

geneous quaternization of crosslinked thiazole copolymer (Scheme I). Therefore, all active sites of them may participate to this reaction.

Furthermore, the crosslinked polymer catalyst was easily recovered from reaction mixture by filtration, and the recycled polymer catalyst had similar activity (run 6) to that of the original polymer catalyst (run 5).

In conclusion, polymer-supported thiazolium salts were sufficient catalysts for "the formose reaction." DHA was selectively produced in this reaction catalyzed by the thiazolium salt polymers. The polymer catalysts were easily recovered and reused. We are now investigating an application of the polymer catalysts for the selective syntheses of more long chain carbohydrates, such as glucose or fructose.

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# Synthesis of AB(BA), ABA and BAB Block Copolymers of *tert*-Butyl Methacrylate (A) and Ethylene Oxide (B)

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## SYNOPSIS

Well-defined AB(BA), ABA, and BAB block copolymers of *tert*-butyl methacrylate (tBMA) (A) and ethylene oxide (EO) (B) have been prepared by sequential living anionic polymerization of the two comonomers, irrespective of their addition order. Diphenyl methyl potassium and naphthalene potassium have been successfully used as mono- and difunctional initiators, respectively. In all cases, molecular weight and composition of the block copolymers can be predicted on the basis of the monomer over initiator molar ratio, and the molecular weight distribution is relatively narrow. Size exclusion chromatography, selective extractions of homopolymers, and <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy support that block copolymerization proceeds without homopolymer formation nor side reactions, e.g., transesterification reactions. The PtBMA blocks have been quantitatively hydrolyzed into polyacid ones with formation of polyacid-b-polyether block copolymers as supported by titration, <sup>1</sup>H-NMR, and IR analysis. © 1992 John Wiley & Sons, Inc.

**Keywords:** bishydrophilic copolymer • block copolymer • poly(*tert*-butyl methacrylate) • poly(ethylene oxide) • sequential living anionic block copolymerization

## INTRODUCTION

It is well known that poly(methacrylic acid) (PMAA) forms complexes with poly(ethylene oxide) (PEO) as well in the bulk state as in solution. The complexation reaction is driven by hydrogen bonding and has proved to be effective in enhancing miscibility of incompatible polymers, stability of colloidal suspensions and micellar systems, performances of associative thickeners, etc.<sup>1,2</sup>

Most of the studies have been devoted to the association of homopolymers. Little attention has been paid to block copolymers of MAA and EO most likely due to the problem of associating polyacid and polyether blocks in a controlled way. For instance, methacrylic acid cannot be polymerized anionically, in contrast to EO, the anionic polymerization of which is a living process. The sequential anionic polymerization of tBMA and ethylene oxide might

however be a convenient way to cope with the problem of the direct block copolymerization of MAA and EO. Indeed poly(*tert*-butyl methacrylate) blocks can be easily hydrolyzed with formation of the expected poly(methacrylic acid) component. Although tBMA and EO are reactive towards anionic species, the successful block polymerization of two monomers is known to depend very critically on the relative reactivity of the comonomers, i.e., on the relative stability of the conjugated anions. By reference to the scale of monomer reactivity,<sup>3</sup> poly(alkyl methacrylate) anions should initiate polymerization of ethylene oxide. However, noxious secondary reactions are expected to perturb the course of the sequential polymerization. Indeed, the rather low reactivity of ethylene oxide requires a polymerization temperature of a least 0°C, at which most alkyl methacrylate anions are essentially unstable. Moreover, the low solubility of PEO in the commonly used solvents (e.g., THF) might request a still higher polymerization temperature (above 20°C) to keep the reaction medium homogeneous. Under such experimental conditions, living

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poly(ethylene oxide) anions can react with the ester groups of poly(alkyl methacrylate) blocks and be responsible for a loss of propagating species together with an ill-defined structure of the final product.<sup>4</sup> Interestingly enough, it has been recently reported that the tBMA anionic polymerization still displays a living character even at a temperature as high as 37°C for lithium counterions and 17°C for sodium in THF.<sup>5</sup> Since Li containing active species are unable to propagate the anionic polymerization of EO, whereas a too high temperature (more than +50°C) is required when Na is used as a counterion, a K containing initiator has been selected assuming that K can provide PtBMA macroanions with a stability comparable to that promoted by Li and Na.

The reverse sequential addition of the comonomers might be considered since Suzuki et al.<sup>4</sup> have shown that the anionic polymerization of both MMA and tBMA can be initiated with alkali metal salts of PEO prepared by metalation of PEO oligomers bearing OH, NH, or methyl isobutyrate  $[(CH_3)_2-CH-COOCH_3]$  end-groups. In addition to a nonstraightforward copolymerization scheme, only block copolymers comprising BA and ABA types and a relatively short PEO (B) segment have been made available. Since metallation of hydroxyl-terminated PEO leads to the formation of oxoanions which do not differ from the growing species of living PEO, the latter polyanions must be able to initiate successfully the polymerization of MMA and tBMA. Actually, Ulbricht et al.<sup>6</sup> have reported the synthesis of poly(EO-b-MMA) based on the polymerization of MMA initiated with living PEO macroanions.<sup>6a</sup>

Very recently, Ulbricht et al. also reported that diblock copolymers could be synthesized by anionic polymerization in the order *tert*-butyl methacrylate-ethylene oxide and ethylene oxide-*tert*-butyl methacrylate using a monofunctional initiator in THF.<sup>6c</sup> However the initiation of the *tert*-butyl methacrylate polymerization by cumyl potassium at +25°C resulted in a tailing in the low molecular region indicative of some side reactions. Consequently, anionic polymerization of EO by PtBMA macroanions does not seem to be perfectly controlled. Actually, an incomplete conversion of EO (80% as an average) and a relatively broad molecular weight distribution (from 1.43 to 1.72) are observed. Furthermore, the reverse sequential addition of the comonomers, i.e., the anionic polymerization of tBMA initiated by PEO macroanions leads to diblock copolymers contaminated with a certain amount of homo-PEO (ca. 2.5–10%).

