Anionic Polymerization of Acrylic Monomers. 6.[†] Synthesis, Characterization, and Modification of Poly(methyl methacrylate)-Poly(*tert*-butyl acrylate) Di- and Triblock Copolymers

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ABSTRACT: Poly(methyl methacrylate)-*b*-poly(*tert*-butyl acrylate) (PMMA-*b*-PtBA) copolymers have been successfully synthesized by the sequential anionic polymerization of methyl methacrylate (MMA) and *tert*-butyl acrylate (tBA) in THF at -78 °C. Although the order of monomer addition makes a difference on the initiation efficiency, it has no significant effect on the final achievement. Mono- and bifunctional initiators based on alkali metals can be used. When the initiators are modified by LiCl as a ligand, the polymerization of each block appears to be living, the molecular weight and composition can be predicted, and the molecular weight distribution is narrow. Size exclusion chromatography supports the absence of homo-PtBA in the PtBA-*b*-PMMA samples. The PtBA blocks can be quantitatively hydrolyzed into polyacid ones as supported by titration and ^1H NMR analysis.

Introduction

It has been reported from this laboratory that inorganic salts potentially able to form a μ-type complex with a growing ion pair and to accordingly displace the classical equilibrium between different types of ion pairs are quite efficient in promoting the truly "living" polymerization of (meth)acrylic esters.[1-3] That discovery opens the way to controlled block copolymerization of alkyl acrylates and alkyl methacrylates. It has been shown, for instance, that some LiCl-modified organolithium initiators make the propagation step of the anionic polymerization of *tert*-butyl acrylate (tBA) and methyl methacrylate (MMA) perfectly living.[2,4,5]

It is reasonable to consider the block copolymerization of these two monomers, which could lead to new multiphase materials that combine a hydrophobic and high T_g block (PMMA T_g = 130 °C for a 80% syndiotactic chain) and a very versatile poly(*tert*-butyl acrylate) (PtBA) component. PtBA can indeed be selectively hydrolyzed with the formation of a hydrophilic poly(acrylic acid) or polysalt. Furthermore, trans-alcoholysis of PtBA can lead to a hydrophobic low T_g polyacrylate (e.g., poly(*n*-butyl acrylate), T_g = -45 °C), of which the association to PMMA in a triblock structure is of great potential in thermoplastic elastomers.[6,7]

The basic question is to know whether the anions derived from one polymer are able to initiate quantitatively the living polymerization of the second comonomer and vice versa. The cross-reactivity of the comonomer pair in an anionic process not only is an appealing problem but is crucial for the successful synthesis of triblock copolymers by further coupling of A-B or B-A diblocks, i.e., the capability to obtain A-B-A as well as B-A-B macromolecules. This paper presents an answer to that challenge.

Experimental Section

Reagents and Solvents. MMA from Aldrich Chemical Co. and tBA from NORSOLOR (France) were first vacuum distilled from CaH_2 after reflux and stored under nitrogen atmosphere at -20 °C. Before polymerization, it was added with a 10 wt % $AlEt_3$ solution in hexane until a persistent yellowish green color was observed.[8] It was then redistilled under reduced pressure just prior to use. Pure LiCl (99.99%) as obtained from Aldrich was dried overnight at +130 °C and then dissolved in dry tetrahydrofuran (THF). A suitable amount of this solution was introduced into the preflamed glass reactor, and THF was distilled off under reduced pressure. THF was purified by refluxing over fresh sodium benzophenone complex (a deep purple color indicating an oxygen- and moisture-free solvent). It was further distilled over oligomers of styryllithium under reduced pressure immediately before use.

