Macromolecules **1990,** *23,* 3893-3898

Anionic Polymerization of Acrylic Monomers.[†] 5. Synthesis, Characterization, and Modification of Polystyrene–Poly(*tert*-butyl acrylate) Di- and Triblock Copolymers

J.-P. Hautekeer, S. K. Varshney, R. Fayt, C. Jacobs, R. Jérôme, and Ph. Teyssié*

Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart-Tilman, B6, 4000 Liège, Belgium

Received October 31, 1989; Revised Manuscript Received February 7, 1990

ABSTRACT: Different polystyrene (PS)–poly(*tert*-butyl acrylate) (PtBuA) block copolymers have been synthesized by first preparing "living" PS using mono- or difunctional initiators, followed by polymerization of tBuA in THF at −78 °C. The chain length of PtBuA blocks can be controlled in a predictable way with a very narrow molecular weight distribution when polystyrene macroanions are modified by LiCl as a ligand. Di- and triblock copolymers are obtained essentially free from homopolystyrene as shown by gel permeation chromatography. The phase morphology of a diblock copolymer of about 50/50 molar composition consists of randomly distributed, short alternating lamellae of PS and PtBuA. The PtBuA blocks can be quantitatively hydrolyzed into polyacid blocks as supported by titration, ^{1}H NMR, and IR analysis. Subsequent neutralization of the polyacid block with a variety of bases leads to two-phase copolymers containing an ionomer type of component.

Introduction

The discovery by Szwarc that some monomers can be polymerized by a living mechanism has paved the way for the fine tailoring of synthetic polymers.[1] Living polymerization is actually a very powerful pathway when the fine control of molecular weight, molecular weight distribution, and polymer architecture is required. This technique allows the controlled synthesis of star-shaped polymers and linear polymers bearing quantitatively a functional group at one end (e.g., macromonomers) or at both chain ends (telechelic polymers).[2-7] Spectacular advances have also been reported in the tailoring of block copolymers as illustrated by the discovery of the thermoplastic elastomers (Kraton, Solprene, etc.). It is worth recalling that the emergence of block copolymerization in the sixties has given rise to an entirely new concept for the design and control of polymer properties. Block copolymers and, as a rule, multiphase polymers are materials of great interest because the general behavior of the corresponding homopolymers is maintained along with the added benefit of some new properties in relation to the phase morphology.[8-10]

The anionic polymerization of hydrocarbon monomers such as styrene and dienes into well-controlled block copolymers works well.[9] However, the anionic "living" polymerization of polar monomers is a challenge because of the occurrence of side-termination reactions.[11] Methacrylate and acrylate esters are examples of polar monomers, the controlled anionic polymerization and block copolymerization of which are still a gap to be filled. This is mainly due to the nucleophilic attack on the carbonyl group and the acidity of the α-hydrogen atom of the acrylates. Furthermore, obtaining these monomers in a sufficiently high level of purity was a problem for a long time, until McGrath et al.[12] discovered that alkylaluminum is a very efficient purification agent. Nowadays, experimental conditions have been documented in the scientific literature[13-15] such as low temperature, polar solvents, sterically hindered initiators, and ultrapure monomers that prevent successfully the occurrence of transfer and termination reactions in the anionic polymerization of alkyl methacrylates but not in that of alkyl acrylates.

The anionic polymerization of alkyl acrylates is so touchy that it has not been as yet controlled under conventional conditions. Recently, a Du Pont Co. research team has succeeded in the living polymerization of α,β-unsaturated carbonyl conjugated monomers by taking advantage of the nucleophile-assisted "group-transfer" reaction of silyl ketene acetals.[16,17] Although a living polymerization process is now available for the molecular engineering of alkyl (meth)acrylate-based polymers and block copolymers, it is still quite a problem to copolymerize these compounds with comonomers missing a carbonyl conjugated group. To cope with that problem we have been interested in controlling the reactivity of the anionic initiators commonly used in the living polymerization of nonpolar monomers. Thus, we have proposed to minimize the relative importance of the secondary transfer and termination reactions by using an appropriate ligand of the anionic species.[18,19] Suitable ligands should either control the dissociation of the active sites or create enough steric hindrance around them. Of course, both effects may occur simultaneously. It has been reported from our laboratory that μ-type ligands, especially LiCl, are quite efficient in promoting the living polymerization of hindered acrylates (e.g., *tert*-butyl acrylate) when organolithium compounds are used as initiators.[20] In addition to that ligand effect, both the bulkiness and the positive inductive effect of the hindered alkyl group of acrylates are expected to contribute to the complete elimination of secondary reactions usually associated with the carbonyl group (1,2 addition).

This paper aims at extending the performance of the lithium chloride modified initiators to the controlled synthesis of polystyrene–poly(*tert*-butyl acrylate) di- and triblock copolymers. Poly(*tert*-butyl acrylate) blocks (PtBuA) are of great interest due to their easy hydrolysis into poly(acrylic acid) blocks. The subsequent neutralization of the acid groups with different bases is a direct way to corresponding ionomer blocks. Finally, the possible

---

[*] To whom correspondence should be addressed.

[†] For preceding papers in this series, see refs 18–20.

