

# Anionic Polymerization of Acrylic Monomers. 8. Synthesis and Characterization of (Meth)acrylic End-Functionalized Polymers: Macromonomers and Telechelics

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Received November 4, 1991; Revised Manuscript Received May 11, 1992

**ABSTRACT:** Tailor-made poly(*tert*-butyl acrylate) macromonomers, which are useful building blocks for the synthesis of comb or multiblock copolymers, have been successfully synthesized by deactivation of living PtBA macroanions with suitable electrophiles bearing either styrene or methacrylic unsaturation. Mono- or bifunctional initiators such as *sec*-butyllithium or naphthalenyllithium can be used. When these initiators were modified by LiCl as a  $\mu$ -type ligand, the macroanions which are known to be living were functionalized with high efficiency. Characterization of the various macromonomers was performed using <sup>1</sup>H NMR spectroscopy and SEC.

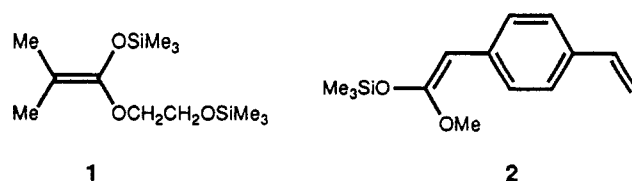
## Introduction

The synthesis of well-defined macromonomers and  $\alpha$ - or  $\omega$ -functionalized (telechelic) polymers by living polymerization techniques is unequivocally preferred to other methods in order to control their molecular parameters: molecular weight, homogeneity of each chain length, i.e. low molecular dispersity, microstructure of the polymer backbone, and finally, nature of the end group of the chain. This opportunity originates from the pioneering work of Szwarc and co-workers on the anionic polymerization carried out in aprotic solvents.<sup>1</sup> By controlling such parameters, these properly tailored macromolecules can then be used to design new polymeric materials. Block- and comblike copolymers are convincing examples of well-defined molecular architectures that comprise at least two polymeric components.

The advent of macromonomers has marked a real breakthrough in the tailoring of comblike copolymers.<sup>2</sup> Preparation of these macromonomers using the living polymerization tool seems to be more appropriate since the length of grafted branches can be easily controlled. Such copolymers are known for versatile applications such as emulsifiers, liquid crystalline materials, adhesives, surface modifiers, etc. In the anionic process, generally, macromonomers synthesis and end functionalization can be achieved by two different strategies, i.e. either by deactivation of the living species with a suitable electrophile or by initiation of the living process with an organic anionic species that bears either the protected required double bond or the protected functionalized group, respectively. However, a disadvantage in following the former route to prepare macromonomers is that any polymer chain that has been terminated during the propagation will not react with the electrophile, therefore impairing quantitative functionalization. If such conventional procedures are not available, a macromonomer can however be obtained in high yield by appropriate chemical modification of a preexisting reactive functional group. In any event, the functionalization with a double bond or with a functional group must be as quantitative as possible.

Macromonomers based on hydrocarbon monomers such as styrenes and dienes and on heterocyclic monomers such as oxiranes,  $\epsilon$ -caprolactone, and cyclosiloxanes have been prepared using end-functionalization and investigated for a number of unique applications.<sup>3,4</sup> On the other hand, few investigations on the synthesis of (meth)acrylic ester macromonomers and telechelic polymers by anionic pathways have appeared, probably owing to the following three main reasons: (a) The anionic true living polymerization of (meth)acrylic ester monomers suffers severe limitations when carried out under classical conditions of initiation and propagation. These problems arise from the possible nucleophilic attack of the active species on the carbonyl groups along the chain, particularly the antepenultimate one, and perhaps the  $\alpha$ -hydrogen atom of the acrylates, resulting in secondary transfer or termination reactions. (b) The reactivity of acrylic anions at low temperature (< -40 °C) is low toward functional electrophiles. (c) The purity of monomers is a critical factor which can perturb the course of polymerization. This last problem has been however practically overcome: high purity monomers are now available by a purification method involving alkyl-aluminum reagents.<sup>5</sup>

The GTP technique allows the preparation of a variety of functionalized polyacrylics by using properly designed initiators.<sup>6</sup> For example, telechelic PMMA can be obtained by the use of [[2-methyl-1-(2-(trimethylsiloxy)ethoxy)-1-propenyl]oxy]trimethylsilane (1)<sup>7</sup> or (vinylphenyl)ketene



methyl trimethylsilyl acetal (2)<sup>8</sup> as initiator of the methacrylic ester polymerization. This method gives polymers with a protected terminated  $\alpha$ -functional group, which generates quantitatively  $\alpha$ -OH or  $\alpha$ -vinyl unsaturated polymers, respectively. Unfortunately, the GTP technique is not able to polymerize monomers lacking a carbonyl group (styrene, dienes, ...).