Initiators. α-Methylstyryllithium (α-MSLi) used as a monofunctional initiator was prepared by reacting *sec*-BuLi with a slight molar excess of α-methylstyrene (α-MS) in THF at room temperature.[9] Other monofunctional initiators were used: diphenylmethyllithium (Ph_2CHLi), diphenylmethylsodium (Ph_2CHNa), and diphenylmethylpotassium (Ph_2CHK). They were prepared at room temperature by reacting diphenylmethane with the corresponding alkali-metal naphthalene in THF for 24 h. The solution of alkali-metal naphthalene resulted by addition of the alkali metal to naphthalene in THF at room temperature.[10]

Polymerization. Anionic block copolymerization of MMA and tBA was carried out in a flamed glass reactor under nitrogen atmosphere. LiCl was first introduced and dried as previously described. THF and initiator were transferred into the glass reactor by using a rubber septum and a stainless steel capillary or a syringe. The initiator solution was added dropwise to THF until the initiator color persisted; 3 or 4 drops of a 0.2 M initiator solution to 100 mL of THF were generally required to get a persistent color, i.e., a highly pure solvent. After adding the desired amount of initiator, the solution was cooled to -78 °C, the required quantity of MMA or tBA (tBA as a dilute solution in THF, 40% v/v) was introduced, and the polymerization was performed for 15 min. Upon addition of the monomer, a sudden change of the initiator color to light yellow was noticed, indicating that the initiation was instantaneous. An aliquot of the reaction medium was withdrawn for analysis by size exclusion chromatography (SEC) in order to determine the molecular weight of the first block. The second monomer was then added to the solution of the first block (PMMA or PtBA) at -78 °C, and the copolymerization was carried out for an additional 15 min. It was then stopped by adding acidic methanol, and the copolymer was recovered by precipitation into methanol or into a methanol/water (80/20 v/v) mixture. The crude polymer was dried under vacuum at 80 °C for 48 h.

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[†] For the preceding papers in this series, see refs 1-7 and 11-13.

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Table I
Effect of the LiCl/Initiator Molar Ratio on the Synthesis of PMMA-*b*-PtBA Diblock Copolymers in THF at −78 °C, Using α-MSLi as an Initiator[a]

			for PMMA			for diblock				
no.	LiCl/initiator molar ratio	% total conversion	$10^{-3}\bar{M}_n$ (SEC value)	$\bar{M}_w/\bar{M}_n$	f	$10^{-3}\bar{M}_n$ (SEC value)	$\bar{M}_w/\bar{M}_n$	f for PtBA	T_g, °C	
1		93.0	33.0	1.20	0.71	76.0[b]	2.30		36	126
2	0.5	100.0	26.5	1.15	0.88	90.0	1.90	0.80	36	126
3	1.0	97.0	25.5	1.15	0.92	79.0	1.25	0.90		
4	5.0	100.0	23.5	1.15	1.00	83.0	1.15	0.76	37	128
5	10.0	98.0	23.5	1.05	1.00	81.0	1.15	0.78		
6	50.0	100.0	23.5	1.05	1.00	83.0	1.15	0.76		
7	100.0	100.0	23.5	1.05	1.00	81.0	1.15	0.78	37	128

[a] MMA = 0.047 mol; tBA = 0.070 mol; α-MSLi = 0.20×10^{-3} mol; THF = 200 mL. T_g's of PtBA and PMMA prepared under the same conditions are 36 and 128 °C, respectively. f(initiation efficiency) = $\bar{M}_n$(calc)/$\bar{M}_n$(SEC); where $\bar{M}_n$(calc) = (moles of monomer/moles of initiator)(MW of monomer)(% yield/100). [b] Bimodal distribution.

