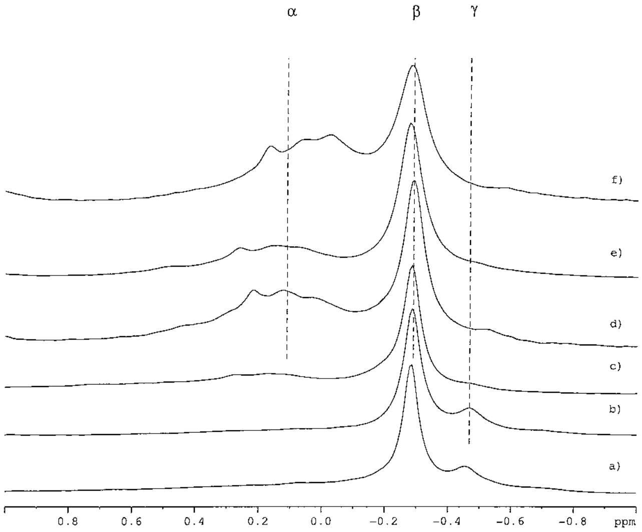


**Figure 3.** The 116.6 MHz $^7$Li NMR spectra of **A** at 253 K in THF-$d_8$/toluene-$d_8$ (v/v %) at 0.08 M: (a) 100/0, (b) 80/20, (c) 40/60, (d) 20/80, (e) 10/90, (f) 2/98.

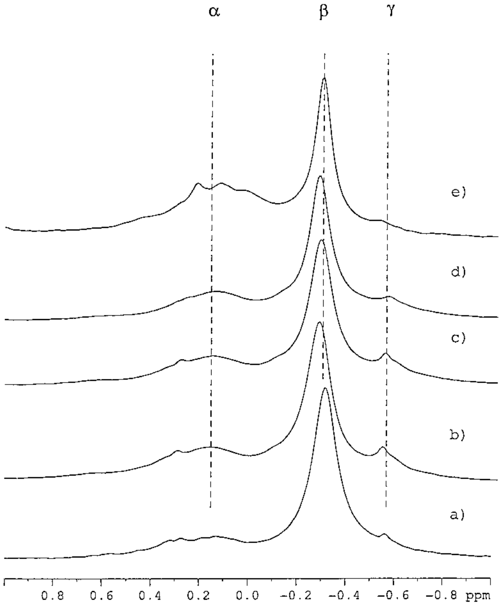


**Figure 4.** The 116.6 MHz $^7$Li NMR spectra of **A** in 20/80 THF-$d_8$/toluene-$d_8$ at 0.08 M at various temperatures: (a) 223, (b) 227, (c) 233, (d) 243, and (e) 253 K.

clear that the strongly prevailing form of **A**, irrespective of temperature or THF/toluene ratio, is the dimeric aggregate (**A$_2$**).

Figure 3 compares the $^7$Li NMR spectra for a 0.08 M solution of **A** in various THF/toluene mixtures at 253 K, whereas Figure 4 shows the temperature dependence of the spectrum for solution in the 20/80 THF/toluene mixture. All the spectra in Figure 3 show one main signal ($\beta$) at ca. $-0.28$ ppm (in reference to a 0.1 M LiCl solution in THF). A broad group of signals (α) is also observed in the range 0.5 to $-0.2$ ppm for the solution containing at least 50 vol % toluene, whose the relative intensity increases with the toluene content. Moreover, the relative intensity of the signals α and $\beta$ in the $^7$Li NMR spectrum changes upon storage at 253 K (as shown in Figure 4 as Supporting Information). These changes can be reversed if the sample is heated to room temperature and then cooled to 253 K. This observation may be explained by the gradual formation of loosely organized and relatively voluminous aggregates in the oversaturated solution prior to crystallization. Furthermore, a third minor signal $\gamma$ at ca. $-0.45$ ppm is observed in THF-rich solutions. Upon increasing toluene content, it becomes broader, being finally undetectable. No separate set of $^1$H and $^{13}$C signals could be assigned to either α or $\gamma$ signals, indicating thus that they are not the signature of radically different structures.

**Table 2. $^7$Li NMR Relaxation Times $T_1$ of Di-*tert*-butyl 2-Lithio-2,4,4′-Trimethylglutarate (A, 0.08 M) in Various THF/Toluene Mixtures at 253 K**

| THF/toluene (vol %) | $^7$Li NMR relaxation times $T_1$ (ms) | | |
|---|---|---|---|
| | α (0.5 ppm) | $\beta$ ($-0.28$ ppm) | $\gamma$ ($-0.85$ ppm) |
| 100/0 | | 90.95 | 65.86 |
| 80/20 | | 86.86 | 68.27 |
| 40/60 | | 71.62 | |
| 20/80 | 46.7 | 66.51 | |
| 10/90 | 42.7 | 66.48 | |

**Table 3. Anionic Polymerization of tBMA in Various THF/Toluene Mixtures at − 78 °C with a Lithium Counterion**[a]

| THF/toluene (vol %) | $M_{n,SEC}$ | MWD |
|---|---|---|
| 100/0 | 3600 | 1.4 |
| 50/50 | 5060 | 1.45 |
| 20/80 | 3800 | 2 |
| 10/90 | 2200 | 2.9 |
| 6/94 | 2700 | 2.9 |

[a] Initiator: DPHLi.