The presence of a stabilizing electron-withdrawing substituent on the (meth)acrylic esters makes them ideal

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partners for an anionic polymerization mechanism. That possibility has been actively revisited during the last decade, despite the already recognized difficulties arising from side reactions of the carbanions with the carbonyl groups and acidic  $\alpha$ -hydrogen.<sup>9</sup> Up to now, the best general answer to that problem has been the use of different ligands able to control the electronic and (mainly) steric environment of the growing ion pair.<sup>10</sup> LiCl has already been proved to be efficient in controlling not only perfectly living homopolymerization of different methacrylates and tertiary or secondary acrylates in solvents of variable polarity but also the precisely tailored synthesis of different block copolymers including PMMA or PtBA sequences,<sup>11</sup> or with other hydrocarbon blocks (styrenes or dienes).<sup>12</sup> This efficiency could be attributed to the formation of a four-membered  $\mu$ -type complex with the growing species, which could be able to displace the classical equilibria between different types of ion pairs, as already suggested.<sup>26</sup>

This paper is concerned with the potentialities of that modified initiator for the synthesis of polyacrylic ester macroanions and their end-functionalization. The reactivity of PMMA and PtBA macroanions are probably not very different. We can however expect a slightly higher reactivity for PMMA<sup>-</sup>, which is due to the presence of the additional methyl group on the carbanionic site. For an efficient functionalization with electrophiles, the reacting macroanions must be truly living. This living character only appears when the polymerizations are carried out in the presence of LiCl, as already described.<sup>10b</sup> The functionalization of acrylate-derived anions has not largely been described, because they generally exhibit more side reactions than methacrylics, thus impairing the living character.

Special attention has been paid to PtBA macroanions for their stability and their specific advantage in the indirect preparation of the corresponding products based on primary acrylates and acrylic acid. The *tert*-butyl group used in this study is indeed a well-known versatile removable group in catalyzed transalcoholysis or hydrolysis reactions.<sup>13</sup> The resulting poly(acrylic acid) exhibits in alkaline media a typical polyelectrolyte behavior. The synthesis of PtBA macromonomers should thus be a route for the synthesis of amphiphilic comb copolymers bearing polyelectrolytic side chains, a new type of polymer that has not been accessible up to now.

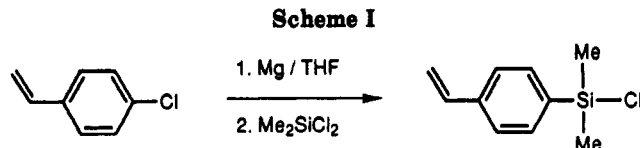
## Experimental Section

LiCl (99.99+ % purity, Aldrich) was dried overnight at 130 °C and then dissolved in dry THF. After introduction into the reactor, the THF was removed under reduced pressure prior to use. THF was purified by refluxing over fresh sodium-benzophenone complex (a deep purple color indicating an oxygen- and moisture-free solvent). Toluene was distilled under dry nitrogen over polystyryllithium after being refluxed over CaH<sub>2</sub> for several days.

*tert*-Butyl acrylate (tBA) obtained from ATOCHEM Co., France, was dried over CaH<sub>2</sub> for 24 h, vacuum-distilled, and stored under a nitrogen atmosphere in the dark at -20 °C. It was finally added with a 10 wt % triethylaluminum solution in toluene until a persistent yellow color was observed. It was then distilled under vacuum and diluted with dried toluene prior to polymerization.

Experimental molecular weights were determined with a Hewlett-Packard 1090 liquid chromatograph equipped with four columns (10<sup>5</sup>, 10<sup>3</sup>, 500, and 100 Å) and a Hewlett-Packard 1030A refractive index detector. Polystyrene standards were used for calibration and the number ( $M_n$ ) and weight ( $M_w$ ) average molecular weights as well as the polydispersity ratio of the samples were accordingly calculated.

**Initiators.** *sec*-Butyllithium (*s*BuLi) or "( $\alpha$ -methylstyryl)-lithium" ( $\alpha$ MSLi) as monofunctional initiators and naphthale-



nyllithium<sup>14</sup> as bifunctional initiator were generally used.  $\alpha$ MSLi was prepared by reacting *s*BuLi with a slight molar excess of  $\alpha$ -methylstyrene ( $\alpha$ MS) in THF at room temperature.

**Electrophiles.** Methacryloyl chloride (Aldrich), oxalyl chloride (99%, bp 64 °C) were fractionally distilled over CaH<sub>2</sub>, and the middle fraction was collected. It was stored over 3-Å molecular sieves and redistilled prior to use. Benzaldehyde (Aldrich) (99+ %, bp 178–170 °C) was first distilled from CaH<sub>2</sub>, stored under nitrogen atmosphere, and redistilled prior to use. 9-Anthraldehyde (Aldrich) (mp 162–163 °C) was sublimed under reduced pressure, dissolved in dried THF and stored under nitrogen pressure. 4-Vinylbenzoyl chloride was synthesized as described in the literature<sup>16</sup> by reacting 4-vinylbenzoic acid (Aldrich) (mp 144 °C) with a 3-fold excess of oxalyl chloride in benzene at 50 °C. 4-Vinylbenzoic acid is sparingly soluble in benzene, but as the reaction proceeds a light clear yellow solution is formed. The reaction mixture was stirred overnight and the product separated by fractional distillation under vacuum. It was then stored over CaH<sub>2</sub> and redistilled under reduced pressure. The final product was characterized by IR and <sup>1</sup>H NMR spectroscopy, both techniques giving results consistent with the desired structure.