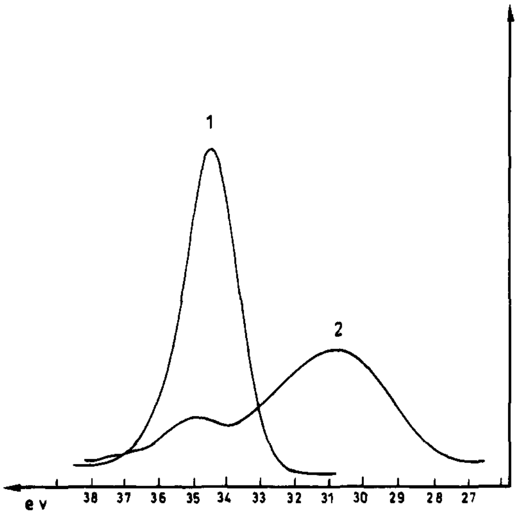

Figure 1. SEC of sample 1 (Table I). (1) PMMA block: $\bar{M}_n$ = 33 000, $\bar{M}_w/\bar{M}_n$ = 1.20. (2) Block copolymer: $\bar{M}_n$ = 76 000, $\bar{M}_w/\bar{M}_n$ = 2.30; prepared in THF at −78 °C using α-MSLi as an initiator in the absence of LiCl.

The PtBA block was hydrolyzed by using *p*-toluenesulfonic acid as a catalyst, as described earlier.[11]

Characterization. SEC was carried out by using a Waters GPC apparatus equipped with two Ultrastyragel linear columns, with THF as the eluent at a flow rate of 1 mL min^{-1} at 30 °C. Polystyrene standards were used for calibration, and the number- and weight-average molecular weights of the first block and the final copolymer were accordingly calculated. The glass transition temperature was measured by differential scanning calorimetry (DSC) using a Du Pont 9000 apparatus. The instrument was calibrated with indium and mercury. Samples were first heated up to 150 °C, cooled rapidly to room temperature, and then scanned again at a rate of 20 °C min^{-1}. The composition of copolymers was determined by ^{1}H NMR using a Bruker AN 400 spectrometer.

Results and Discussion

Synthesis of PMMA-*b*-PtBA Diblock Copolymers. Living PMMA anions, prepared as described in the Experimental Section and complexed with various well-defined amounts of LiCl, have been used to initiate tBA copolymerization. Table I reports the quite remarkable influence of the LiCl/initiator molar ratio on the molecular weight (MW) and polydispersity (MWD) of both the initial PMMA block and the final copolymer. It is worth noting that conversion of each monomer is nearly quantitative even in the absence of LiCl. However, the SEC trace of the copolymer synthesized without that additive shows a very broad MW distribution, i.e., $\bar{M}_w/\bar{M}_n$ = 2.3, which is actually bimodal (Figure 1). The chromatogram indicates the presence of ca. 20% homo-PMMA in the final raw product.

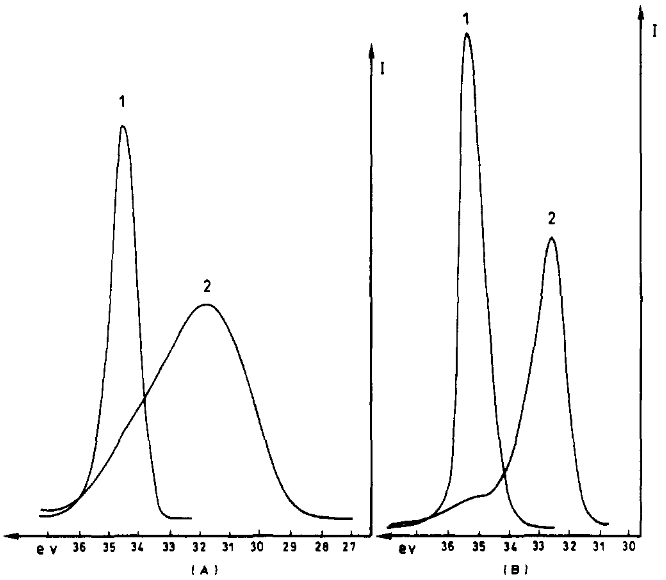

Figure 2. SEC of samples 2 and 4 (Table I). (A) (1) PMMA block: $\bar{M}_n$ = 26 500, $\bar{M}_w/\bar{M}_n$ = 1.15. (2) Block copolymer: $\bar{M}_n$ = 90 000, $\bar{M}_w/\bar{M}_n$ = 1.90. (B) (1) PMMA block: $\bar{M}_n$ = 23 500, $\bar{M}_w/\bar{M}_n$ = 1.15. (2) Block copolymer: $\bar{M}_n$ = 83 000, $\bar{M}_w/\bar{M}_n$ = 1.15; prepared in THF at −78 °C using α-MSLi as an initiator in the presence of LiCl ((A) LiCl/initiator molar ratio = 0.5; (B) LiCl/initiator molar ratio = 5.0).