0024-9297/90/2223-3893$02.50/0

Table I
Characterization of PSt-*b*-PtBuA Diblock Copolymers Prepared in THF at −78 °C Using α-MeSt$^-$Li$^+$ as a LiCl-Modified Initiator[a]

sample	theor comp ($\bar{M}_n \times 10^{-3}$) PSt-*b*-PtBuA	total $\bar{M}_n$ ($\times 10^{-3}$) theor[b]	total $\bar{M}_n$ ($\times 10^{-3}$) exptl SEC	total $\bar{M}_n$ ($\times 10^{-3}$) exptl osmom	$\bar{M}_w/\bar{M}_n$ SEC	tBuA content,[c] wt %	T_g, °C	
1	66–4	70	70		1.05	7		109
2	61–39	100	100		1.05	39	43	107
3	105–80	185	185.5		1.05	44	41.5	107
4	60–50	110	110	106	1.05	50	41.5	107
5	11–43	54	54	48	1.05	77	46.4	107
6	7–63	70	72	69.5	1.05	91	46	
7[d]	25–25	50	42		1.75	55	41	100

[a] LiCl/initiator molar ratio = 5. [b] $\bar{M}_{n,calcd}$ = (weight of reacted monomer)/(moles of initiator). [c] By ^{1}H NMR analysis. [d] In the absence of LiCl.

transalcoholysis of PtBuA makes available a series of block copolymers of the same molecular features (chain length, polydispersity) but containing different poly(alkyl acrylate) blocks (2-ethylhexyl acrylate, *n*-butyl acrylate, etc.).

Experimental Section

Styrene (Aldrich) was dried over CaH$_2$ for 24 h, distilled in vacuo, and stored under a nitrogen atmosphere at −20 °C. Finally, the required amount of styrene was added to fluorenyllithium for 8 h at 25 °C and subsequently distilled under vacuum just before polymerization.

tert-Butyl acrylate (tBuA) (Norsolor) was also dried over CaH$_2$ for 24 h, vacuum distilled, and stored under a nitrogen atmosphere in the dark at −20 °C. It was finally added to a 10 wt % triethylaluminum solution in hexane until a persistent yellow color was observed. It was then distilled under vacuum prior to polymerization.

LiCl (99.99+ purity) was obtained from Aldrich. It was dried under vacuum overnight at +130 °C in a glass reactor to be used for the block copolymerization.

THF was purified by refluxing over the deep purple sodium-benzophenone complex. It was further distilled from polystyryllithium under reduced pressure immediately before use.

Initiators. The monofunctional initiator ((α-methylstyryl)lithium (α-MeSt$^-$Li$^+$)) was prepared by reacting *sec*-BuLi with a slight molar excess of α-MeSt at room temperature in dry THF.[21] Li-naphthalene resulted by addition of lithium to naphthalene in THF at room temperature and was used as a bifunctional initiator.[22]

Polymerization. The anionic block copolymerization of styrene and tBuA was carried out under a nitrogen atmosphere in a previously flamed glass reactor. A typical example involved introducing 0.02 g (0.5×10^{-3} mol) of LiCl (dried as previously explained) into the flask. THF (100 mL) and the initiator (1 mL, 0.1 M) were transferred into the reactor by means of a stainless steel capillary or a syringe. After the catalyst solution was cooled to −78 °C, 6 g of styrene was added. The polymerization was performed for 30 min. tBuA (4.0 g) was then added to the polymerization medium as a dilute solution (25% in THF). Upon addition of a few drops of the tBuA solution, the red (or orange) color of the living polystyryl anions changed suddenly to a very light yellow color. The block copolymerization was allowed to proceed for 30 min at −78 °C. It was then stopped by adding methanol, and the copolymer was recovered by precipitation into methanol or a methanol/water (80/20 (v/v)) mixture. The polymer was dried under vacuum at 80 °C for 48 h.

Hydrolysis. Triblock copolymers were hydrolyzed as follows: *p*-Toluenesulfonic acid (PTSA) was used as a catalyst (5 mol % relative to the polyacrylate content).[23] The block copolymer was dissolved in toluene (5 wt %), added with the catalyst, and heated to 100 °C for 8 h. Triblock copolymers containing more than 70 wt % of tBuA gelified under such conditions, and addition of methanol was required to restore the copolymer solubility. However, this treatment gave rise to the esterification of the acrylic acid block to a methyl acrylate block, as evidenced by ^{1}H NMR spectroscopy (disappearance of the *tert*-butyl ester's signal at 1.39 ppm and appearance of the signal characteristic of the methyl ester group of the poly(methyl acrylate) block at 3.6 ppm).

Finally, these block copolymers were hydrolyzed in a higher power solvating solvent such as 1,4-dioxane (δ, 10 (cal cm^{-3})$^{1/2}$) in the presence of PTSA or HCl without any premature precipitation. The final polymers were then precipitated into heptane, filtered, washed several times to remove any trace of catalyst, and freeze-dried in benzene.[24]

Characterization. Size exclusion chromatography (SEC) was carried out with a Waters GPC 501 apparatus equipped with two Ultrastyragel linear columns with THF as the eluent at a flow rate of 1 mL/min (30 °C). Standard polystyrenes were used for calibration, and the number- and weight-average molecular weights of the polystyrene block and the final copolymers were accordingly calculated.