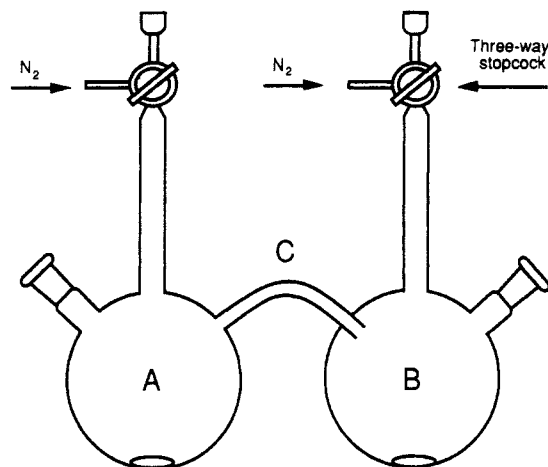
(*p*-Vinylphenyl)dimethylchlorosilane was prepared by adding dropwise (*p*-vinylphenyl)magnesium chloride (0.2 mol in 100 mL of THF) to dimethyldichlorosilane (0.4 mol) (Scheme I).

The reaction mixture was then refluxed for 30 min and further allowed to settle down in order to separate formed MgCl<sub>2</sub>. The solution containing (*p*-vinylphenyl)dimethylchlorosilane was separated by capillary tubing. The solvent was removed, the crude compound was purified by fractional distillation and redistilled over CaH<sub>2</sub> under vacuum (bp 65 °C/0.5 mmHg). The yield was 50% (lit. 51%<sup>4c</sup>). The compound was stored under nitrogen pressure. Its <sup>1</sup>H NMR spectrum indicated the desired structure as reported in the literature.<sup>4c-16</sup>

4-(Chlorodimethylsilyl)- $\alpha$ -methylstyrene was synthesized with 4-chloro- $\alpha$ -methylstyrene as starting material following the same procedure. It was purified by distillation under vacuum (bp 85 °C/0.5 mmHg). The yield was 60%. IR (neat liquid): 3080, 2969, 1627, 1598, 1454, 1386, 1255, 1094, 895, 811, 680 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.13–7.03 (AB, 4 H, aromatic, <sup>3</sup>J = 7.9 Hz), 4.95 (s, 1 H, =CH), 4.66 (s, 1 H, =CH), 1.69 (s, 3 H, CH<sub>3</sub>-C=), 0.22 (s, 6 H, CH<sub>3</sub>-Si-CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  143.09, 142.82, 135.71, 133.08 (CH aromatic), 125.12 (CH aromatic), 113.42 (=CH<sub>2</sub>), 21.61 (CH<sub>3</sub>-C=), 2.05 (CH<sub>3</sub>-Si-CH<sub>3</sub>).

**Synthesis of Macromonomers—Termination of PtBA Macroanions with Benzaldehyde.** The best suited experimental procedure involves the slow addition of the diluted monomer<sup>24</sup> (~70% in toluene v/v) into the initiator solution cooled at -78 °C. In a typical example 2.53  $\times$  10<sup>-2</sup> mol of LiCl (dried as previously explained) was introduced into the preconditioned nitrogen-filled flask. THF (200 mL) and the initiator *s*BuLi (5.06  $\times$  10<sup>-3</sup> mol) were transferred into the reactor by means of a stainless-steel capillary or a syringe. After the catalyst solution was cooled to -78 °C, 7.0 g of tBA diluted with 3 mL of toluene was added slowly. The polymerization was performed for 10 min. Thereafter, a fraction of the solution was sampled out and deactivated protonically with acidic methanol, and the polymer was recovered by precipitation into a cold (-30 °C) methanol/water (7/3 v/v) mixture for the purpose of characterization. SEC analysis of the product shows  $M_n$  = 1750 with  $M_w/M_n$  = 1.10. The rest of the reaction medium still kept at -78 °C was treated with 6.0  $\times$  10<sup>-3</sup> mol of benzaldehyde. The reaction was allowed to proceed for 1 h. The polymer was recovered by precipitation into heptane at -40 °C,<sup>25</sup> redissolved in benzene, and freeze-dried. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.30–7.20 (m, 5 H, C<sub>6</sub>H<sub>5</sub>), 5.3 and 4.7 (m, 1 H, CH-Ph), 2.8–2.5 (m, 1 H, OH), 2.18 (s, CH-COOtBu), 1.76–1.50 (s, CH<sub>2</sub>), 1.39 (s, tBu), 0.78 (s, 3 H, CH<sub>3</sub>).

**Termination of PtBA Macroanions with Anthracenaldehyde.** The same experimental procedure was followed using



**Figure 1.** Schematic representation of the glass reactor used in the preparation of  $\alpha$ - or  $\alpha,\omega$ -benzoyl chloride terminated PtBA.

anthracenaldehyde instead of benzaldehyde.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.30–7.10 (m, 9 H, aromatic), 5.80 and 5.10 (m, 1 H,  $\text{CH}-\text{C}_{14}\text{H}_9$ ), 3.05 and 2.50 (m, 1 H, OH), 2.18 (s,  $\text{CH}-\text{COOtBu}$ ), 1.76–1.50 (s,  $\text{CH}_2$ ), 1.37 (s, tBu).

**Termination of living PtBA macroanions with terephthaloyl chloride** has been carried out at  $-78^\circ\text{C}$  initiated with either sBuLi/10 LiCl or Li naphthalene/10 LiCl as the mono- or bifunctional initiator, respectively. The polymerization reaction was performed in a special reactor, schematically described in Figure 1.

Poly(*tert*-butyl acrylate) macroanions were prepared as described above in flask A. Flask B contained terephthaloyl chloride (4-fold excess with respect to the initiator) solution in THF kept at  $-78^\circ\text{C}$ . The solution of PtBA macroanions was transferred to the solution of terephthaloyl chloride through connector C. An immediately appearing light blue color very quickly turned to light yellow. The solution was stirred for 1 h at  $-78^\circ\text{C}$ . The polymer was recovered by precipitation into heptane at  $-30^\circ\text{C}$  and purified as described above.