Table 2 shows $^7$Li $T_1$ relaxation times measured at increasing toluene contents. The $T_2$ values of the α and $\beta$ signals are almost identical, and accordingly, the signal shape of the central $\beta$ peak is Lorentzian, showing thus that the extreme narrowing conditions are fulfilled. Therefore, only $T_1$ data will be discussed further. In accordance with the $^1$H relaxation, the $T_1$ decrease with increasing toluene content can thus be attributed to increasing viscosity rather than to any pronounced structural or solvation change. As expected, the more voluminous aggregates (α, $\gamma$) have shorter relaxation times, but again, the change is not dramatic, indicating thus that the corresponding species are stabilized by rather weak Li bonding and can be characterized as a pseudophase rather than tight aggregates.

We can thus conclude that **A** forms a dimer (**A$_2$**) in THF and THF/toluene mixed solvents. Additionally, the increase in the toluene content is responsible for the formation of relatively voluminous metastable pseudoaggregates whose structure and solvation state would be comparable to **A$_2$**, although their reactivity might be markedly different toward the monomer.

**Solvent Effect on Living *tert*-Butyl Methacrylate Oligomers Studied by $^{13}$C and $^7$Li NMR.** The macromolecular parameters of the living oligomers studied in this work are shown in Table 3. Figure 5 compares the $^7$Li NMR spectra for living oligomers prepared in situ (0.01 M Li solutions) in different THF/toluene mixtures and measured at temperatures in the 200−280 K temperature range. In all the cases, the lithium signal has a slightly twisted and super-Lorentzian shape which indicates a rather tight bonding of Li to a slowly rotating voluminous species. When the solution contains more than 10% (v/v) THF, the spectra are mostly dominated by the two resonances observed at $-0.56$ and $-0.73$ ppm (A and B, respectively) in pure THF. The relative A/B intensity changes when the temperature

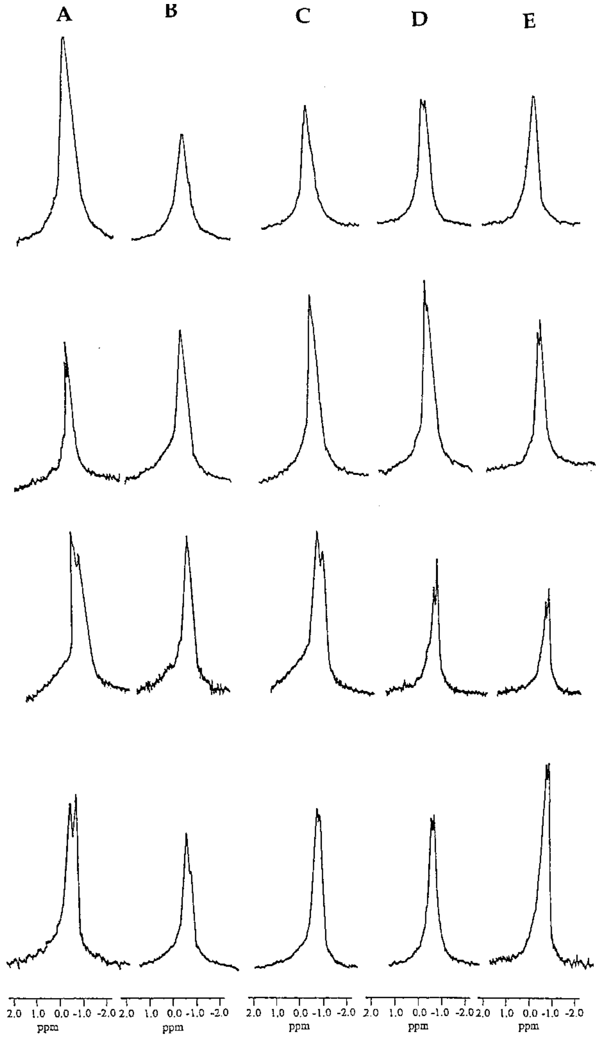


**Figure 5.** The 155.5 MHz $^7$Li NMR spectra of [PtBMA$^-$,Li$^+$] in THF/toluene mixtures of various compositions ([RLi]: 0.01 M): (a) 35/65 THF/toluene, (b) 20/80 THF/toluene, (c) 10/90 THF/toluene, (d) 2/98 THF/toluene. (A) 200, (B) 220, (C) 240, (D) 260, and (E) 280 K. The molecular weight ($M_n$) measured by SEC (polystyrene standards) is ca. 3000.

is increased from 195 to 280 K for the samples containing more than 10% THF. Although this modification seems to be quite independent of the mixed solvent composition, the poor resolution of the spectra (as a result of fast measurements) prevents any definite conclusion to be drawn. In the 2/98 THF/toluene mixture, mainly one broad signal is observed at −0.2 ppm ($\Delta\nu_{1/2}$ = 100 Hz at 200 K), which changes with increasing temperature and splits into A and B at 280 K. This signal broadening in THF-poor media is reminiscent of the behavior of the model dimer and could be explained, at least partly, by the increased viscosity.

A shoulder on the left side of the signals is observed in some spectra due to the presence of a third broad signal (C). When the living PtBMA is prepared at 253 K instead of 195 K, the $^7$Li NMR spectrum shows the three signals (A, B, C), the signal C being well-defined (Figure 6). The shape of the spectrum is not modified by cooling the solution. One possible explanation is the limited stability of the living chains at 253 K and formation of some lithium *tert*-butoxide. Complexation of the living oligomers by this byproduct could lead to a new species responsible for the signal C.