This article considers the synthesis of a series of well-defined block copolymers based on the sequential living anionic polymerization of tBMA and EO under suitable conditions. The sequential addition of the two comonomers will be reversed and its possible effect on the efficiency of the block copolymerization will be considered. Both mono- and difunctional initiators will be used in order to make available AB, ABA, and BAB types of block copolymers. Finally, the PtBMA blocks will be hydrolyzed with formation of copolymers consisting of PEO and polymethacrylic acid sequences.

## EXPERIMENTAL

### Reagents and Solvents

tBMA from Norsolor (France) was first dried by refluxing over CaH<sub>2</sub>, distilled under reduced pressure and stored under inert atmosphere at -20°C. Just before polymerization, tBMA was treated with a 10% Al(Et)<sub>3</sub> solution in toluene at 0°C until a persistent yellow-green color was obtained,<sup>5</sup> and then distilled under reduced pressure. Ethylene oxide was first purified with KOH and CaH<sub>2</sub> and then twice distilled over *n*-Buli just before use.

THF was purified by refluxing over a freshly prepared sodium benzophenone complex. A deep-purple colour indicated that THF is oxygen and moisture free. It was further distilled over styryllithium oligomers under reduced pressure for final purification.

### Initiator

Diphenyl methyl potassium ( $\Phi_2CHK$ ) was prepared at room temperature by reacting diphenyl methane with naphthalene potassium in THF for 24 h. Naphthalene potassium resulted from the reaction of potassium with naphthalene in THF at room temperature.

### Block Copolymerization

Anionic block copolymerization of tBMA and EO was usually carried out in a flamed glass reactor under nitrogen atmosphere. THF and initiator were transferred into the reactor using rubber septums and stainless-steel capillaries and/or syringes.

Depending on the sequence of monomer addition di- and tri-block copolymers were prepared as follows.

### Poly(tBMA-b-EO) (AB) and Poly(EO-b-tBMA-b-EO) (BAB) Copolymers

After the addition of the desired amount of initiator into THF, the solution was cooled to -78°C and added with the required quantity of tBMA. Upon the addition of the monomer a sudden change of color from deep red to light yellow occurred as a result of an instantaneous initiation. tBMA polymerization lasted 2 h at -78°C. Then an aliquot of the reaction medium was withdrawn for analysis by GPC in order to determine the molecular weight of the first block. Ethylene oxide was cooled down to -78°C and added into the glass reactor, the temperature of which was then slowly increased from -78 up to +35°C (ca. 0.5 h). Copolymerization was allowed to occur for 20 h at that temperature.

### Poly(EO-b-tBMA) (BA) and Poly(tBMA-b-EO-tBMA) (ABA) Copolymers

EO was added to the initiator solution in THF at -78°C. Temperature was then raised to 35°C and ethylene oxide was polymerized for 24 h. An aliquot of the reaction medium was withdrawn for GPC analysis in order to determine the molecular weight of the PEO block. The glass reactor was cooled down to +20°C and added with the desired amount of tBMA. Copolymerization was continued for 5–15 min.

In all cases, polymerization was stopped by addition of acidified methanol. Copolymers were recovered by precipitation into a large excess of petroleum ether at a low temperature (ca. -20°C), filtered, washed, and dried under vacuum at room temperature to constant weight. Copolymers of a high PtBMA content (> 50 mol %) were dissolved in benzene and freeze-dried.

### Hydrolysis

The representative procedure for the hydrolysis of PtBMA containing block copolymers was as follows. A stirred mixture of the copolymer (1.0 g, 4.5 mmol based on tBMA units) and sodium iodide (4.0 g, 28 mmol) in acetonitrile (60 mL) was added with 4.0 mL (30 mmol) of trimethylsilyl chloride at +50°C. The reaction mixture immediately turned yellow, and a white precipitate of sodium chloride appeared. After 10 h, the mixture was concentrated by solvent evaporation, redissolved in THF, and precipitated into 0.1 N HCl aqueous solution containing Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, i.e., a discoloring agent. The final polymer was purified by repeated precipitation from THF

into H<sub>2</sub>O and from THF into hexane, respectively. It was finally dried in a vacuum oven (80°C), and collected as a white powder. The degree of hydrolysis was determined by titration of the carboxylic acid groups with tetramethyl ammonium hydroxide (TMAH) in a 90/10 (v/v) THF/methanol mixture using phenolphthalein as an indicator.

### Characterization

Size exclusion chromatography (SEC) was carried out in THF at 45°C using a Hewlett-Packard 1090 liquid chromatograph equipped with four Gel Columns (10<sup>5</sup>, 10<sup>3</sup>, 500, and 100 Å) and a Hewlett-Packard 1037 A Refractive Index Detector. Polystyrene standards were used for calibration, and the number- and weight-average molecular weights were accordingly calculated.

<sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded at 400 and 100 MHz, respectively, in the FT mode on a Bruker AN 400 Super conducting magnet system. 20% solutions in CDCl<sub>3</sub> or CD<sub>3</sub>OD were prepared for <sup>13</sup>C-NMR measurements. Inverse-gated proton decoupling was used when high resolution <sup>13</sup>C-NMR spectra were recorded.