**Termination of PtBA Macroanions with Benzaldehyde Followed by Methacryloyl Chloride.** The procedure described above for deactivation of PtBA macroanions with benzaldehyde was followed. After addition of benzaldehyde, the reaction was allowed to proceed for 1 h. Methacryloyl chloride ( $10^{-2}$  mol) was added, and the reaction was stirred for 1 h at  $-78^\circ\text{C}$ . The polymer was recovered as usual.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.26 (m, 5 H, aromatic), 6.21 (m, 1 H,  $=\text{CH}$ ), 5.88 (m, 1 H,  $=\text{CH}$ ), 5.66 and 5.64 (m, O—CH—Ph), 3.86 (s, 3 H,  $\text{CH}_3-\text{C}=\text{O}$ ), 2.20 (s,  $\text{CH}-\text{COOtBu}$ ), 1.80–1.50 (s,  $\text{CH}_2$  polymer), 1.40 (s, tBu).

**Termination of PtBA Macroanions with 4-(Chlorodimethylsilyl)- $\alpha$ -methylstyrene.** The same experimental procedure was followed using 4-(chlorodimethylsilyl)- $\alpha$ -methylstyrene as a deactivating agent instead of benzaldehyde.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.50–7.00 (m, 4 H, aromatic), 5.35 (s, 1 H,  $=\text{CH}$  trans), 5.05 (s, 1 H,  $=\text{CH}$  cis), 2.20 (s,  $\text{CH}-\text{COOtBu}$ ), 2.10 (s, 3 H,  $\text{CH}_3-\text{C}=\text{O}$ ), 1.75–1.50 (m,  $\text{CH}_2$ ), 1.35 (s, tBu), 0.80 (m, 3 H,  $\text{CH}_3$  initiator), 0.31 (s, 6 H,  $\text{CH}_3-\text{Si}-\text{CH}_3$ ).

## Results and Discussion

It has been disclosed from our laboratory that a  $\mu$ -type ligand can provide a "true living" anionic process for the tBA monomer.<sup>10b</sup> That approach offers interesting prospects for the macromolecular engineering in designing macromolecules with well-defined molecular architecture. Obviously, the living PtBA macroanions, instead of being used in block copolymers, can also be end-functionalized by reacting their terminal carbanion(s) with appropriate electrophiles. A very broad series of  $\alpha$ -monofunctional and  $\alpha,\omega$ -difunctional macromolecules, which can be useful in polyaddition and polysubstitution reactions are now accessible using this rather straightforward practical method.

sBuLi as an anionic initiator combined with LiCl as a  $\mu$ -type ligand was preferred over more sterically hindered initiators such as (1,1-diphenylhexyl)lithium, (diphenylmethyl)lithium, or oligomeric  $\alpha\text{MSLi}$  to polymerize tBA in THF at  $-78^\circ\text{C}$ , despite a somewhat lower efficiency factor. This approach allows easy quantitative determination of the functionalization based on aromatic groups of the deactivation partner with the help of  $^1\text{H}$  NMR spectroscopy or a specific UV absorption technique. Since the sterically hindered aromatic initiators also absorb in the same spectral region as the electrophile normally employed to generate functionalized macromonomers, it was indeed easier to use a sBuLi/10 LiCl initiator system. It is also worth mentioning here, that the use of sBuLi alone as an initiator in THF at  $-78^\circ\text{C}$  does not lead to a good control of MMA polymerization in the presence or absence of LiCl as additive. The tBu group of the ester moiety plays an important role (inductive as well as a more pronounced steric one) to suppress to a large extent the nucleophilic attack on the  $\text{C}=\text{O}$  group of the ester moiety even by a strong nucleophile such as sBuLi when modified with LiCl as a ligand.

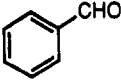
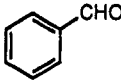
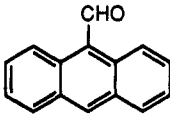
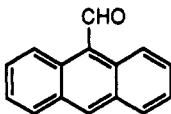
The tBA polymerization is itself an extremely fast reaction under the conditions stated above, typically ensuring a quantitative monomer conversion within less than 1 s. The homopolymerization is typically free from significant self-termination and chain-transfer reactions since the degree of polymerization is close to that calculated from the monomer/initiator molar ratio assuming a perfectly living system.<sup>10c</sup>

As reported by Rempp et al.,<sup>17a</sup> attempts to functionalize PtBA macroanions with ethylene oxide leading to the formation of primary hydroxyl terminated  $\alpha$ - and  $\alpha,\omega$ -PtBA telechelic polymers were up to now not very successful. However, in the methacrylate series, we<sup>17b</sup> and others<sup>18</sup> have shown that PtBMA macroanions could react with ethylene oxide, leading to PtBMA-*b*-PEO block copolymers. An indirect approach has been recommended in order to develop  $\alpha$ -primary hydroxyl terminated poly(meth)acrylic ester polymers by effectively utilizing a protected hydroxyl group bearing initiator such as 3-lithiopropyl acetaldehyde acetal.<sup>19</sup>

It has also been reported by Sogah et al.<sup>6</sup> and by Smith et al.<sup>15</sup> that the use of benzaldehyde as an electrophile was promising for the development of  $\omega$ -hydroxyl-terminated polymethacrylic ester by GTP and by conventional anionic technique, respectively. In such a case the macroanion addition across the carbonyl group of benzaldehyde leads to a benzyl alcohol type of structure.