Absolute number-average molecular weights were determined by osmometry with a HP 502 high-speed membrane osmometer.

The glass transition temperature of the polymers was measured by differential scanning calorimetry using a Du Pont 9000 apparatus. The instrument was calibrated with indium and mercury. Samples were first heated to 150 °C, cooled rapidly to room temperature, and then scanned again at a rate of 20 °C/min.

The composition and degree of hydrolysis or esterification of the polymers were determined by ^{1}H NMR using a Bruker AN 400 spectrometer. The degree of hydrolysis was also determined by potentiometric titration with tetramethylammonium hydroxide in a 90/10 (v/v) toluene/MeOH mixture. Determination of the degree of both hydrolysis and neutralization can also be achieved by titration with methanolic potassium hydroxide in THF using phenolphthalein as an indicator.

IR spectra were recorded on a Perkin-Elmer 197 infrared spectrophotometer.

The morphology of polystyrene–poly(*tert*-butyl acrylate) block polymer films cast from 0.2 wt % toluene solution was investigated by transmission electron microscopy. Natural phase contrast was sufficient to avoid staining of the acrylate phase.

Results and Discussion

Synthesis of Diblock Copolymers. It has been shown previously[20] that a μ-type ligand can provide the anionic polymerization of tBuA with a living character. This substantial progress offers interesting prospects for the controlled block copolymerization of tBuA with nonpolar monomers such as styrene and dienes. To evaluate this opportunity, we prepared living polystyryllithium in THF at −78 °C using a monofunctional (*sec*-BuLi added with a few α-methylstyrene units) and a difunctional (Li-naphthalene) initiator. The initiator was added with LiCl in a defined molar ratio before starting the anionic polymerization of styrene. Thus, polyanions with a Li counterion and LiCl as a ligand were made available to initiate the tBuA copolymerization. Table I reports the experimental values of molecular weight, polydispersity ($\bar{M}_w/\bar{M}_n$), and composition of a series of block copolymers

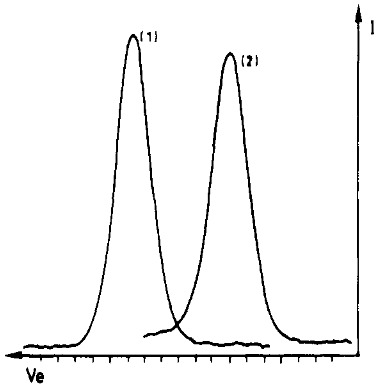

Figure 1. SEC of sample 5 (Table I): (1) polystyrene block, $\bar{M}_n$ = 11 000, $\bar{M}_w/\bar{M}_n$ = 1.05; (2) block copolymer, $\bar{M}_n$ = 54 000, $\bar{M}_w/\bar{M}_n$ = 1.05, prepared in THF at −78 °C using α-MeSt$^-$Li$^+$ as a LiCl-modified initiator.

accordingly prepared. Conversion of the comonomers is quantitative in all cases. It must be mentioned that tBuA has already been block copolymerized with styrene[25] and 2-vinylpyridine[26] in the absence of any added ligand. Unfortunately, these earlier papers do not report on the possible contamination of the diblocks by homopolymers. When prepared in the presence of LiCl with a fivefold molar excess of LiCl compared to the carbanion, block copolymers are essentially free from homopolystyrene as evidenced by the size exclusion chromatograms. Figure 1 compares the SEC traces of polystyrene used as the macroinitiator and the related diblock copolymers with tBuA as recovered before precipitation in methanol. Clearly, no homopolystyrene contaminates the diblock copolymer, which has a unimodal distribution with a very narrow polydispersity ($\bar{M}_w/\bar{M}_n$ = 1.05). The latter observation is consistent with the absence of homopoly(*tert*-butyl acrylate). Furthermore, the experimental molecular weights as determined by SEC with polystyrene standards are very close to the theoretical values ($\bar{M}_{n,\text{calcd}}$ on the basis of the reacted monomer/initiator molar ratio). Since the molecular weight of block copolymers determined by SEC has no absolute meaning, the agreement observed between experimental and calculated values cannot serve as evidence for a living process.

For the foregoing reasons, the absolute number-average molecular weight was measured by osmometry for several copolymers. As shown in Tables I and II, all values are in close agreement with both the theoretical values and the ones determined by SEC.

This clearly shows that the use of LiCl as a ligand of the active species in the block copolymerization of styrene with *tert*-butyl acrylate allows the mechanism to be truly living.

The composition of the block copolymers was determined from ^{1}H NMR spectroscopy. The resonance peaks of the aromatic protons (PSt) and the protons in the α-position of the ester groups (PtBuA) were integrated and compared. The experimental composition is in close agreement with the theoretical value. All of the evidence gathered in Table I is thus in favor of a closely controlled block polymerization process.