The amount of LiCl added is obviously a critical parameter. Compared to Figure 1, Figure 2A shows how much the situation is already improved when only 0.5 mol of LiCl is used per mole of initiator. The MWD of the final block copolymer has been reduced from 2.3 to 1.9, and the percentage of homo-PMMA has been decreased to such an extent that only a faint shoulder is now observed on the low molecular weight side of the distribution curve. At the same time, the initiator efficiency, f, has increased by ca. 20% (from 0.71 to 0.88) in the synthesis of the first PMMA block. An additional beneficial effect is observed when equimolar amounts of LiCl and initiator are used (Table I). A 5 M excess of LiCl compared to the initiator allows the situation to be improved further. The SEC trace of the final block copolymers (Figure 2B) shows that a very small amount of homo-PMMA still contaminates the diblock copolymer (ca. 5%).

Table I shows that any further excess of LiCl does not change the course of the two-step block copolymerization of MMA and tBA. Actually the initiator efficiency is almost 100% for the MMA polymerization, and it drops to ca. 78% for the second block; this expectedly reflects the partial deactivation of the first block upon addition of the second comonomer solution. The molecular weight distribution is very narrow, i.e., 1.05 for the first block and

Table II
Characterization Data for PMMA-*b*-PtBA Diblock Copolymers Synthesized in THF at −78 °C, Using Different Alkali-Metal-Based Initiators (LiCl/Initiator Molar Ratio = 10.0)

			monomers, mol			for PMMA			for diblock		
no.	type of initiator	initiator × 10^{-3}, mol	MMA	tBA	% total conversion	$10^{-3}\bar{M}_n$ (SEC value)	$\bar{M}_w/\bar{M}_n$	f	$10^{-3}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	f for PtBA
1	α-MSLi	3.60	0.800	2.145	100.0	24.0	1.05	0.92	125.0	1.10	0.81
2[a]	α-MSLi	0.11	0.047	0.070	100.0	43.5	1.05	0.98	147.5	1.10	0.80
3	Ph_2CHLi	0.25	0.020	0.038	99.5	8.5	1.05	0.94	30.5	1.05	0.95
4	Ph_2CHLi	0.20	0.047	0.070	99.5	24.5	1.05	0.95	77.5	1.10	0.87
5	Ph_2CHNa	0.20	0.047	0.070	99.5	24.0	1.05	0.97	78.0	1.10	0.85
6	Ph_2CHK	0.15	0.047	0.070	99.5	34.0	1.05	0.92	113.0	1.15	0.82

[a] That experiment has been carried out on a pilot scale (10-L apparatus, 5 L of THF, total quantity of monomer 360 g).

Table III
Characterization Data for PtBA-*b*-PMMA Diblock Copolymers Synthesized in THF at −78 °C, Using Different Alkali-Metal-Based Initiators (LiCl/Initiator Molar Ratio = 10.0)

			monomers, mol			for PtBA			for diblock		
no.	type of initiator	initiator × 10^{3}, mol	tBA	MMA	% total conversion	$10^{-3}\bar{M}_n$ (SEC value)	$\bar{M}_w/\bar{M}_n$	f	$10^{-3}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	f for PMMA
1[a]	α-MSLi	0.45	0.040	0.050	100	27.0	1.65	0.42	51.0	1.55	
2	α-MSLi	0.45	0.040	0.050	100	12.0	1.14	0.91	24.0	1.20	0.97
3	α-MSLi	1.06	0.195	0.150	100	25.5	1.10	0.92	42.0	1.10	0.93
4	Ph_2CHLi	0.20	0.034	0.080	100	23.0	1.05	0.95	67.0	1.05	0.96
5	Ph_2CHNa	0.20	0.034	0.080	100	24.5	1.05	0.89	68.0	1.05	1.03
6	Ph_2CHK	0.20	0.040	0.080	100	27.0	1.07	0.95	74.5	1.10	0.93

[a] Block copolymerization carried out in the absence of LiCl.