**$\omega$ -OH-Terminated PtBA.** Table I describes the experimental values of molecular weight and polydispersity ( $\bar{M}_w/\bar{M}_n$ ) for the functionalized PtBA polymers prepared by deactivating the macroanions with benzaldehyde and anthracenaldehyde. Several methods could be used for the determination of the OH functionality. Chemical reaction of the OH group using a suitable reagent (e.g. hexafluoroacetone) has been used by Rempp et al.<sup>17a</sup> However, we preferred to use  $^1\text{H}$  NMR spectroscopy because the OH functionality is directly related to the amount of aromatic hydrogens present in the polymer.  $^1\text{H}$  NMR spectra of such compounds are reported in Figure 2. The aromatic protons of the terminating agent can be directly observed between 7.2 and 7.3 ppm. The integrations of these signals indicate an almost quantitative reaction of benzaldehyde with the macroanions of PtBA. Weak signals due to the presence of hydrogen adjacent to the hydroxyl group (4.7 and 5.3 ppm) and the alcoholic proton at 2.5–2.8 ppm are also present. These signals,

Table I  
Characteristics of  $\omega$ -Hydroxyl-Terminated Poly(*tert*-butyl acrylate) Macromonomers<sup>a</sup>

| entry | type of initiator  | type of aldehyde as terminating agent   | $\bar{M}_n(\text{calc})^b$ | $\bar{M}_n(\text{SEC})$ | $\bar{M}_n(^1\text{H NMR})$ | $\bar{M}_w/\bar{M}_n$ | $f$  |
|-------|--------------------|---|----------------------------|-------------------------|-----------------------------|-----------------------|------|
| 1     | sBuLi/LiCl         |  | 1400                       | 1450                    | 1440                        | 1.10                  | 0.93 |
| 2     | sBuLi/LiCl         |  | 1800                       | 2100                    | 2300                        | 1.14                  | 0.91 |
| 3     | $\alpha$ MSLi/LiCl |  | 3700                       | 4500                    |                             | 1.09                  |      |
| 4     | sBuLi/LiCl         |  | 3000                       | 3700                    | 4300                        | 1.10                  | 0.86 |

<sup>a</sup> Polymerization of tBA was initiated by the RLi/10 LiCl system in THF at  $-78^\circ\text{C}$  and terminated with different aldehydes. <sup>b</sup> Calculated from the monomer to initiator ratio.

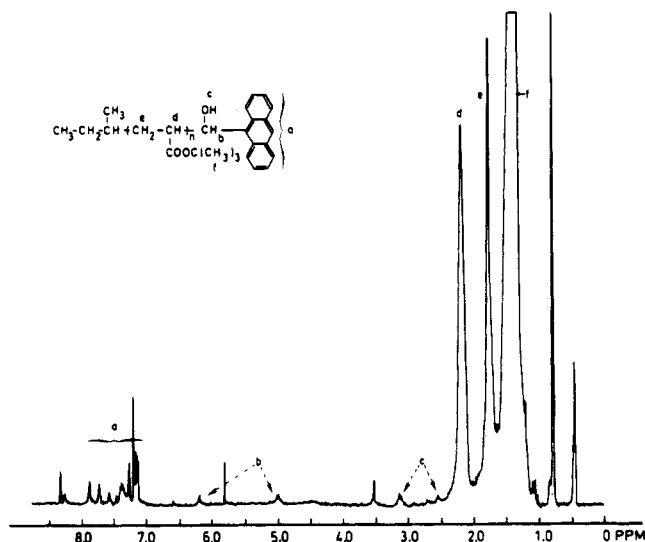
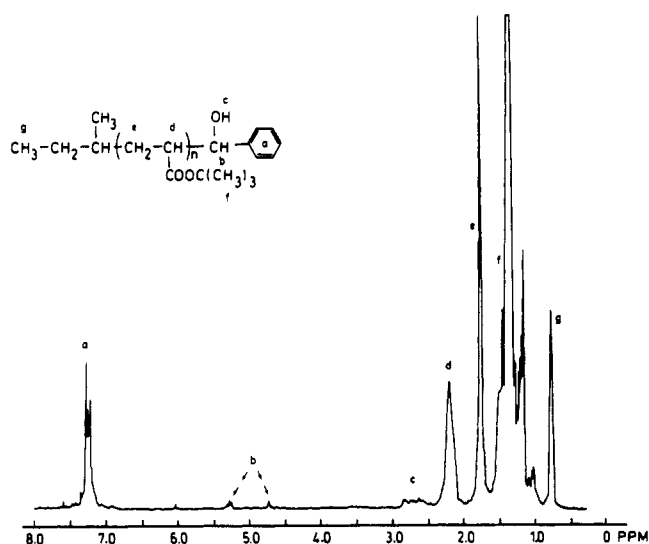
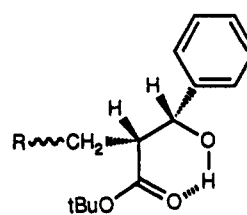


Figure 2.  $^1\text{H}$  NMR spectra (samples 1 and 4 in Table I) of  $\omega$ -OH-terminated PtBA: (A, top) PtBA macroanions terminated with benzaldehyde and (B, bottom) with anthracenaldehyde.