IR spectra (KBr disk) were obtained on a Perkin-Elmer 197 infrared spectrophotometer.

## RESULTS AND DISCUSSION

As mentioned in the Introduction, two different direct pathways can be envisioned in order to prepare PtBMA (A) and PEO (B) block copolymers of various architectures.

### Synthesis of Poly(tBMA-b-EO) (AB) and Poly(EO-b-tBMA-b-EO) (BAB)

When tBMA is first polymerized with a counterion (K) compatible with the EO polymerization, it is of critical importance to know whether the anionic polymerization of tBMA is living and whether the related macroanion is stable enough to initiate quantitatively the EO polymerization at a relatively high temperature (ca. 0°C). Tables I and II report the characteristic features of di- and triblock copolymers prepared from polyanions of the tBMA type. When these precursors are synthesized in THF at -78°C by using diphenyl methyl potassium as an initiator, Table I shows that the expected molecular weight is actually observed, in agreement with a possible living mechanism. Furthermore, the molecular

Table I. Characterization of PtBMA-b-PEO Diblock Copolymers Synthesized in THF Using  $\phi_2\text{CHK}$  as Initiator<sup>a</sup>

Sample	Theoretical Composition (wt %)		$\bar{M}_n \times 10^{-3}$ (PtBMA)		Total Conversion (wt %)	tBMA Content in the Copolymer <sup>d</sup>	$\bar{M}_w/\bar{M}_n^c$ (PtBMA)		$\bar{M}_w/\bar{M}_n^c$ Block Copolymers
	tBMA	EO	Theoretical <sup>b</sup>	Experimental (SEC)			$\bar{M}_w/\bar{M}_n^c$	Experimental <sup>f</sup>	
1	89.0	11.0	8.0	8.5	93.5	92.0	1.05	8.4	1.20
2	40.0	60.0	2.2	2.2	97.5	38.5	1.10	5.4	1.40
3	30.0	70.0	2.0	2.2	95.0	29.5	1.10	6.8	1.40
4	20.0	80.0	4.2	4.3	95.0	19.0	1.09	21.0	1.40

<sup>a</sup> Polymerization of tBMA, 2 h at  $-78^\circ\text{C}$ ; copolymerization of EO: 24 h at  $+35^\circ\text{C}$ .

<sup>b</sup>  $\bar{M}_n$ , calcd =  $\frac{\text{weight of reacted monomer (g)}}{\text{mole of initiator}}$ .

<sup>c</sup> SEC value.

<sup>d</sup> By  $^1\text{H-NMR}$  analysis.

<sup>e</sup>  $\bar{M}_n$ , copolymers =  $\frac{\text{weight of comonomers (g)}}{\text{mole of initiator}} \times \text{wt \% conversion}$ .

<sup>f</sup>  $\bar{M}_n$ , copolymers =  $\frac{\bar{M}_n, \text{ first block (SEC value)}}{\text{wt \% first block (}^1\text{H-NMR value)}}$ .

Table II. Characterization of PEO-b-PtBMA-b-PEO Triblock Copolymers Synthesized in THF Using K-Naphthalene as Initiator<sup>a</sup>

Sample	Theoretical Composition (wt %)		$\bar{M}_n \times 10^{-3}$ PtBMA		Total Conversion (wt %)	tBMA Content in the Copolymer <sup>d</sup>	$\bar{M}_w/\bar{M}_n^c$ (PtBMA)		$\bar{M}_w/\bar{M}_n^c$ Block Copolymers
	tBMA	EO	Theoretical <sup>b</sup>	Experimental (SEC)			$\bar{M}_w/\bar{M}_n^c$	Experimental <sup>f</sup>	
1	90.0	10.0	35.0	35.7	96.0	89.0	1.25	38.9	1.25
2	50.0	50.0	2.5	2.6	97.0	51.0	1.10	5.0	1.35
3	40.0	60.0	9.0	9.7	92.0	42.0	1.20	22.5	1.45
4	20.0	80.0	4.0	4.1	97.0	19.0	1.15	20.0	1.20

<sup>a</sup> Polymerization of tBMA, 2 h at  $-78^\circ\text{C}$ ; copolymerization of EO: 24 h at  $+35^\circ\text{C}$ .

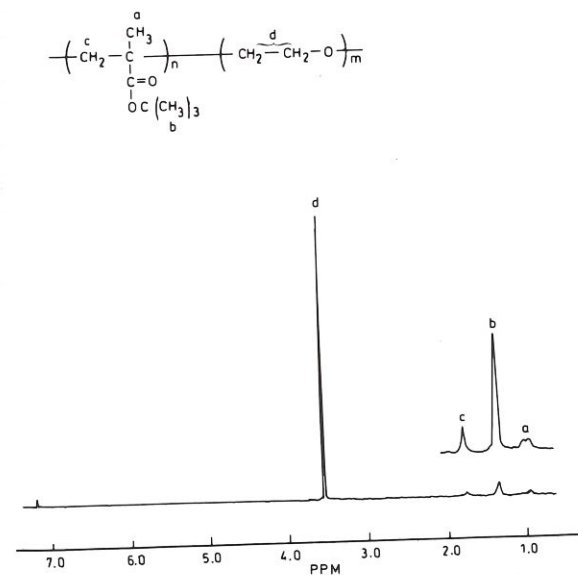
<sup>b</sup>  $\bar{M}_n$ , calcd =  $2 \times \frac{\text{weight of reacted monomer (g)}}{\text{mole of initiator}}$ .

<sup>c</sup> SEC value.

<sup>d</sup> By  $^1\text{H-NMR}$  analysis.