1.15 for the diblock. Finally, the MW as determined by SEC is very close to the theoretical value expected for a perfectly living process as already observed for the PSt-*b*-PtBA diblock copolymers.[11] This is in sharp contrast, with the significant discrepancy found for the products prepared in the absence of LiCl. That f for the second block is less than the value calculated for the first block might be due to several facts: partial deactivation of the first block upon addition of the second monomer, determination of the diblock molecular weight by SEC, and secondary reactions in the initiation of tBA by PMMA macroanions. It will be further seen that the third effect would be the most contributing one.

When the LiCl/initiator molar ratio is further increased over that value of 5, no other beneficial effect is observed. It means that regularly increasing the amount of LiCl improves the control of the anionic block copolymerization up to an asymptotical situation close to the ideal one but is limited at that point as expected for a complex equilibrium formation between the growing ion pairs and the inorganic salt.

Extension to the Other Initiators. Table II shows that the use of other initiating carbanions, even comprising a cation different from Li, does not perturb the regulating influence of an excess of LiCl; in all cases, the MWD is narrow, the comonomer conversion is quantitative, and the efficiency of the initiator is high (over 90% for the first block and over 80% for the second block). It should, however, be mentioned that, in the series of diphenylmethyl alkaline initiators, the potassium gegenion seems to be less effective than lithium in the initiation of tBA by the first PMMA block. However, it would be surprising that potassium counterion initiator allows perfect control of the MMA polymerization in the first step and not that of tBA by macroanions of PMMA. The data of Table III, described hereafter, will support that Ph_2CHK actually initiates the tBA polymerization properly and that the initiator efficiency of 82% for experiment 6 in Table II is more likely due to a partial deactivation of the living MMA-type macroinitiator upon the addition of the solution of tBA.

These data provide a clear indication that coordination of LiCl to R^-M^+ is a generally efficient strategy for avoiding the noxious secondary reactions potentially promoted by the R^-M^+ organometallic species. As reported elsewhere,[12] ^7Li and ^{35}Cl NMR spectroscopies have shown the existence of an interaction between the growing ion pair of living PMMA and LiCl, and this convincingly supports the ideas discussed above.

Synthesis of PtBA-*b*-PMMA Diblock Copolymers. In order to demonstrate the feasibility of the reverse reaction sequence, living PtBA anions were first prepared in THF at −78 °C using various monofunctional alkali-metal initiators in the presence of a 10-fold excess of LiCl. The experimental data summarized in Table III indicate still better control of the block copolymerization process than in the PMMA-*b*-PtBA case, in striking contrast to the blank carried out in the absence of the salt: a very narrow MWD (1.05–1.10), a high efficiency (above 90–95%), and above all the absence of any homo-PtBA in the raw final product (see SEC trace in Figure 3). f values are now comparable for the first and second block, and this is in contrast to what has been observed in the PMMA-*b*-PtBA case. Possible reasons might be found in favored backbiting intramolecular reactions when PMMA anions are initiators as described previously.[13] As already reported in Table I, T_g's of the blocks closely correspond to those of the homopolymers,[2,4] indicating an extensive phase separation.