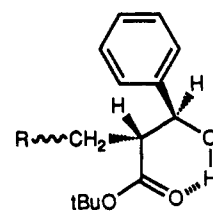
which disappeared when the spectrum was recorded in the presence of  $\text{D}_2\text{O}$ , could be explained by the presence of two diastereoisomers, both having hydroxyl hydrogen associated intramolecularly with the ultimate ester group of the polymer backbone.

Protons  $\alpha$  to the hydroxyl group of erythro or threo diastereoisomers of  $\beta$ -hydroxy esters are known to appear at different chemical shifts. According to the literature,<sup>27</sup> the more deshielded signal at 5.3 ppm could be assigned to the erythro diastereoisomer. On the other hand, the signal at 4.7 ppm has been attributed to the threo chain end.



5.3 ppm

3 erythro



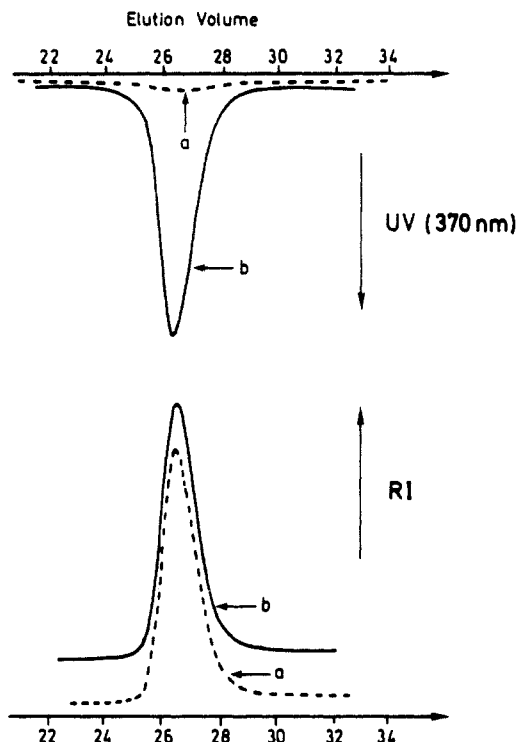
4.7 ppm

4 threo

Furthermore, these  $\omega$ -OH-terminated PtBA synthesized by deactivation with anthracenaldehyde were also characterized by SEC in the UV mode. Figure 3 represents the chromatograms obtained in the refractive index as well as in UV mode at  $\lambda = 370\text{ nm}$  (characteristic absorption of the anthracene unit). Using a refractive index detector, the SEC profiles of functionalized PtBA and of PtBA prepolymer are identical. However, using a UV detector, we can observe a sharp absorption for anthracene end-capped PtBA, which is absent in the prepolymer. The end group functionality of PtBA was checked to be close to quantitative ( $>85\%$ ) by using the calibration curve obtained from a mixture of PtBA prepolymer and anthracenaldehyde.

Quantitative termination of PtBA macroanions by anthracenaldehyde provided a polymer bearing luminescent labels (chromophores) at the end of the polymer chain. A variety of homopolymers and block copolymers of PtBA end-capped with an anthracene chromophore could be prepared by this deactivation process similar to the initiation technique already described.<sup>20</sup>

$\alpha,\omega$ -Dicarboxylic acid PtBA polymers were prepared starting from a difunctional initiator (i.e. naphthalenyl lithium<sup>14</sup>/10 LiCl) by the polymerization of tBA and deactivation of the resulting "living" polymers with a large excess of dried  $\text{CO}_2$ . A dicarboxylic telechelic PtBA of  $\bar{M}_n = 16\,000$  displaying a functionality of 1.95 and a MWD of

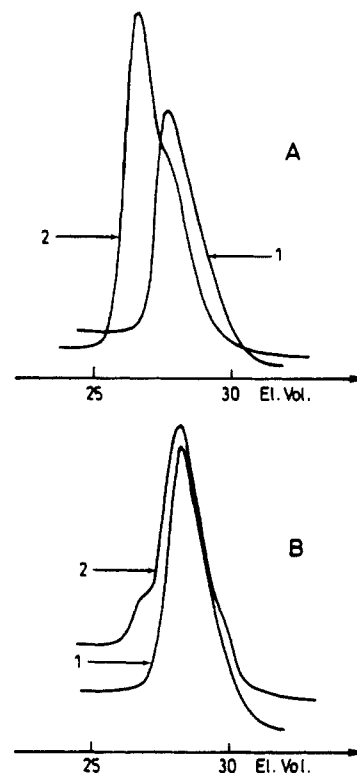


**Figure 3.** SEC traces of the  $\omega$ -functionalized PtBA bearing an anthracene unit (sample 4 in Table I): (a) PtBA prepolymer; (b) polymer after terminating PtBA macroanions with anthracen-aldehyde ( $\bar{M}_n = 3700$ ; MWD = 1.10).