<sup>e</sup>  $\bar{M}_n$ , copolymers =  $\frac{\text{weight of comonomers (g)}}{\text{mole of initiator}} \times \text{wt \% conversion}$ .

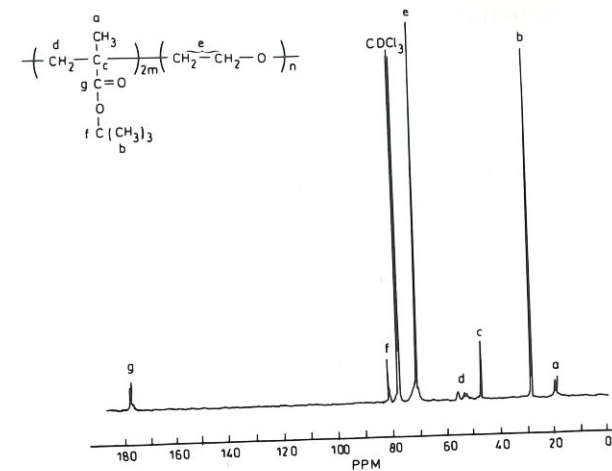
<sup>f</sup>  $\bar{M}_n$ , copolymers =  $\frac{\bar{M}_n, \text{ first block (SEC value)}}{\text{wt \% first block (}^1\text{H-NMR value)}}$ .

Figure 1. 400 MHz  $^1\text{H-NMR}$  spectrum of a PtBMA-b-PEO diblock copolymer (sample 3, Table I).

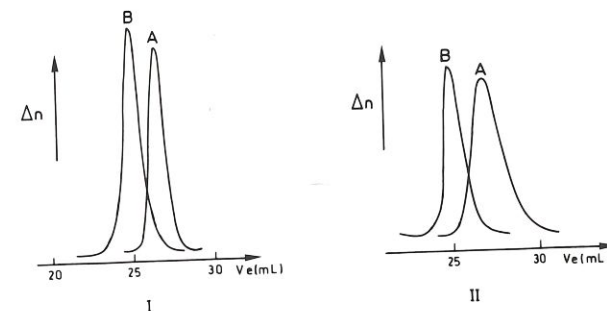
weight distribution is rather narrow, in contrast to the observation by Ulbricht et al.<sup>6c</sup> who reported a tailing on the low molecular weight side when the tBMA polymerization was initiated with cumylpotassium in THF at  $25^\circ\text{C}$ . The authors agreed that the occurrence of some side reactions could not be completely precluded under these experimental conditions.

The same conclusion is drawn when naphthalene-K is used as a difunctional initiator for the tBMA polymerization. Indeed, theoretical molecular weights and values determined by SEC are in good agreement in the investigated range. It must be mentioned here that the absolute molecular weight of PtBA has been observed to be in a close agreement with the value determined by SEC on the basis of a polystyrene calibration.<sup>7</sup> The molecular weight distribution is still narrow although slightly broader when tBMA is initiated with  $\phi_2\text{CHK}$  (1.2 vs. 1.1). This first series of experimental data do show that the anionic polymerization of tBMA is free from noxious side reactions when it is performed at a sufficiently low temperature ( $-78^\circ\text{C}$  in THF) and when the initiator is either a highly delocalized and sterically hindered monofunctional diphenyl methyl potassium, or a bifunctional naphthalene-K complex.

Mono- and di-functional polyanions of the tBMA type have been used as macroinitiators for the EO polymerization. Tables I and II demonstrate that the overall conversion is nearly quantitative (95% as an average).  $^1\text{H-}$  and  $^{13}\text{C-NMR}$  spectra of the

Figure 2. 100 MHz  $^{13}\text{C-NMR}$  spectrum of a PEO-b-PtBMA-b-PEO triblock copolymer (sample 3, Table II).

copolymers clearly show the typical resonance of the methylene group of PEO at 3.58 ppm ( $^1\text{H}$ )/70.6 ppm ( $^{13}\text{C}$ ) and of the *tert*-butyl group of PtBMA at 1.33 ppm ( $^1\text{H}$ )/27.7 ppm ( $^{13}\text{C}$ ) (Figs. 1 and 2). The weight composition of the purified copolymers has been calculated from  $^1\text{H-NMR}$  spectra and found to be very close to the theoretical composition within the limits of experimental errors (mainly due to the accuracy on the amount of initiator when the theoretical molecular weight is high). Composition and molecular weight of the recovered block copolymers fit very closely the expected values. The molecular weight distribution is not very much broader than the precursor; it seems however to be narrower for the copolymers of an extreme composition. SEC