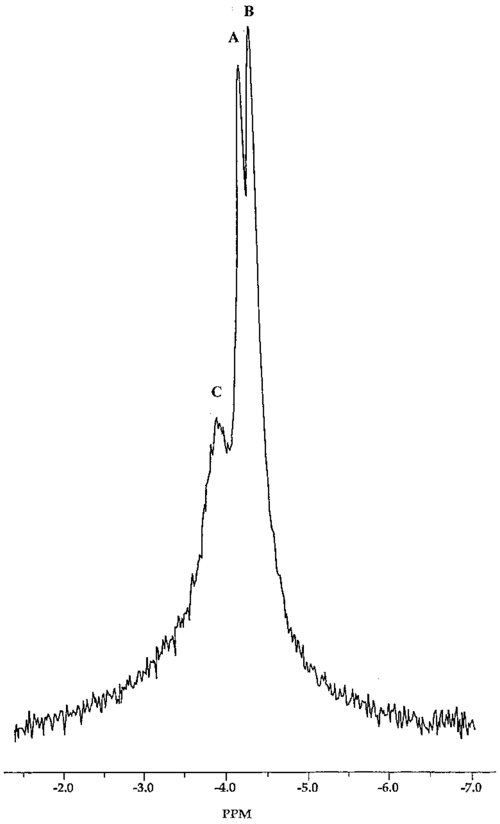


**Figure 6.** The 155.5 MHz $^7$Li NMR spectra of [PtBMA$^-$,Li$^+$] in 10/90 THF/toluene mixture ([RLi]: 0.01 M) prepared at 253 K and observed at 253 K. The molecular weight ($M_n$) measured by SEC (polystyrene standards) is ca. 3000.

**Table 4. Difference in Chemical Shifts for the A and B Signals, and Crude Approximation of the Rate of Exchange Extracted from the $^7$Li NMR Spectra of [PtBMA$^-$,Li$^+$] in Various THF/Toluene Mixed Solvents at 200 K**

| THF/toluene (vol %) | $\Delta\nu = (\nu_A - \nu_B)$ | $k_{\text{exchange}}$ |
|---|---|---|
| 100/0 | 0.17 | 0.06 |
| 20/80 | 0.24 | 0.04 |
| 10/90 | 0.27 | 0.037 |
| 4/96 | 0.28 | 0.036 |
| 2/98 | 0 | |

In previous studies,[4,8] the two $^7$Li NMR signals (A and B) observed in THF solution were assigned to a dimeric aggregated form and nonaggregated species of [PtBMA$^-$, Li$^+$], respectively. At 203 K and in pure THF, the exchange between these A and B species is slow (i.e., in the 0.1−0.05 s$^{-1}$ range as estimated from the $^7$Li NMR chemical shifts), in rather good agreement with the 0.2 s$^{-1}$ value proposed by Müller from kinetic measurements.[12] The estimated exchange rates between A and B in THF/toluene mixed solvents (in the limits of the quality of the spectra) are reported in Table 4. No profound change is observed when the toluene content is increased.

So, the increase in the toluene content of the polymerization medium does not markedly influence the two main species observed, i.e., the living oligomers and the dimeric aggregates, their equilibrium, and their interconversion rate.

To get more information about the structure of the terminal lithium ester enolate group,$^{13}$C NMR spectra were measured for the living oligomers whose few terminal monomer units contained $^{13}$C-enriched carbonyl groups. The $^{13}$C NMR spectra of [PtBMA$^-$,Li$^+$] in

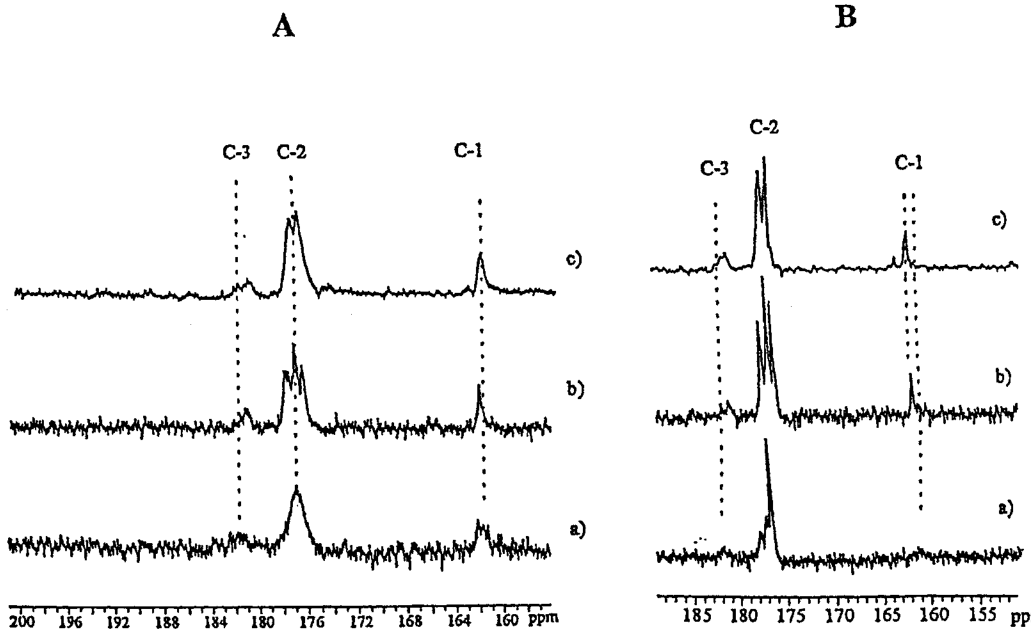
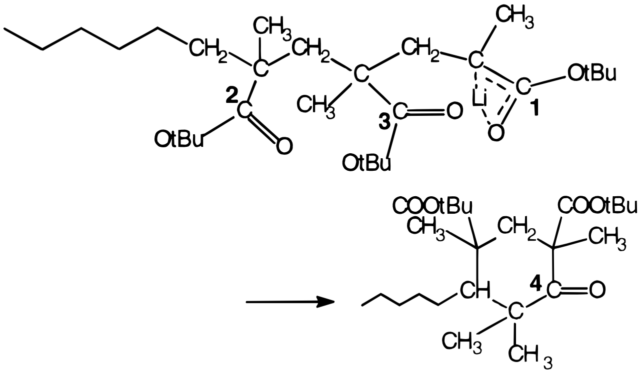