A–B–A- and B–A–B-type triblock copolymers should represent a straightforward and valuable extension of the results discussed in the foregoing sections, since there is no problem of cross-reactivity when the sequential anionic polymerization of MMA and tBA is considered. It is thus feasible for substitution of monofunctional initiator by a difunctional one in order to synthesize A–B–A or B–A–B triblock copolymer. Purposely, the MMA polymerization has been initiated by lithium naphthalene in the presence of a 10-fold excess of LiCl, leading to a macrodianion, i.e., a potential central block ($\bar{M}_n$ = 15 000, MWD = 1.25, f = 0.78). In the second step, tBA propagation takes place on both sides of that first sequence. The resulting product

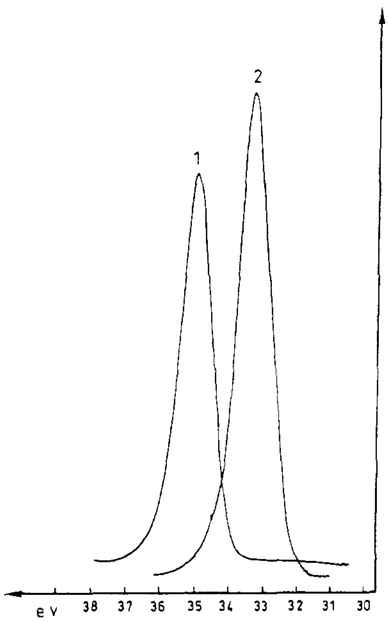

Figure 3. SEC of sample 4 (Table III). (1) PtBA block: $\bar{M}_n$ = 23 000, $\bar{M}_w/\bar{M}_n$ = 1.05. (2) Block copolymer: $\bar{M}_n$ = 67 000, $\bar{M}_w/\bar{M}_n$ = 1.05; prepared in THF at −78 °C using Ph_2CHLi as an initiator in the presence of LiCl (LiCl/initiator molar ratio = 10.0).

has the following characteristics: $\bar{M}_n$ = 17 800, MWD = 1.20 f = 0.80, tBA = 14% by ^1H NMR analysis. PMMA-*b*-PtBA-*b*-PMMA can also be prepared following a similar strategy.

Obviously enough, these techniques offer an extremely versatile strategy for the synthesis of a number of new products, particularly since the PtBA block may be easily and quantitatively converted into other polyacrylates or poly(acrylic acid) by trans-alcoholysis or hydrolysis reactions, respectively.[11]

As an example, the above-described PtBA-*b*-PMMA-*b*-PtBA copolymer has been hydrolyzed in toluene in the presence of *p*-toluenesulfonic acid (5 mol % relative to the polyacrylate content) at 100 °C for 4 h; completion of the reaction has been ascertained by ^1H NMR (complete disappearance of the peak at 1.39 ppm characteristic of the *tert*-butyl group protons) and by titration of the polyacid with a tetramethylammonium hydroxide solution in a toluene–methanol mixture (9/1 v/v). Neutralization of this hydrolyzed triblock with metal bases provides for a very valuable extension for the carboxylato-telechelic polymers (HTP's) thoroughly studied in our laboratory,[14,15] instead of consisting of linear chains selectively end-capped at both ends by a metal carboxylate. The present triblock copolymer represents a controlled central sequence surrounded by two (small) ionomer blocks.

The present results confirmed in a broad range of MW's and compositions are a striking illustration of the efficiency and practicality of salt additives, i.e., LiCl, since it is normally difficult to reinitiate the methacrylate polymerization from polyacrylate anions or vice versa using more classical initiators, including GTP ones.[16]

In conclusion, ligated carbanionic initiators appear as an efficient tool for controlling the living polymerization of methacrylic and hindered acrylate esters. It opens extremely attractive potentialities in the macromolecular engineering of (meth)acrylate-based materials (such as organized anisotropic heterophase systems, physically cross-linked elastomers, polymeric emulsifiers, etc.), thus ensuring further development of a valuable class of ionomers.

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Registry No. α-MSLi, 92503-87-2; Ph_2CHLi, 881-42-5; Ph_2CHNa, 5152-68-1; Ph_2CHK, 10060-17-0; (MMA)(tBA) (block copolymer), 131589-87-2; LiCl, 7447-41-8; lithium naphthalene, 27939-69-1.