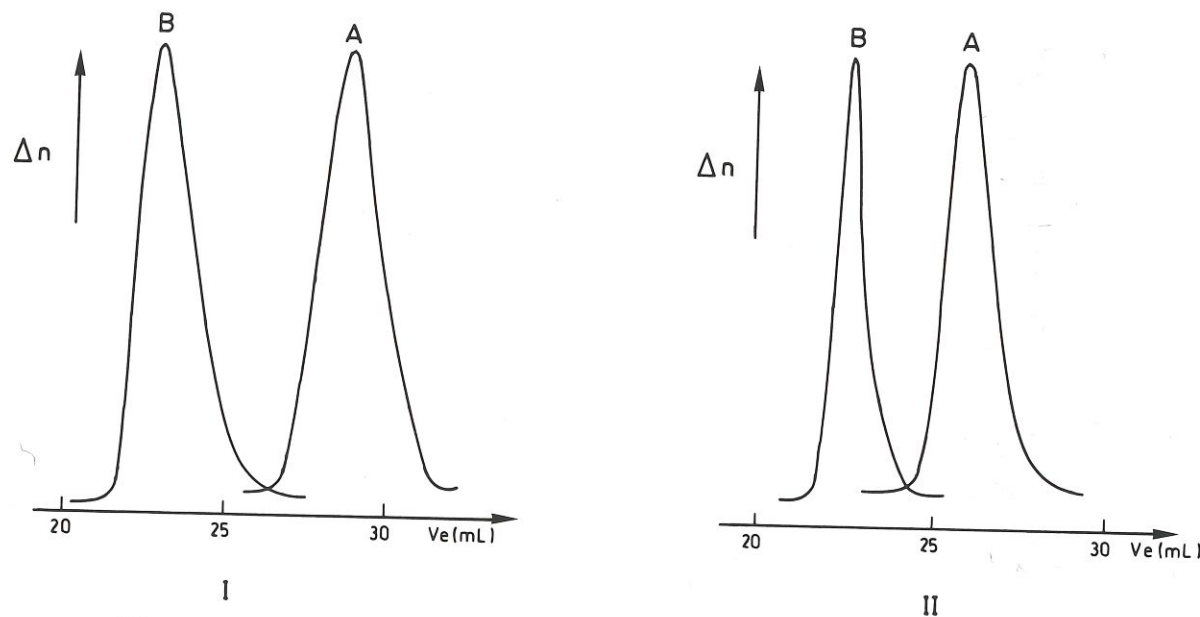
Figure 3. SEC chromatograms of di- and triblock copolymers synthesized in THF using living PtBMA precursors. [I] PtBMA-b-PEO diblock copolymer (sample 4, Table I): (A) PtBMA block,  $\bar{M}_n$ : 4200;  $\bar{M}_w/\bar{M}_n$ , 1.09; (B) diblock copolymer,  $\bar{M}_n$ : 22,600;  $\bar{M}_w/\bar{M}_n$ , 1.40. [II] PEO-b-PtBMA-b-PEO triblock copolymer (sample 4, Table II): (A) PtBMA block,  $\bar{M}_n$ : 4100;  $\bar{M}_w/\bar{M}_n$ , 1.15; (B) triblock copolymer,  $\bar{M}_n$ : 21600;  $\bar{M}_w/\bar{M}_n$ , 1.20.

chromatograms typical of di- and tri-block copolymers are shown in Figure 3 and compared to the elution curve of the PtBMA; practically no homo-PtBMA contaminates the di- and tri-block copolymers within the limits of sensitivity of the method. In order to confirm that pure block copolymers have actually been synthesized, several samples reported in Tables I and II (e.g., samples reported on Fig. 3 have been extracted with hexane, a selective solvent of PtBMA and found to be free of homopolymer of that type.

As a conclusion of this first series of syntheses, essentially pure di- and tri-block copolymers result from the anionic polymerization of EO initiated with mono- and di-functional polyanions of tBMA in THF and in the presence of a potassium counterion.

### Synthesis of Poly(EO-b-tBMA) (BA) and Poly(tBMA-b-EO-b-tBMA) (ABA)

In order to demonstrate the feasibility of the reverse sequence of monomer addition, living PEO anions have been first prepared in THF at 35°C and used to initiate the subsequent tBMA polymerization. Experimental data of Tables III and IV highlight a very well-controlled block copolymerization process: high conversion of comonomers, relatively narrow and symmetric molecular weight distribution, ab-



**Figure 4.** SEC chromatograms of di- and triblock copolymers synthesized in THF using living PEO precursors. [I] PEO-b-PtBMA diblock copolymer (sample 1, Table III): (A) PEO block,  $\bar{M}_n$ : 2100,  $\bar{M}_w/\bar{M}_n$ , 1.13; (B) di-block copolymer,  $\bar{M}_n$ : 13500;  $\bar{M}_w/\bar{M}_n$ , 1.45. [II] PtBMA-b-PEO-b-PtBMA triblock copolymer (sample 3, Table IV): (A) PEO block,  $\bar{M}_n$ : 6900;  $\bar{M}_w/\bar{M}_n$ , 1.09; (B) tri-block copolymer,  $\bar{M}_n$ : 10300;  $\bar{M}_w/\bar{M}_n$ , 1.40.

sence of homo-PEO in the raw final products (see SEC traces in Fig. 4), and close matching of the theoretical and experimental composition and molecular weight. These results are in contrast to those reported by Ulbricht et al.,<sup>6c</sup> who observed contamination of block copolymers by small amounts of homo-PEO (6% as an average).

Side transesterification reactions have been reported to occur when methyl methacrylate is polymerized by living PEO in THF at ambient temperature.<sup>4,6b</sup> In order to assess the absence of such side reactions in the course of the herein reported block copolymerization, high resolution <sup>13</sup>C-NMR spectra of several samples have been recorded using the inverse-gated proton decoupling method. <sup>1</sup>H-NMR spectroscopy has to be disregarded due to the overlapping of <sup>1</sup>H resonances of the  $\alpha$ -methyl and  $-\text{OC}(\text{CH}_3)_3$  groups of PtBMA. The relative intensities of the <sup>13</sup>C resonances of C=O and O-*tert*-butyl are essentially the same, and the intensity ratio of the carbonyl and the three methyl groups of the *tert*-butyl moiety is 1 : 3, strongly suggesting the absence of transesterification reactions under the polymerization conditions reported in the experimental part.