To answer the question of the role played by LiCl, we performed the sequential anionic polymerization of styrene and tBuA in the absence of LiCl. Although the copolymer conversion is still quantitative, size exclusion chromatography (SEC) shows that the maximum of the elution peak of polystyrene has been shifted to smaller elution volumes to a much lesser extent than expected (0.075 mL instead of 0.6 mL). Furthermore, a very broad tail extends now toward the higher molecular weight side (Figure 2). Comparison of Figures 1 and 2 illustrates convincingly the beneficial effect that LiCl has on the course of styrene and tBuA block copolymerization. In contrast to block copolymers synthesized in the presence of LiCl, the one prepared without any ligand shows a significant discrepancy between the theoretical molecular weight and the experimental value derived from SEC data (Table I). Furthermore, the molecular weight distribution ($\bar{M}_w/\bar{M}_n$) jumps from 1.05 to 1.7 when no ligand is used. Thus Table I provides a piece of information suggesting that coordination of LiCl is an efficient means of avoiding the attack of the carbonyl group or the tertiary hydrogen atom of tBuA by both polystyryllithium during the initiation step and polyacrylate type ion pairs during the propagation step. Interactions between the organolithium ion pairs and LiCl have been put in evidence by ^{7}Li NMR spectroscopy as reported elsewhere,[27] although their exact nature has not been completely clarified as yet.

Synthesis of Triblock Copolymers. Table II shows that using naphthalene–Li added with LiCl as an initiator in the styrene polymerization allows again well-defined triblock copolymers to be obtained. Figure 3 provides evidence for the nearly quantitative participation of polystyryllithium dianions to the initiation of tBuA. Once again theoretical molecular weights and values determined by SEC are in good agreement in the whole series. The molecular weight distribution is still narrow although slightly broader than that of the diblocks (1.15 as an average in contrast to 1.05). The elution peak seems to be slightly asymmetric with a tail on the lower molecular weight side. Figure 4 is a convincing illustration of the poor result obtained when the triblock copolymerization is performed in the absence of any ligand. Figures 3 and 4 deserve a direct comparison since all the experimental conditions are the same except for LiCl.

Characterization of Diblock and Triblock Copolymers. A poly(St-*b*-tBuA) copolymer of 43 wt % polyacrylate was cast from toluene solution and characterized by transmission electron microscopy. Figure 5 shows a two-phase morphology of seemingly alternating lamellae of PS andd PtBuA: actually small-size lamellae are randomly distributed throughout the sample. Such a morphology is consistent with the near 50/50 composition of the diblock.

The T_g's of all samples, shown in Tables I and II, were determined by differential scanning calorimetry. When the weight percentage of any block was <15%, the limited sensitivity of this technique did not allow us to record the T_g of the corresponding phase. Tables I and II show that the T_g values for all the copolymers correspond to those reported for the homopolymer, indicating that phase separation is complete. Nevertheless, in examples 5 and 6 of Table I, the higher values reported for the acrylate block might be explained by a partial miscibility of the short polystyrene chains of these diblocks. Similarly, when the acrylate blocks of the copolymer are very short (examples 5–7 in Table II), the lower values observed for the central polystyrene block might be accounted for by a slight plasticization of the polystyrene matrix by the short polyacrylate sequences.

Hydrolysis and Neutralization of the Hydrolyzed PtBuA Blocks. To illustrate the range of end products made available by living block copolymerization of tBuA, we hydrolyzed triblock copolymers by acid catalysis. Conversion of *tert*-butyl ester groups into carboxylic acids or methyl esters was ascertained by ^{1}H NMR. Figure 6 shows the disappearance of the resonance at 1.39 ppm

Table II
Characterization of PtBuA-*b*-PSt-*b*-PtBuA Triblock Copolymers Prepared in THF at −78 °C Using Li–Naphthalene as a LiCl-Modified Initiator[a]

sample	theor comp ($\bar{M}_n \times 10^{-3}$) PtBuA-*b*-PSt-*b*-PtBuA	total $\bar{M}_n$ ($\times 10^{-3}$) theor[b]	total $\bar{M}_n$ ($\times 10^{-3}$) exptl SEC	total $\bar{M}_n$ ($\times 10^{-3}$) exptl osmom	$\bar{M}_w/\bar{M}_n$ (SEC)	tBuA content,[c] wt %	T_g, °C	T_g, °C
1	30.0–30.0–30.0	90.0	82.0		1.2	68.6	45	107
2	7.5–95–7.5	110.0	106.0		1.2	15.0	40	107.5
3	5.0–90–5.0	100.0	100.0		1.2	10.8		107
4	1.5–90–1.5	93.0	95.5	95	1.2	2.8		107.5
5	0.8–23–0.8	24.6	24		1.15	6.0		104
6	0.5–24–0.5	25.0	25		1.2	5.0		104
7	0.3–34–0.3	34.6	35		1.15	1.8		104
8[d]	60–60–60	180.0	88.0		2.0		45.5	106.5

[a] LiCl/initiator molar ratio = 5. [b] $\bar{M}_{n,calcd}$ = (weight of reacted monomer)/(moles of initiator). [c] By ^{1}H NMR analysis. [d] In the absence of LiCl.