1.3 was efficiently obtained with 98% yield and 90% initiation efficiency. Exactly neutralized with a  $\text{Ba}^{2+}$  salt, it generates a halatotelechelic polymer which is one of the first ion-containing polymers to exhibit a small- and large-scale organization, as seen from its SAXS diagram (8 Bragg spacings from 14 to 67 nm, probably indicating an overall hexagonal lattice).<sup>21</sup>

**$\omega$ -Terminated Benzoyl Chloride PtBA.** An attempt has been made to prepare  $\omega$ -benzoyl chloride functionalized PtBA by deactivating the PtBA macroanions ( $\bar{M}_n = 2200$ ; MWD = 1.10) by addition of a large excess of terephthaloyl chloride to the living PtBA solution. SEC analysis of the final product exhibits an increase in average molecular weight ( $\bar{M}_n = 3600$ ) (Figure 4A). The molecular weight of this sample has been calculated from its  $^1\text{H}$  NMR spectrum, and integration of the aromatic protons at 8.26 ppm indicates a  $\bar{M}_n$  value of 6400. This polymer clearly results from a coupling reaction taking place at both ends of the electrophile. In order to avoid this noxious side reaction, PtBA- $\text{Li}^+$  macroanions were transferred into a large excess of terephthaloyl chloride (solution in THF) by utilizing the apparatus described in Figure 1 (Experimental Section). Although the SEC chromatogram of the final product (Figure 4B) exhibits a tailing toward the high molecular weight side, indicating that about 10% of PtBA macroanions were coupled,  $^1\text{H}$  NMR analysis of the product gives  $\bar{M}_n = 2800$ ; i.e. about 80% of the PtBA chains are end-capped with one benzoyl chloride moiety.

**$\alpha,\omega$ -Benzoyl Chloride Terminated PtBA.** A similar procedure has been applied to prepare  $\alpha,\omega$ -benzoyl chloride terminated PtBA by treating tBA in THF at  $-78^\circ\text{C}$  with the naphthalenyl lithium/10 LiCl initiator system. SEC analysis of the product shows  $\bar{M}_n = 4600$ , MWD = 1.5, with no further increase in their molecular weight after reacting the PtBA macroanions with a large excess of terephthaloyl chloride. In order to confirm unambiguously that PtBA is end-capped by the benzoyl chloride group at both ends, the recovered and purified PtBA has been



**Figure 4.** SEC traces of PtBA macroanions terminated with terephthaloyl chloride. (A) Terephthaloyl chloride solution was added onto macroanions of PtBA in THF at  $-78^\circ\text{C}$ : (1) prepolymer ( $\bar{M}_n = 2200$ ; MWD = 1.10); (2) polymer after adding terephthaloyl chloride ( $\bar{M}_n = 3600$ ; MWD = 1.20). (B) Macroanions of PtBA were added onto a solution of terephthaloyl chloride at  $-78^\circ\text{C}$  in THF: (1) prepolymer ( $\bar{M}_n = 2200$ ; MWD = 1.10); (2) polymer after adding macroanions of PtBA onto terephthaloyl chloride ( $\bar{M}_n = 2500$ ; MWD = 1.16).

characterized by  $^1\text{H}$  NMR spectroscopy, which indicated a functionality of 1.66.

**Synthesis of  $\omega$ -Methacryloyl PtBA.** An attempt has been made to terminate PtBA macronions with a large excess of methacryloyl chloride. It was found that the molecular weight of the final polymer was increased with a broadening in its MWD. The SEC trace of the polymer is reported in Figure 5.  $^1\text{H}$  NMR analysis of the product shows only 17% remaining unsaturation. This is probably due to the preferable attack of the carbanions onto the unsaturation of methacryloyl chloride competing with the expected fast acylation reaction. In order to avoid that possible addition of PtBA macroanions onto the double bond, we decided to end-cap the living macroanions with one unit of benzaldehyde before adding methacryloyl chloride. The resulting alkoxy anions have now a more suitable nucleophilicity and are capable of selectively attacking the acid chloride function of the electrophile (Scheme II). A similar strategy has been followed by Asami et al.<sup>22</sup> in order to synthesize  $\omega$ -methacrylate-terminated polystyrene macromonomers. This technique allowed us to obtain  $\omega$ -methacrylate-terminated PtBA macromonomers with high yield (>87%), as calculated from their  $^1\text{H}$  NMR spectrum.

**Synthesis of  $\omega$ -Styryl PtBA Macromonomers.**  $\omega$ -Styryl-PtBA and -PMMA have already been synthesized by Rempp et al.<sup>17a,23a</sup> who used *p*-vinylbenzyl bromide as a deactivating agent. On the other hand,  $\omega$ -methacryloyl-PtBA and -PMMA were obtained by the same research team using (chlorodimethylsilyl)propyl methacrylate as a functional terminating agent.<sup>23b</sup> We have now extended the scope of these procedures by the use of other electrophiles, e. g. acid chlorides or chlorosilane derivatives

Table II  
Characteristics of  $\omega$ -Functionalized Styrene Poly(*tert*-butyl acrylate) Macromonomers<sup>a</sup>

| entry | type of electrophile | $\bar{M}_n(\text{calc})$ | $\bar{M}_n(\text{SEC})$ | $\bar{M}_w/\bar{M}_n$ | $\bar{M}_n(^1\text{H NMR})$ | end vinylphenyl group (per chain) |
|-------|----------------------|--------------------------|-------------------------|-----------------------|-----------------------------|-----------------------------------|
| 1     |                      | 2200                     | 3000                    | 1.07                  | 3300                        | 0.91                              |
| 2     |                      | 4500                     | 6000                    | 1.10                  | 6200                        | 0.97                              |
| 3     |                      | 1500                     | 1800                    | 1.15                  | 1900                        | 0.95                              |
| 4     |                      | 2100                     | 2900                    | 1.16                  | 3200                        | 0.91                              |

<sup>a</sup> Polymerization of tBA was initiated by the sBuLi/10 LiCl system in THF at -78 °C.