Up to this point, one can safely state that di- and tri-block copolymers of tBMA (A) and EO (B) can be made available in a highly predictable and con-

**Table III.** Characterization of PEO-b-PtBMA Diblock Copolymers Synthesized in THF Using  $\Phi_2\text{CHK}$  as Initiator<sup>a</sup>

Sample	Theoretical Composition (wt %)		$\bar{M}_n \times 10^{-3}$ PEO		Total Conversion (wt %)	tBMA Content in the Copolymer <sup>d</sup>	$\bar{M}_n \times 10^{-3}$ Block Copolymers	
	tBMA	EO	Theoretical <sup>b</sup>	Experimental (SEC)			Theoretical <sup>e</sup>	Experimental <sup>f</sup>
1	85.0	15.0	2.0	2.1	100	84.5	13.0	13.5
2	70.0	30.0	2.3	2.3	99.5	70.5	7.7	7.8
3	60.0	40.0	6.0	6.5	100	59.0	15.0	15.9
4	40.0	60.0	12.0	12.9	97	37.0	20.0	20.5
5	10.0	90.0	11.0	12.0	99	10.5	13.1	13.5

<sup>a</sup> Polymerization of EO: 24 h at +35°C; copolymerization of tBMA: 15 min at +20°C.

<sup>b</sup>  $\bar{M}_n$ , cal. =  $\frac{\text{weight of reacted monomer (g)}}{\text{mole of initiator}}$ .

<sup>c</sup> SEC value.

<sup>d</sup> By <sup>1</sup>H-NMR analysis.

<sup>e</sup>  $\bar{M}_n$ , copolymers =  $\frac{\text{weight of comonomers (g)}}{\text{mole of initiator}} \times \text{wt \% conversion}$ .

<sup>f</sup>  $\bar{M}_n$ , copolymers =  $\frac{\bar{M}_n, \text{ first block (SEC value)}}{\text{wt \% first block (}^1\text{H-NMR value)}}$ .

**Table IV.** Characterization of PtBMA-b-PEO-b-PtBMA Triblock Copolymers Synthesized in THF Using K-Naphthalene as Initiator<sup>a</sup>

Sample	Theoretical Composition (wt %)		$\bar{M}_n \times 10^{-3}$ PEO		Total Conversion (wt %)	tBMA Content in the Copolymer <sup>d</sup>	$\bar{M}_n \times 10^{-3}$ Block Copolymers	
	tBMA	EO	Theoretical <sup>b</sup>	Experimental (SEC)			Theoretical <sup>e</sup>	Experimental <sup>f</sup>
1	70.0	30.0	2.2	2.4	97.0	69.0	7.0	7.7
2	40.0	60.0	10.0	11.2	95.0	38.0	17.1	18.1
3	35.5	65.5	6.7	6.9	93.0	33.0	10.3	10.3
4	20.0	80.0	10.0	11.1	96.0	19.0	12.5	13.7

<sup>a</sup> Polymerization of EO: 24 h at +35°C; copolymerization of tBMA: < 5 min at +20°C.

<sup>b</sup>  $\bar{M}_n$ , cal. =  $2 \times \frac{\text{weight of reacted monomer (g)}}{\text{mole of initiator}}$ .

<sup>c</sup> SEC value.

<sup>d</sup> By <sup>1</sup>H-NMR analysis.

<sup>e</sup>  $\bar{M}_n$ , copolymers =  $\frac{\text{weight of comonomers (g)}}{\text{mole of initiator}} \times \text{wt \% conversion}$ .

<sup>f</sup>  $\bar{M}_n$ , copolymers =  $\frac{\bar{M}_n, \text{ first block (SEC value)}}{\text{wt \% first block (}^1\text{H-NMR value)}}$ .

trolled way whatever the sequence of the comonomers addition and the functionality of the organo-K initiator. These data provide a clear indication that PtBMA-K<sup>+</sup> can efficiently initiate the copolymerization of EO monomer and vice-versa. It is quite easy to understand the former situation since PtBMA anions possess a higher reactivity than those conjugated to PEO. According to the classical scale of reactivity, the PEO anions should not be reactive enough to initiate the block copolymerization of alkyl methacrylates. However, as it was pointed out by Suzuki et al.,<sup>4</sup> complexation of the counterion by the polyether chain should be responsible for that unexpected phenomenon. That hypothesis has in fact been confirmed by UV spectroscopy since upon the addition of PEO to a THF solution of fluorenyl potassium, the band characteristic of contact ion pairs (362 μm) completely disappears in favor of a new band at 373 μm, which is characteristic of ion pairs separated by a solvating agent, i.e., ethylene oxide subunits.<sup>8a</sup> That important shift is exactly the same as that one promoted by the addition of dimethyl dibenzo-18-crown-6 to fluorenyl sodium in THF.<sup>8b</sup> It has also been reported that a metal alkoxide which is unable to polymerize MMA becomes an effective initiator when the metal cation is complexed with cryptand [222].<sup>8c</sup> Similarly the anionic polymerization is endowed with a living character when the tBuOK initiator is used in the presence of PEO oligomers.<sup>8d</sup> All these experimental observations give credit to an enhancement in the nucleophilicity of the alkoxide anions by intra- and intercomplexation of K<sup>+</sup> by PEO chain segments.<sup>4</sup>

Finally, the effect of the PEO subunits on the propagating ion pairs might also be supported by a significant modification in the microstructure of the PtBMA blocks of PEO-PtBMA diblock copolymers. Usually a decrease in temperature is in favor of the syndiotacticity of PtBMA. Table V shows a completely different behavior, since the PtBMA blocks which have been initiated by PEO<sup>-</sup>K<sup>+</sup> at +20°C

(nos. 2 and 3) are more syndiotactic than PtBMA chains initiated by Φ<sub>2</sub>CHK at -78°C (no. 1). This effect might be accounted for by the inter- or intramolecular solvation of the counterion by PEO units. Interactions between the growing chain ends and the potassium counterions are thus expected to be weakened and to favor the formation of syndiotactic-rich PtBMA chains.<sup>4c</sup>

#### Hydrolysis of the PtBMA Block

<sup>1</sup>H-NMR and IR analysis have shown that the acidic hydrolysis (*p*-toluene sulfonic acid/THF or 1,4-dioxane) of a block copolymer comprising PtBMA and PEO blocks is incomplete even at high temperatures. This might be due to the insolubility of the partially hydrolyzed copolymer in an acidic medium, i.e., complexation of PEO segments with carboxylic acid groups.