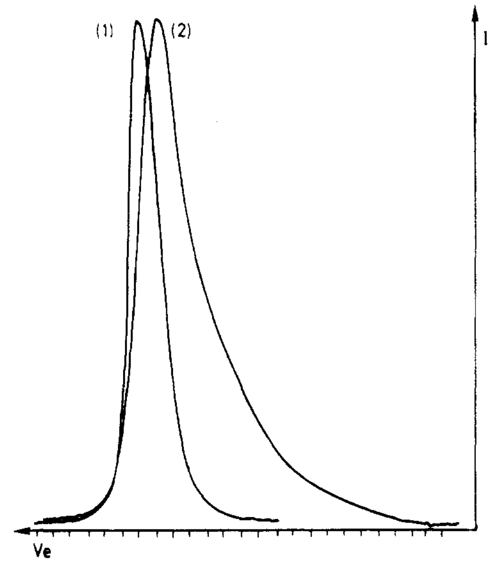

Figure 2. SEC of sample 7 (Table I): (1) polystyrene block, $\bar{M}_n$ = 25 000, $\bar{M}_w/\bar{M}_n$ = 1.05; (2) block copolymer, $\bar{M}_n$ = 42 000, $\bar{M}_w/\bar{M}_n$ = 1.75, prepared in THF at −78 °C in the absence of LiCl.

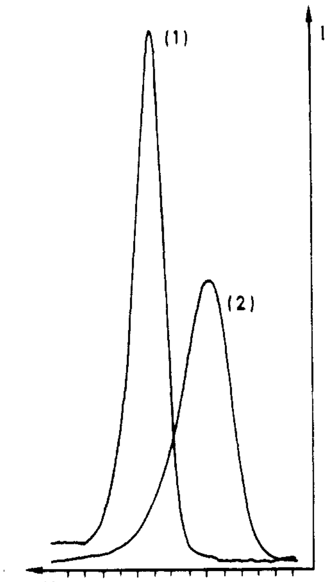

Figure 3. SEC of sample 1 (Table II): (1) polystyrene block, $\bar{M}_n$ = 30 000, $\bar{M}_w/\bar{M}_n$ = 1.15; (2) block copolymer, $\bar{M}_n$ = 82 000, $\bar{M}_w/\bar{M}_n$ = 1.20, prepared in THF at −78 C using Li–naphthalene as a LiCl-modified initiator.

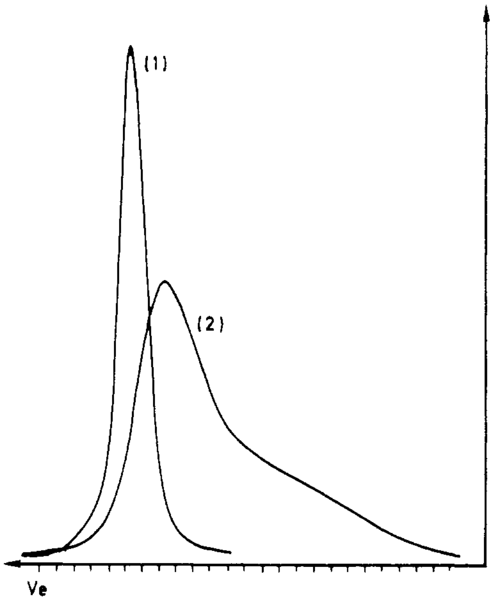

Figure 4. SEC of sample 8 (Table II): (1) polystyrene block, $\bar{M}_n$ = 60 000, $\bar{M}_w/\bar{M}_n$ = 1.10; (2) block copolymer, $\bar{M}_n$ = 88 000, $\bar{M}_w/\bar{M}_n$ = 2.0, prepared in THF at −78 °C using Li–naphthalene as an initiator in the absence of LiCl.

which is characteristic of the protons of the *tert*-butyl groups. The remaining weak resonance at ca. 1.4 ppm is still present after hydrolysis and has to be assigned to the β-methylene protons of the styrene block which generally give a multiplet centered at 1.5 ppm. The quantitative conversion of the polyacrylate block into a poly(carboxylic acid) block is also supported by titration of the polyacid using a solution of tetramethylammonium hydroxide (TMAH) in a 90/10 (v/v) toluene/MeOH mixture. As reported in Table III, results of the potentiometric titrations indicate a practically complete hydrolysis. Figure 7 compares the IR spectra of the triblock copolymer of example 1 (Table II) recorded before and after hydrolysis and neutralization with TMAH, respectively. Hydrolysis is clearly responsible for the occurrence of a broad absorption between 3400 and 2400 cm^{-1}, which is characteristic of the OH groups. After neutralization, the stretching absorption of the carbonyl which is observed in the range 1730–1700 cm^{-1} disappears in favor of the stretching absorption of the carboxylate salts at 1600 (asymmetric) and 1400 cm^{-1} (symmetric), respectively. Characteristic peaks of the stretching absorption of the C–N groups of the neutralized samples which occurs generally in the range from 1350 to 1000 cm^{-1} cannot be precisely attributed because of the absorptions due to the polystyrene block.