**Figure 7.** The 100.13 MHz $^{13}$C spectra of [P(tBMA-*b*-tBMA$^{*-}$,Li$^+$)] in THF/toluene mixtures of various compositions ([RLi]: 0.01 M). The molecular weight estimated by SEC (polystyrene standards) is 4000, and the chains are end-capped by ca. three $^{13}$C-labeled tBMA units: (A) 220 K, (B) 240 K; (a) 2/98 THF/toluene, (b) 20/80 THF/toluene, (c) 35/65 THF/toluene.

**Scheme 2. Structure of the End Units of [PtBMA−,Li$^+$]**



different THF/toluene mixed solvents are shown in Figure 7. The concentration of lithium ester enolate was 0.01 M, and ca. 3 equiv of $^{13}$C-labeled tBMA units was added in the final step of the oligomerization reaction, so that the chemical shift for the penultimate carbonyl could be detected. Due to the stochastic nature of the monomer addition, the length of the $^{13}$C-labeled blocks is not uniform, but a distribution has to be considered.

Figure 7 shows three main types of carbonyl signals in the 150−190 ppm range. The assignment of the $^{13}$C NMR signals corresponds to the superscripts in Scheme 2. The C-1 (around 163 ppm) and C-3 (around 182 ppm) signals correspond to the living end groups and to the penultimate carbonyl groups, respectively. The chemical shift of the terminal carbonyl carbon is identical to that one of classical α-lithio ester enolate. The C-3 carbon has a chemical shift quite comparable to the penultimate carbonyl carbon in the dimer model, whether it is lithiated or not.[4] C-2 is the contribution of the carbonyl ester of the other monomeric units.[4,8,9] Parts A and B of Figure 7 (that differ in temperature, i.e., 220 and 240 K, respectively) show similar chemical shifts for the C-1 and C-3 signals in different THF/toluene mixtures. The group of signals C-2 reflects changes in the chain stereoregularity with the THF content. When this content is only 2%, mainly one signal for the highly isotactic mmmm pentad is observed in the C-2 region.

Both the C1 and C3 signals are broad at 220 K, particularly at higher toluene contents. In contrast to C2, this broadness is not decreased when the temperature is increased. (An analogous behavior was observed in the $^{13}$C NMR spectra for the model dimer **A.)** At 240 K, the C1 signal is almost lost. The signal resolution of the $^7$Li NMR spectra decreases as result of broadening in the 220 and 240 K range that might be due to an intermediate exchange rate, probably between two different solvation states.

The striking similarity in the chemical shifts for the above-discussed $^{13}$C spectra and those ones observed in pure THF[4] suggests that the structure of the propagating chains is not deeply changed by the gradual substitution of THF by toluene. The only marked distinction between pure THF and mixtures with toluene is the loss of the C1 signal splitting more likely due to signal broadening.

By analogy with pure THF, no intramolecular complexation of the lithium counterion by the penultimate ester function can be detected up to the 2/98 THF/toluene ratio at −78 °C. In this solvent mixture, the chemical shift of the C-3 carbonyl carbon remains identical to that one of the neutral version of the dimer model, in which no coordination can occur. This observation is rather surprising since the vastly predominating termination reaction of the living species is a backbiting reaction that leads to the formation of a cyclic $\beta$-keto ester (Scheme 2), as illustrated by Figure 8 in the case of [PtBMA$^-$,Li$^+$] in 20/80 THF/toluene at 263 K. The C-1 resonance slowly disappears in favor of a cyclic ketone signal C-4 at 212 ppm (cf. Scheme 2). The backbiting reaction is fast at 263 K in THF/toluene mixtures, compared to 298 K in THF. Since self-condensation of simple ester enolates is known to be easier in more polar and more solvating solvents, the more important propensity of the [PtBMA$^-$,Li$^+$] oligomers to backbiting in the less polar media might be the sign of the vicinity of the penultimate carbonyl groups

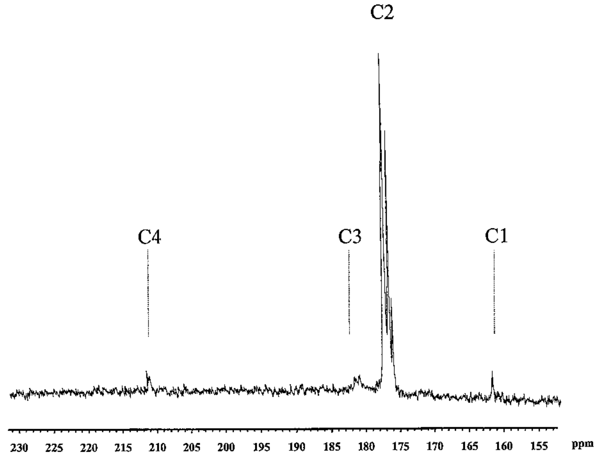


**Figure 8.** The 100.13 MHz $^{13}$C spectra of P[tBMA-*b*-tBMA$^{*-}$,Li$^+$] in 20/80 THF/toluene mixture at 264 K: termination process.