Recently, trimethylsilyl iodide (TMSI) has been proposed as an effective reagent for the dealkylation of ester under mild neutral conditions.<sup>9</sup> Bugner has shown that when the hydrolysis of PMMA-*b*-PtBMA is promoted by TMSI, the *tert*-butyl ester is completely cleaved at room temperature, whereas the methyl ester remains unchanged.<sup>10</sup> Instead of using preformed TMSI, Nakahama et al.<sup>11</sup> have used trimethylsilyl chloride (TMSCl) in conjunction with NaI. The *in situ* formed TMSI has proved to promote the complete hydrolysis of poly(*tert*-butyl 4-vinylbenzoate) with formation of poly(4-vinylbenzoic acid).

According to the method reported by Nakahama et al.,<sup>11</sup> block copolymers of PtBMA and PEO have been treated with TMSCl, and NaI at 50°C for a few hours in acetonitrile. Conversion of the *tert*-butyl ester groups into carboxylic acids was ascertained by <sup>1</sup>H-NMR. Figure 5 shows the complete disappearance of the resonance of the *tert*-butyl protons at 1.33 ppm. Similarly, it could be seen from Fig. 6 that the IR absorption of the ester carbonyl (1722

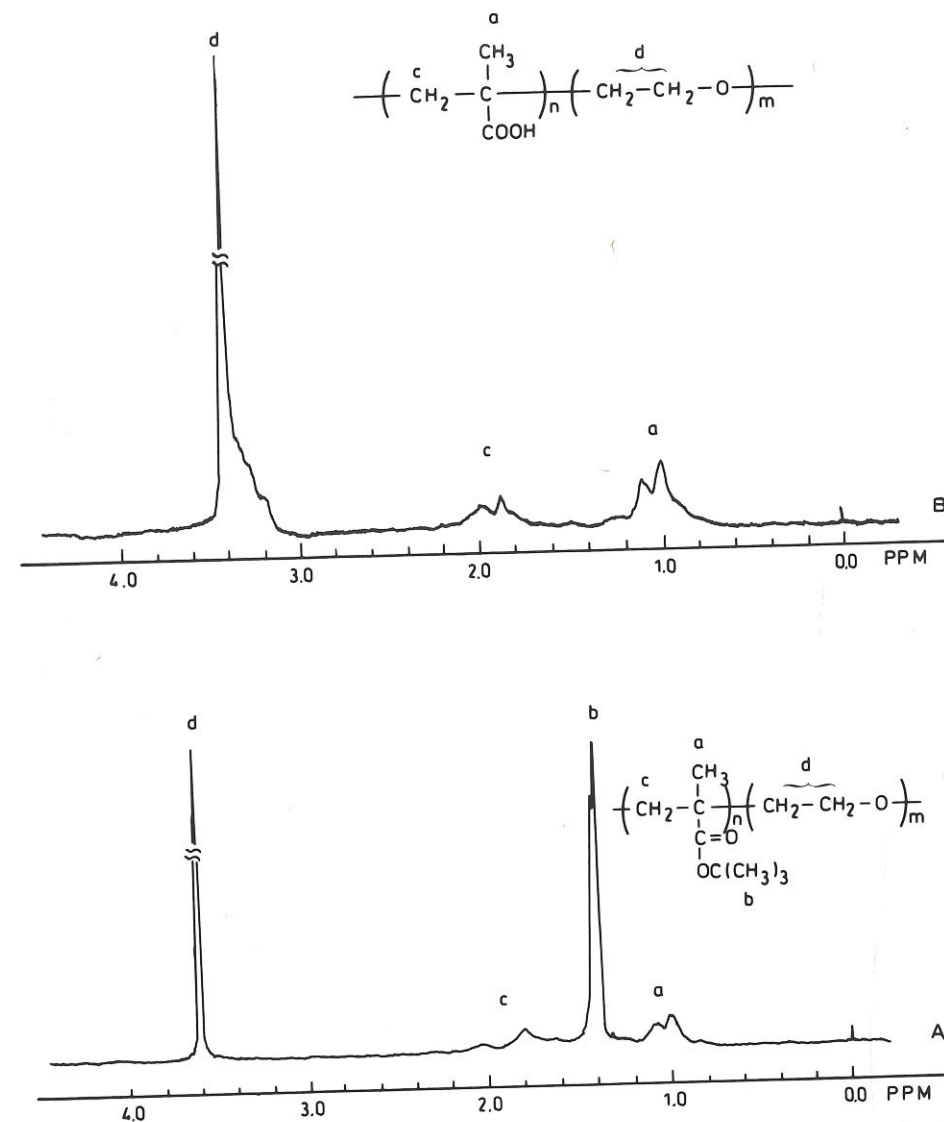


Figure 5. <sup>1</sup>H-NMR of PtBMA-*b*-PEO block copolymer (A) before and (B) after hydrolysis by a TMSCl/NaI mixture in acetonitrile.