Finally, the DSC traces of these smaples are reported in Figure 8. It is obvious that the glass transition of the polyacrylate block at 45 °C is no longer observed after the

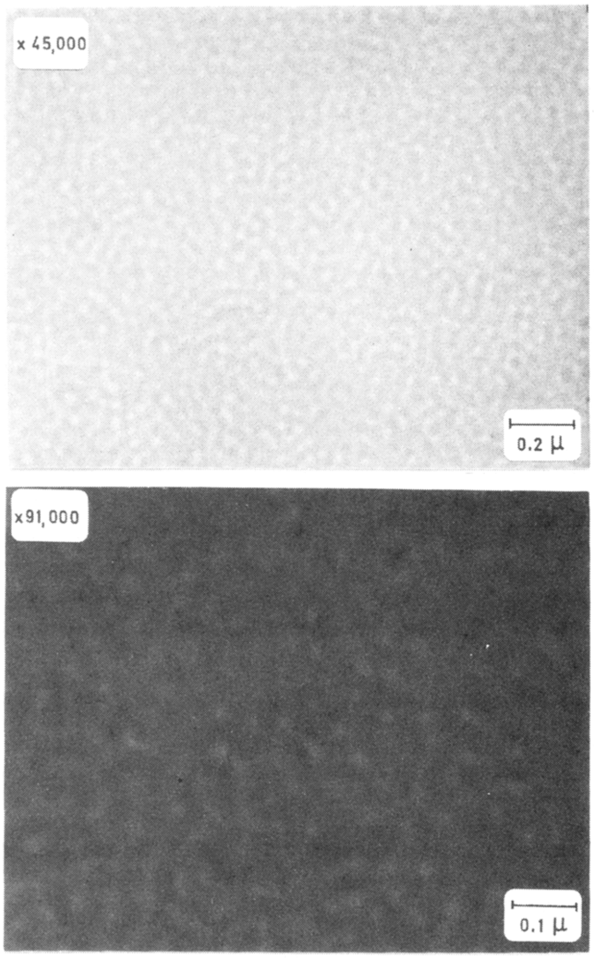

Figure 5. TEM of sample 3 (Table I): PSt-*b*-PtBuA.

acid hydrolysis followed or not by neutralization of the acid groups with sodium methoxide.

In the limits of their sensitivity, NMR, IR, and DSC conclude that the polyacrylate blocks of a poly(tBuA-*b*-St-*b*-tBuA) triblock can be quantitatively hydrolyzed into polyacid and further neutralized into ionomeric blocks. The polyacid component can be neutralized with a variety of bases such as KOH in methanol, TMAH in a 90/10 (v/v) toluene/MeOH mixture, or metal alkoxides.

Figure 9 shows the entire thermogram of the hydrolyzed sample (example no. 1, Table II). It indicates a transition at 124.5 °C, which can be attributed to the polyacid block and which might result from the overlapping of the glass transitions of the polyacid and the polystyrene blocks, respectively.[24] Figure 9B shows the DSC analysis of the ABA block ionomer obtained after neutralization of the hydrolyzed triblock copolymer with sodium methoxide. Two glass transitions can be detected in the vicinity of 95 and 160 °C. The lower value can be attributed to the polystyrene block. Tentatively, the aggregates resulting from the interactions between the ion pairs distributed along the outer blocks might be responsible for a decrease in mobility and for the upper T_g value.

It is worth noting that hydrolysis of triblocks containing ca. 15 wt % or more of PtBuA results in an insoluble product after freeze-drying. Anhydride formation might be responsible for this effect.[24,28]

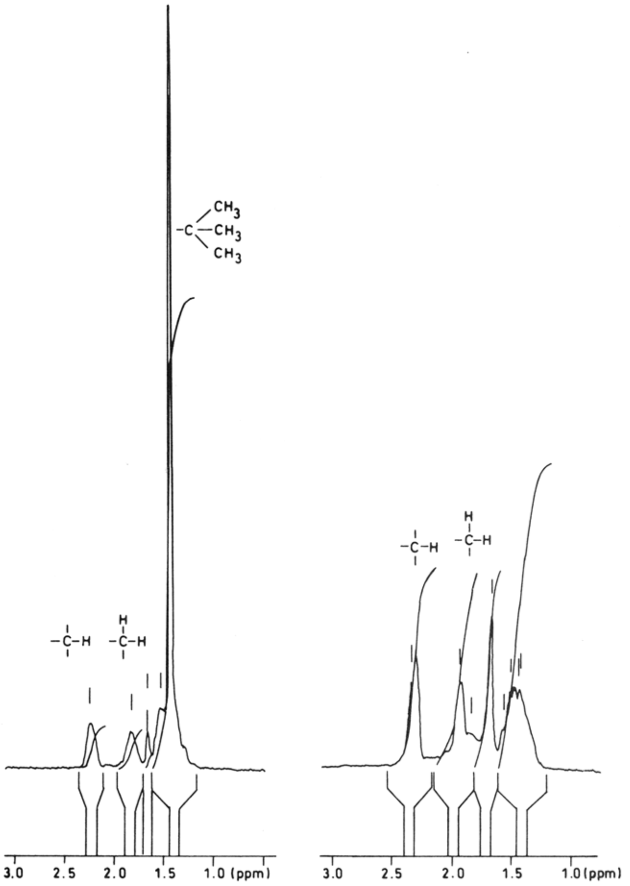

Figure 6. ^1H NMR of triblock copolymer after and before hydrolysis by PTSA (5 mol %) in toluene.