**Table 5. Data for the Anionic Polymerization of tBMA in THF/Toluene Mixtures at −78 °C Initiated by DPHLi as Initiator**[a]

| THF/toluene (vol %) | reaction times (s) | $X_p$ (%)[b] | $M_n$(cal) | $M_n$[b] (SEC) | $M_w/M_n$ |
|---|---|---|---|---|---|
| 100/0[c] | 30 | 34 | | *d* | *e* |
| | 60 | 50 | 1000 | 1700 | 1.5 |
| | 120 | 81 | 2200 | 3000 | 1.5 |
| | 300 | 94 | 3200 | 4000 | 1.4 |
| 12/88 | 30 | 22 | 2800 | 4900 | 1.7 |
| | 60 | 30 | 3800 | 5400 | 1.8 |
| | 120 | 39 | 5000 | 6800 | 2.0 |
| | 180 | 55 | 7000 | 9200 | 2.2 |
| 6/94 | 15 | 7 | 900 | 3600 | 1.4 |
| | 30 | 9 | 1200 | 7800 | 1.3 |
| | 60 | 23 | 3000 | 9500 | 1.4 |
| | 120 | 36 | 4600 | 12600 | 1.8 |

[a] [tBMA] = 0.27 mol/L, [I$_0$] = 0.003 mol/L. [b] The contribution of the oligomers has not been taken into account. [c] See ref 14, [tBMA] = 0.31 mol/L, [I$_0$] = 0.013 mol/L. [d] Bimodal. [e] Broad.

as shown in Scheme 2. Although this situation could be favored by intramolecular coordination, there is no spectral evidence for such a coordination.

**Effect of the Toluene Content of the Polymerization Medium on Reactivity and Molecular Weight Distribution of PtBMA.** As already reported, the anionic polymerization of tBMA in THF/toluene mixtures leads to PtBMA of broad MWD when the toluene content exceeds 50% v/v.[2] The effect of the solvent polarity on the monomer conversion for the anionic polymerization of tBMA initiated by (1,1-diphenyl-3-methylpentyl)lithium (DPHLi) has been analyzed by gravimetry of the polymer formed. Table 5 summarizes the characteristic data for the tBMA polymerization in two different THF/toluene mixtures. SEC-RI analysis of the polymer prepared in the two solvent mixtures shows a broad and multimodal MWD. The increase of $M_{n,SEC}$ with the monomer conversion is worth pointing out (Table 5).

Figures 9 and 10 show that the chain polydispersity increases at high monomer conversion in the 12/88 THF/toluene mixture. Low-molecular weight oligomers ($M_n \sim 2000$), formed in the early stage of polymerization, become relatively less important although they persist at higher monomer conversions (SEC-RI chromatograms). The SEC-UV detector is sensitive to the aromatic fragment of the initiator and shows that both the polymeric and the oligomeric chains are initiated by DPHLi.

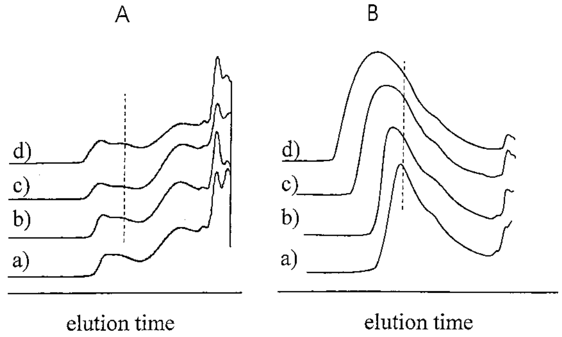


**Figure 9.** SEC-UV (A) and SEC-RI (B) traces of PtBMA initiated by DPHLi at −78 °C in a 20/80 THF/toluene mixture. tBMA conversion: (a) at 22%, (b) 30%, (c) 39%, and (d) 55%.

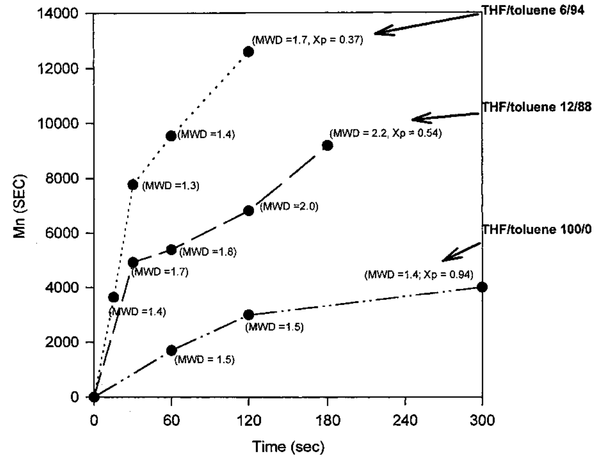


**Figure 10.** Time dependence of the molecular weight ($M_{n,SEC}$) for the tBMA polymerization in THF/toluene mixture at −78 °C, initiated by DPHLi. The polydispersity index is added to the figures.