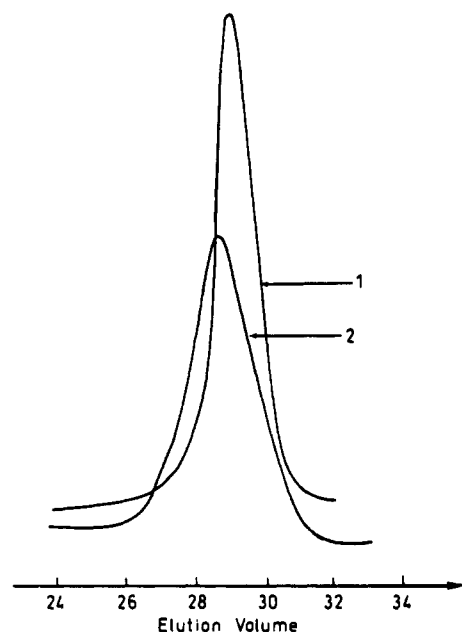
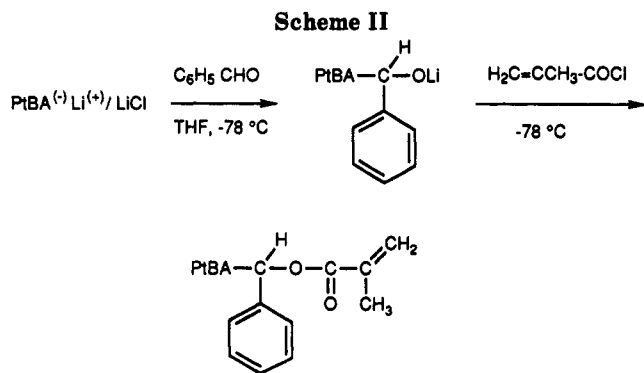


Figure 5. SEC traces of PtBA macroanions terminated with methacryloyl chloride: (1) prepolymer ( $\bar{M}_n = 1200$ ; MWD = 1.2); (2) polymer after adding methacryloyl chloride ( $\bar{M}_n = 2100$ ; MWD = 1.4).



such as 4-vinylbenzoyl chloride, 4-(chlorodimethylsilyl)-styrene, or 4-(chlorodimethylsilyl)- $\alpha$ -methylstyrene. The data shown in Table II clearly demonstrate that the end-capping reaction with these terminating agents is close to quantitative (>90%), as confirmed by  $^1\text{H NMR}$  and UV analysis. It is known that chlorosilanes may react with ester anions either at oxygen or carbon. Silylation on negative oxygen generally occurs at the first stage of the

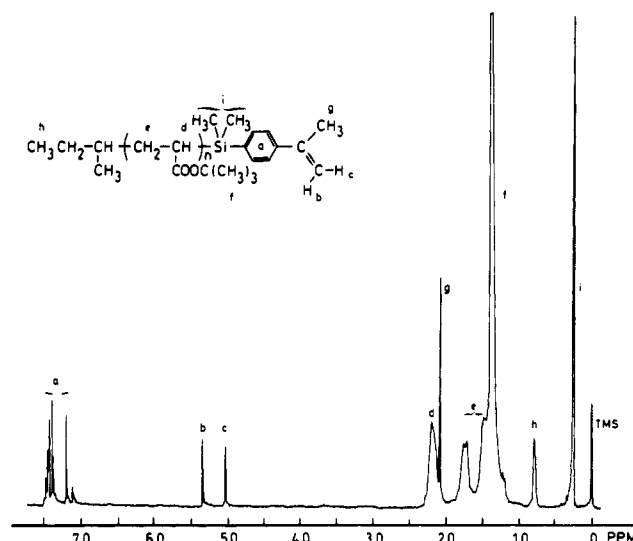


Figure 6.  $^1\text{H NMR}$  spectrum of  $\omega$ -( $\alpha$ -methylstyrene)-terminated PtBA macromonomer (sample 3 in Table II).

reaction. Rearrangement of ketene *O*-silyl *O*-alkyl acetal to give the thermodynamically more stable 2-silyl carboxylate is often observed.<sup>28</sup> Figure 6 depicts the  $^1\text{H NMR}$  spectrum obtained for an  $\omega$ -functionalized (dimethylsilyl)- $\alpha$ -methylstyrene PtBA macromonomer.

In conclusion, the results described above clearly demonstrate that the carbanionic sites of the living PtBA are—under the proper experimental conditions—sufficiently nucleophilic to react quantitatively with a number of electrophiles. These reactions lead to interesting end-functionalized polymers (i.e. macromonomers and telechelics). Such functionalized PtBA polymers represent of course a source of new comb-shaped copolymers readily available via the free radical process. In all these cases, the post hydrolysis of the PtBA branches may lead to very interesting amphiphilic materials, and the same method may be applied to the networks formed from  $\alpha,\omega$ -difunctional macromonomers. These results will be the subject of future investigations.

**Acknowledgment.** We are deeply indebted to CIPARI (Luxembourg) and NORSOLOR (France) for generous financial support and collaboration, as well as to the "Services de Programmation de la Politique Scientifique". We also thank Mrs. M. C. Guesse and Miss N. Price for their skillful technical assistance. NMR spectra were

recorded by Dr. R. Warin at the CREMAN facility (University of Liège) funded by a grant from the "Fonds National de la Recherche Scientifique".

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**Registry No.** *s*BuLi, 598-30-1;  $\alpha$ MSLi, 128554-17-6; LiCl, 7447-41-8; naphthalenyllithium, 27939-69-1.