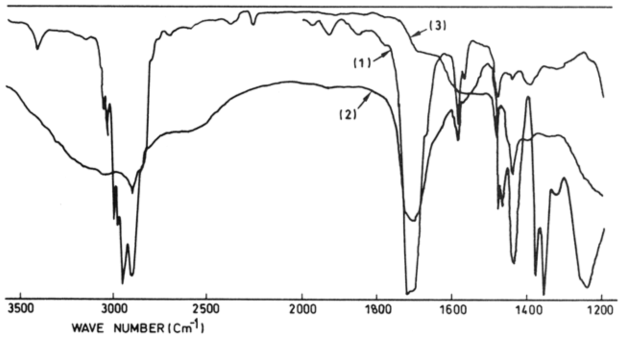

Figure 7. IR spectra of sample 1 (Table II): (1) PtBuA-*b*-PSt-*b*-PtBuA; (2) after hydrolysis by PTSA in dioxane; (3) after neutralization with TMAH.

Table III
Potentiometric Acid–Base Titration of PtBuA-*b*-PSt-*b*-PtBuA (Sample 1, Table II) Hydrolyzed by TMAH in a 90/10 Toluene/MeOH Mixture

no.	wt of polymer, mg	COOH titrated, mol	COOH theor, mol	yield of hydrolysis, %
1	30	1.66×10^{-4}	1.61×10^{-4}	100
2	30	1.57×10^{-4}	1.61×10^{-4}	97.5
3	53	2.74×10^{-4}	2.85×10^{-4}	96

Neutralization of the hydrolyzed triblock copolymers provides an interesting extension for the carboxylato-telechelic polymers, extensively studied in our laboratory.[29,30] This type of halato-telechelic polymers consists of linear chains selectively end capped by a metal carboxylate group. They have been synthesized and investigated as models for the more complex ionomers. Now, there is an opportunity to increase regularly the number of metal carboxylate groups at both ends of linear polystyrene chains. The same strategy has also been proposed recently by McGrath et al.[31] In the traditional ionomers, the electrostatic interactions of randomly distributed metal carboxylate ion pairs generally improve the physicomechanical behavior of the base polymer.

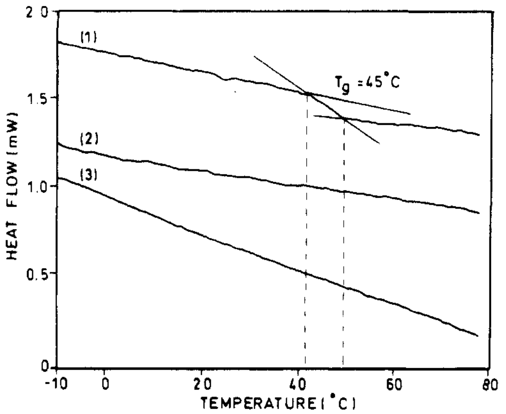

Figure 8. DSC analysis of sample 1 (Table II): (1) PtBuA-*b*-PSt-*b*-PtBuA; (2) after hydrolysis by PTSA in dioxane; (3) after neutralization with NaOMe.

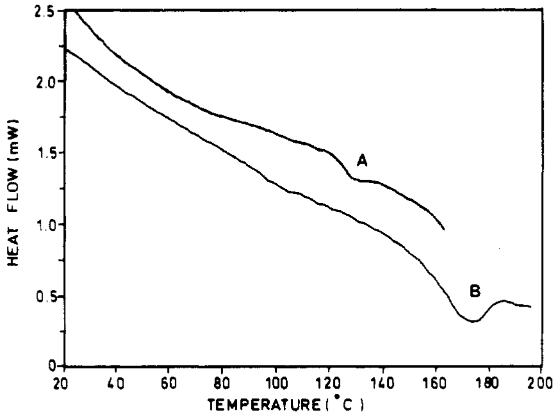

Figure 9. (A) DSC analysis of sample 1 (Table II) after hydrolysis by PTSA in dioxane. (B) DSC analysis of sample 1 (Table II) after hydrolysis and neutralization with NaOMe.

Undoubtedly, the sequential grouping of the ion pairs should favor their mutual interaction and association into microphases. Formation of mesophases as often observed for tailored block copolymers might occur rather than the poorly defined clustering of ion pairs as reported in ionomers.[32]

Acknowledgment. We are indebted to Cipari and Norsolor for financial support and collaboration as well as to the Service de la Programmation de la Politique Scientifique. 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. The skillful technical assistance of Mrs. M. C. Guesse and Miss A. M. Vincent is very much appreciated, as well as the help of Mrs. A. Palumbo in obtaining the electron micrographs.