At low monomer conversion (22%), the SEC-UV analysis indicates that ca. 82% initiator is part of the oligomers (mixture of dimers, trimers, tetramers, etc.) and thus 18% of the polymer ($M_w/M_n = 1.7$). Even the DPH-tBMA 1/1 adduct can be detected. At 50% monomer conversion, the polydispersity of the polymer has increased up to 2.3, and 23% initiator contributes to the SEC-UV signal of the polymeric chains. At complete conversion, oligomers are still present and the polydispersity is 2.9. So, the initiation efficiency is less than 1 for the high molecular weight chains, since part of the initiator is involved in slowly growing or even dormant oligomers. In this respect, Figure 11 illustrates the relative DPH intensity calculated from the area for the DPH−tBMA adduct, the oligomers, and the polymeric fraction. Part of the initiator is still reacting when long chains are already formed, whereas part of the DPH−tBMA adduct forms short oligomers. A comparable observation is reported in the 6/94 THF/toluene mixed solvent, although the initiation efficiency is still lower (cf. Table 5).

The polymerization time is significantly longer in the THF/toluene mixtures compared to that in pure THF. However, the actual concentration of the active species, [P*], which can be extracted from the dependence of the experimental molecular weight on the monomer conversion (Figure 12), is higher in THF, e.g., 10 times higher than in the 6/94 THF/toluene mixture. These data reveal that the initiation efficiency (*f*) decreases when the toluene content of the solvent mixture is increased. It must be noted that the initiator which is originally

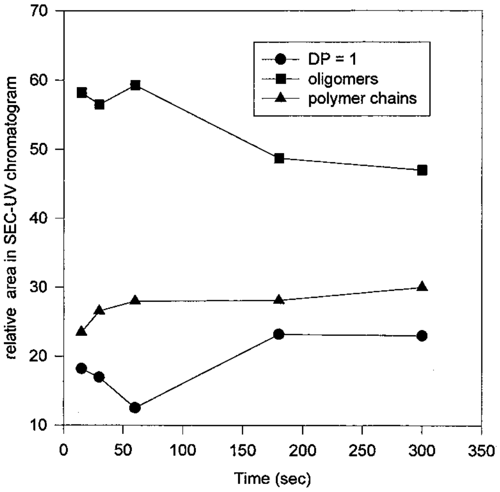


**Figure 11.** Data for the oligomerization of tBMA in 12/88 THF/toluene mixture at −78 °C using DPHLi as initiator.

inactive is converted into low molecular weight oligomers and that part of these oligomers are activated along the polymerization process. Therefore, the concentration of the active species is not constant, as confirmed by the change in the SEC curves versus time, and [P*] are average values. Within the limits of this restriction, the apparent rate constant ($k_{app}$) has been calculated from the first-order plot of $-\ln(1 - X_p)$ versus time ($X_p$ is the molar fraction of tBMA that has been converted). From [P*], the propagation rate constant ($k_p$) has been calculated from $k_{app}$, and [P*] and found to increase from pure THF (0.77 L mol$^{-1}$ s$^{-1}$) to THF/toluene mixtures of increasing toluene content ($k_p = 3.2$ L mol$^{-1}$ s$^{-1}$, in 6/94 THF/toluene mixture). It thus appears that the propagation rate is higher in apolar media than in pure THF.

**Anionic Polymerization of tBMA in Pure Toluene.** The anionic polymerization of tBMA in toluene with a lithium counterion leads to a highly isotactic polymer with a narrow MWD ($M_w/M_n = 1.2$).[1,2] However, the polymer is contaminated by low molecular weight chains.[2] Compared to what happens in THF/toluene mixtures, the oligomers formed in toluene are shorter ($M_n = 615$ compared to 2200 in THF/toluene mixed solvent), and they contain 80% of the C−Li bonds of the [PtBMA$^-$,Li$^+$] solution.

## Discussion

The NMR results reported in this study lead to the conclusion that only one type of structure has to be assigned to the ester enolate group of both [PtBMA$^-$, Li$^+$], parent oligomers, and the dimeric model, whatever the polarity of the polymerization medium. The anionic species would merely be involved in association equilibria, i.e., dimeric aggregation or formation of kind of a pseudophase. SEC analysis of the polymerization product suggests, however, that growing species of markedly different reactivity coexist, particularly in media of a lower THF content. This apparent contradiction should be discussed in reference to previous studies reported in this field.

Solvation effects have been extensively studied in the anionic polymerization of polar monomers.[13] From the kinetics of the tBMA anionic polymerization in toluene,[1] Müller has proposed that the Li counterion of the active species is intramolecularly coordinated to the ester function, whereas an association equilibrium between THF-solvated dimeric and THF-solvated monomeric active species is operative in pure THF.[12] Therefore, the intramolecularly coordinated growth center is expected to be modified when various amounts of THF are added to toluene. This could explain, for instance, why the MW distribution of PMMA and PtBMA becomes broad and even multimodal when the polymerization is conducted in THF/toluene solvents, rather than in toluene.[2,3] Moreover, solvation dominates the stereoregularity of the final polymer from highly isotactic in pure toluene to predominantly syndiotactic in THF. These phenomena are usually explained by a Coleman−Fox multistate stereochemistry model[15,16] i.e., a shift of the equilibria toward more THF-solvated active species when the THF content is increased, which results in a stepwise increase in syndiotactic placements.[2]

Another characteristic of the anionic polymerization of MMA in THF/toluene mixed solvents at low temperature is the presence of low-molecular weight compounds.[3] Indeed, a large number of chains initiated by fluorenyllithium (FluLi) do not participate in propagation, but rather form oligomers that coexist with the growing chains. Although these oligomers contain a terminal C−Li bond since they are able to react with tritiated acetic acid, they are apparently unreactive to MMA.[3] The same phenomenon is observed in this work, when the anionic polymerization of tBMA is initiated by DPHLi in THF/toluene mixtures at −78 °C. Indeed, when this polymerization is resumed by addition of a second monomer feed, some oligomers proved to be inactive[2] or pseudoterminated according to Glüsker et al.[3] Formation of pseudoterminated oligomers in the 12/88 THF/toluene mixture has been confirmed by SEC ($M_n$ = ca. 2000), whereas no trace of backbiting reaction has been found by $^{13}$C NMR (no evidence of ketone at the early stage of polymerization).

From kinetic analysis, Glüsker et al.[3] have concluded that the propagation rate constant of the MMA polymerization is decreased when the mixed solvent is rich in toluene. When the anionic polymerization of MMA is initiated by FluLi at −60 °C in a 15/85 THF/toluene mixture, the propagation rate constant ($k_p$) is $7.3 \times 10^{-3}$ s$^{-1}$ compared to $1.3 \times 10^{-3}$ s$^{-1}$ in the 1/99 THF/toluene mixed solvent.[3] However, these data have been calculated on the assumption that the molar ratio of the active polymer to the pseudoterminated chains is constant whatever the monomer conversion. This assumption is not confirmed by this study. The fraction of the initiator contained in the oligomers at the early stage of polymerization in the 12/88 THF/toluene mixture decreases with increasing conversion, so that some oligomers are able to grow to longer chains (Figure 10).

Kinetic data for the anionic polymerization of tBMA have also been published by Müller,[17,1] who reported $k_p = 45$ mol/L$^{-1}$ s$^{-1}$ in toluene at −40 °C, compared to 6 mol/L$^{-1}$ s$^{-1}$ in THF at the same temperature. The same general dependence of the propagation rate constant on the solvent polarity is thus observed in this work.

The polymerization experiments reported in this work are consistent with three types of species in the anionic polymerization of tBMA in THF/toluene mixtures: (i) dormant or pseudoterminated species at the origin of oligomerization, (ii) much less reactive species of short or intermediate length, and (iii) highly reactive species leading to chain of high polymerization degree.

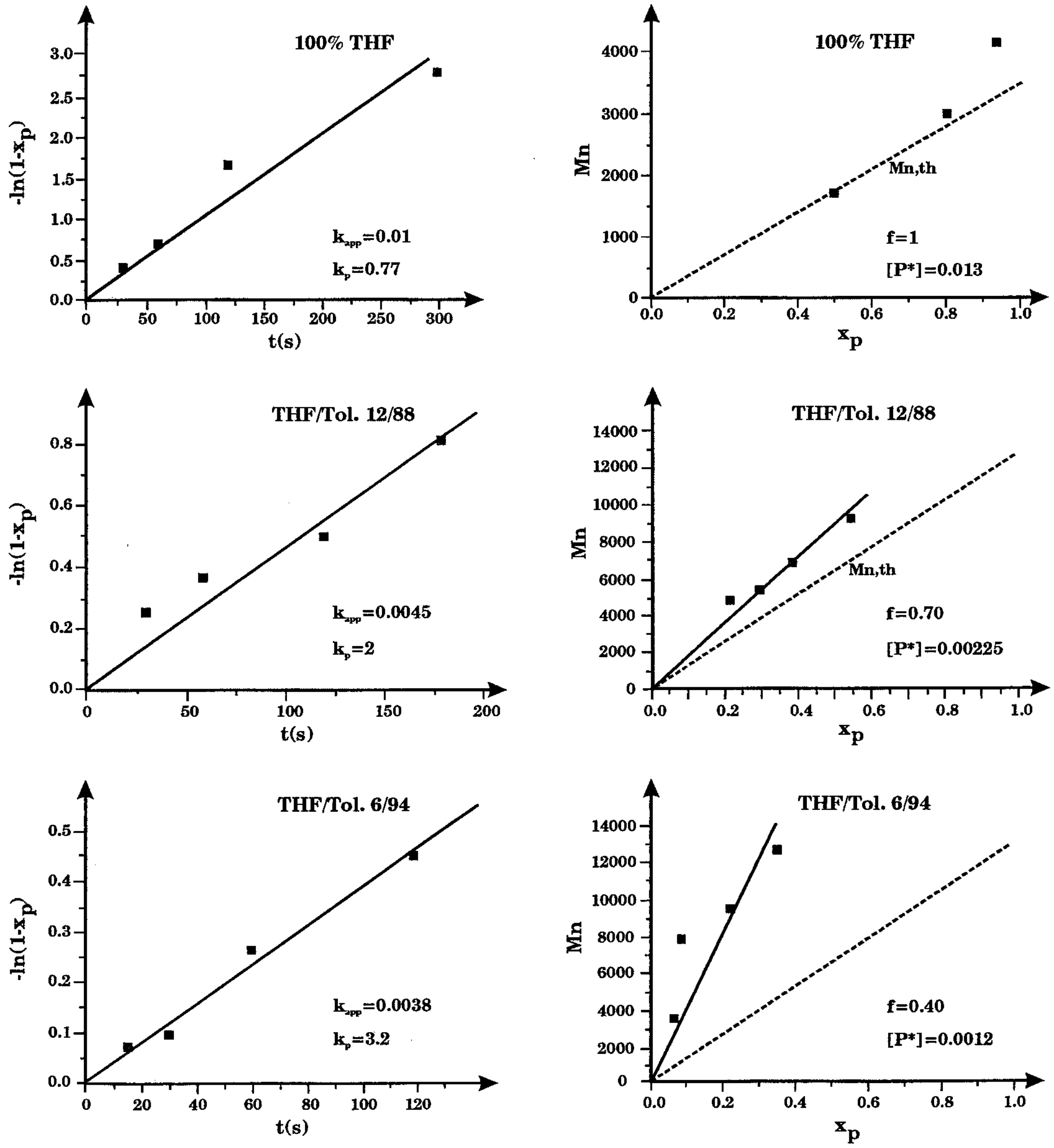
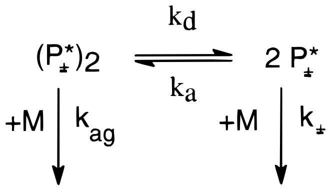