References and Notes

(1) Szwarc, M. *Ions and Ion Pairs in Organic Reactions*; Wiley-Interscience: New York, 1972, Vol. 1; 1974, Vol. 2.
(2) Roovers, J. E. L.; Bywater, S. *Macromolecules* **1974**, *7*, 443.
(3) Lutz, P.; Masson, P.; Beinert, G.; Rempp, P. *Polym. Bull.* **1984**, *12*, 79. Rempp, P.; Lutz, P. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1988**, *29* (2), 15.
(4) Kinning, D. J.; Thomas, E. L.; Alward, D. B.; Fetters, L. J.; Handlin, D. L., Jr. *Macromolecules* **1986**, *19*, 1288.
(5) Tant, M. R.; Sung, J. H.; Wilkes, G. L.; Horrion, J.; Jérôme, R. *Polymer* **1986**, *27*, 1815.
(6) Smith, S. D. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1988**, *29* (2), 48.
(7) Quirk, R. P.; Guo, S. H.; Alsamarraie, M.; Hoover, F. I. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1988**, *29* (2), 298.
(8) Holden, G.; Milkovich, R. Belgian Patent 627,652 (July 29, 1963). U.S Patent 3,265,765 (Aug 9, 1965). Holden, G.; Bishop, E. T.; Legge, N. R. *J. Polym. Sci.* **1969**, *C26*, 37.
(9) Morton, M.; McGrath, J. E.; Juliano, P. C. *J. Polym. Sci.* **1969**, *C26*, 99.
(10) Teyssié, Ph. In *ACS Symp. Ser.* **1981**, *No. 175*, 307. Jérôme, R.; Fayt, R.; Ouhadi, T. *Progr. Polym. Sci.* **1984**, *10*, 87. Morton, M. In *Thermoplastic Elastomers—A Comprehensive Review*; Legge, N. R., Holden, G., Schroeder, H. E., Eds.; 1987; Chapter 4, p 67.
(11) Wiles, D. M. *Structure and Mechanism in Vinyl Polymerization*; Tsurata, T., O'Driscoll, K. F., Eds.; Marcel Dekker: New York, 1969; p 233.
(12) Allen, R. D.; Long, T. E.; McGrath, J. E. *Polym. Bull.* **1986**, *15*, 127.
(13) Wiles, D. M.; Bywater, S. *Trans. Faraday Soc.* **1965**, *61*, 150.
(14) Anderson, B. C.; Andrews, G. D.; Arthur, P.; Jacobson, H. W.; Melby, L. R.; Playtis, A. F.; Sharkey, W. H. *Macromolecules* **1981**, *14*, 1599.
(15) Mueller, A. H. E. *Makromol. Chem.* **1981**, *182*, 2863.
(16) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajan Babu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.
(17) Farnham, W. B.; Sogah, D. Y. U.S. Patent 4,414,372 (Nov 8, 1983).
(18) Jérm̂e, R.; Forte, R.; Varshney, S. K.; Fayt, R.; Teyssié, Ph. In *Recent Advances in Mechanistic and Synthetic Aspects of Polymerization*; Fontanille, M., Guyot, A., Eds.; *NATO ASI, Ser. C* **1987**, *215*, 101.
(19) Forte, R.; Ouhadi, T.; Fayt, R.; Jérôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 2233.
(20) (a) Varshney, S. K.; Hautekeer, J. P.; Fayt, R.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1990**, *23*, 2618. (b) Fayt, R.; Forte, R.; Jacobs, C.; Jérôme, R.; Ouhadi, T.; Teyssié, Ph.; Varshney, S. K. *Macromolecules* **1987**, *20*, 1442. (c) Ouhadi, T.; Forte, R.; Jérôme, R.; Fayt, R.; Teyssié, Ph. Luxembourg Patent 85,627 (Nov 5, 1984); U.S. Patent 4767824, 1988.
(21) Teyssié, Ph.; Jérôme, R.; Ouhadi, T.; Fayt, R. U.S. Patent 4,461,874 (July 4, 1984).
(22) Smid, J. *J. Am. Chem. Soc.* **1965**, *87*, 655.
(23) Matsuzaki, K.; Uryu, T.; Kanai, T.; Hosonuma, K.; Matsubara, T.; Tachikawa, H.; Yamada, M.; Okuzono, S.; *Makromol. Chem.* **1977**, *178*, 11.
(24) Maurer, J. J.; Eustace, D. J.; Ratcliffe, C. T. *Macromolecules* **1987**, *20*, 196.
(25) Tsukahara, Y.; Izumi, A.; Hashimoto, T.; Kawai, H. *Polym. J.* **1982**, *14*, 887.
(26) Price, C.; Briggs, N.; Quintana, J. R.; Stubbersfield, R. B.; Robb, I. *Polym. Commun.* **1986**, *27*, 292.
(27) Hautekeer, J. P.; Jacobs, C.; Fayt, R.; Jérôme, R.; Teyssié, Ph.; Varshney, S. K.; Warin, R., to be published.
(28) Jin, Y.; Huang, R. Y. *J. Appl. Polym. Sci.* **1988**, *36*, 1799.
(29) Broze, G.; Jérôme, R.; Teyssié, Ph.; Marco, C. *Polym. Bull.* **1981**, *4*, 241; *Macromolecules* **1983**, *16*, 996; *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 2205; *Macromolecules* **1983**, *16*, 1771; *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 237.
(30) Horrion, J.; Jérôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Lett. Ed.* **1986**, *24*, 69.
(31) De Porter, C. D.; Long, J. E.; Venkateshwaren, L. N.; Wilkes, G. L.; McGrath, J. E. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1988**, *29* (1), 343.
(32) Eisenberg, A.; King, M. *Ion-Containing Polymers: Physical Properties and Structures.* *2*; Academic Press: New York, 1977.

Registry No. (PSt)(P*t*BuA) (block copolymer), 127972-36-5; (PSt)(P*t*BuA)·Na (block copolymer), 127972-37-6; LiCl, 7447-41-8; αMeSt$^-$Li$^+$, 63949-25-7; Li-naphthalene, 7308-67-0.