**Figure 12.** (A) First-order plot of $-\ln(1 - X_p)$ versus time and (B) plot of molecular weight ($M_{n,SEC}$) versus conversion ($X_p$) for the polymerization of tBMA at −78 °C using DPHLi as initiator in (a) pure THF, (b) 12/88 THF/toluene mixture, and (c) 4/96 THF/toluene mixture.

The dormant or pseudoterminated species (also observed in THF[14]) would be the result of an early stabilization. Glusker et al.[3] have proposed a stabilization mechanism based on intramolecular complexation. This hypothesis is however unable to explain why this mechanism would be no longer operative when the chain length exceeds a definite value. The aggregation of low-molecular weight oligomers could be an alternative explanation. Indeed, the dimeric aggregation of the dimer **A** has been observed even in pure THF.[9] Furthermore, $^7$Li NMR spectra of dimer **A** confirmed aggregation into loosely organized voluminous aggregates in toluene-rich (more than 50%) mixed solvents. In pure toluene, the very poor resolution of the NMR spectra of **A** could also result from strong self-aggregation. We thus propose that the aggregation of the oligomers formed in the early polymerization stage is the main reason for the observed phenomena. Thus, aggregates or pseudophases containing a different number of living species and being of a different reactivity toward the monomer would coexist: the monomeric species being most reactive, the dimeric one being slightly less reactive, and the larger aggregates being basically nonreactive for steric reasons. According to NMR spectra, the propensity of the living oligomers to aggregate decreases as the polarity of the mixed solvent is increased, THF being a solvating agent for the organolithium species and increasing the dielectric constant of the medium.

The species responsible for polymerization would result from the tendency for the Li ester enolate to be less associated in good solvents for PtBMA (THF and toluene) as the length of the chains is increased. If the exchange rate is slower than the propagation one, a fraction of nonaggregated or dimeric living species could initiate polymerization according to the two-state mechanism shown in Scheme 3.[12] The MWD of a two-state mechanism is predicted by the following equation: $M_w/M_n = 1 + k_{\pm}/\alpha k_a$,[12] where $k_a$ is is the exchange rate between the aggregated and the nonaggregated species, $\alpha$ the aggregation fraction, and $k_{\pm}$ the propagation rate. Any modification of these parameters will affect strongly the polydispersity. On the basis of the $^7$Li NMR spectra, this study fails to indicate that the substitution of up

**Scheme 3. Two-State Mechanism of Polymerization**



to 90% of THF by toluene markedly brings changes in the interconversion rate ($k_d$) and the fraction $\alpha$ shown by the $^7$Li NMR spectra. Moreover, the increase in the propagation rate ($k_p$) from 0.77 to 3.2 L mol$^{-1}$ s$^{-1}$ could also affect profoundly the polydispersity of the PtBMA prepared in more apolar media.

Scheme 3 is only valid to the highly reactive species responsible for the formation of chains of high polymerization degree. The SEC chromatograms of PtBMA formed in THF/toluene mixed solvents versus time show that a fraction of the dormant species is partly deaggregated along the polymerization process. The change in the aggregation state of these oligomers allows them to propagate slowly and to contribute to the broadening of the MWD.

In conclusion**,** the similarity of the $^7$Li and $^{13}$C NMR spectra confirms that the structure of the growth sites in the anionic polymerization of tBMA in THF/toluene mixed solvents is close to that one observed in pure THF.[4] Furthermore, the toluene content strongly affects the efficiency of the polymerization, which is drastically lower in apolar media. Higher toluene content in THF/toluene mixtures increases strongly the polydispersity of PtBMA. Therefore, the course of the tBMA polymerization in different THF/toluene mixtures appears to be controlled by changes in the aggregation of the active species rather than by modifications of their structure.

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**Supporting Information Available:** $^1$H−$^{13}$C COSY, $^{13}$C, and $^7$Li NMR spectra of **A**. This material is available free of charge via the Internet at http://pubs.acs.org.

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