cm<sup>-1</sup>) has disappeared in favor of two carbonyl bands associated with the carboxylic acid dimer (1701 cm<sup>-1</sup>)<sup>1</sup> and with the carboxylic acid-ether oxygen interaction (1727 cm<sup>-1</sup>),<sup>1</sup> respectively, at the

expense of that of the ester group (1722 cm<sup>-1</sup>). Furthermore a broad band, characteristic of OH groups is observed from 3730 to 3100 cm<sup>-1</sup>. The quantitative conversion of the polymethacrylate block into a

Table V. Triad Tacticity of the PtBMA Block in the Copolymers<sup>a</sup>

No.	Monomer Sequence in the Copolymer	Temperature (for Synthesis of PtBMA) (°C)	I (%)	H (%)	S (%)
1	PtBMA- <i>b</i> -PEO (sample 3, Table I)	-78	14	56	30
2	PEO- <i>b</i> -PtBMA (sample 1, Table III)	+20	5	47	48
3	PtBMA- <i>b</i> -PEO- <i>b</i> -PtBMA (sample 2, Table IV)	+20	7	50	43

<sup>a</sup> <sup>13</sup>C-NMR.

Table VI. Acid-base Titration of PEO-*b*-PtBMA Hydrolyzed (sample 2, Table III) by TMAH in a 90/10 THF/MeOH Mixture

Experiment	Polymer Weight (mg)	COOH Titrated (mol)	COOH Theoretical (mol)	Yield of Hydrolysis (%)
1	30	1.41 × 10 <sup>-4</sup>	1.48 × 10 <sup>-4</sup>	95.5
2	40	1.87 × 10 <sup>-4</sup>	1.97 × 10 <sup>-4</sup>	94.5
3	50	2.46 × 10 <sup>-4</sup>	2.47 × 10 <sup>-4</sup>	99.5

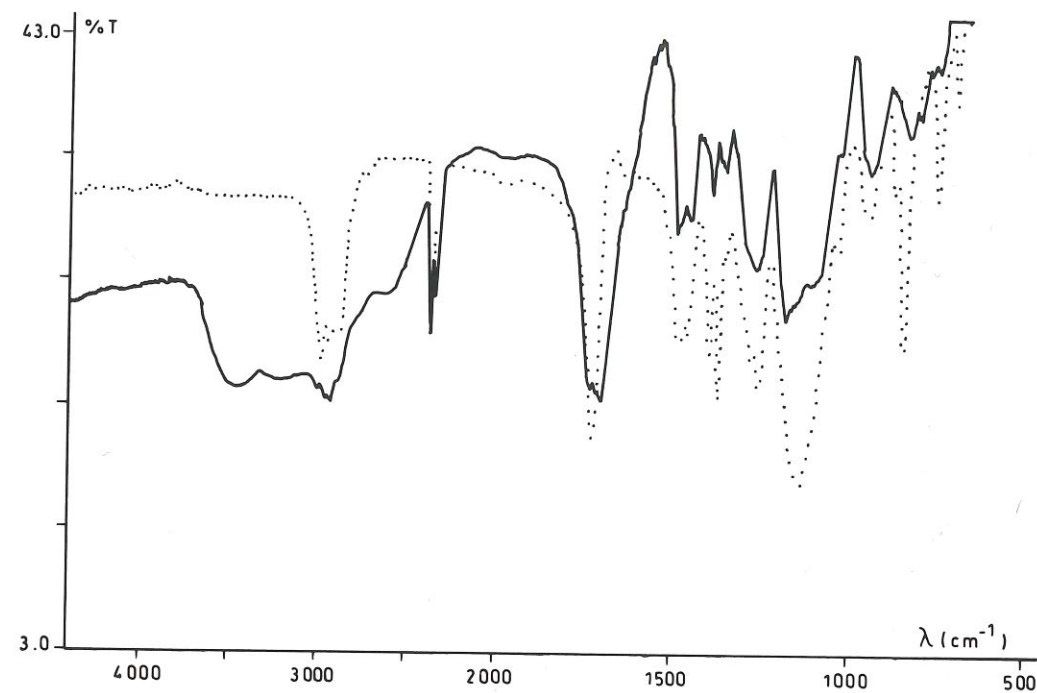


Figure 6. IR spectra of sample 2 (Table III): (----) PEO-b-PtBMA, (—) after hydrolysis.

poly(methacrylic acid) block is further confirmed by direct titration of the polyacid. As it is reported in Table VI, acid-base titrations indicate a practically complete hydrolysis.

#### Solubility of the PMAA-b-PEO

Table VII summarizes the solubility of a PtBMA-b-PEO copolymer and its hydrolyzed counterpart. The original copolymer is soluble in most solvents except for hexane and water. In contrast, the hy-

drolyzed material is soluble in methanol, THF, 1,4-dioxane, *N,N*-dimethylformamide, and insoluble in nonpolar solvents such as hexane, toluene, and chloroform. Very interestingly, the hydrolyzed block copolymer is soluble in water at higher pH, whereas it precipitates under acidic conditions. That behavior should arise from the intra- or intercomplexation of the polyacid and the polyether blocks as pH of the polymer solution is decreased.<sup>12</sup> It has been reported that bishydrophilic block copolymer are very

Table VII. Solubility of PtBMA-b-PEO and Resulting PMAA-b-PEO<sup>a</sup>

Solvent	PtBMA-b-PEO	PtBMA-b-PEO
Hexane	no	no
Toluene	yes	no
Chloroform	yes	no
1,4-Dioxane	yes	yes
Tetrahydrofuran	yes	yes
<i>N,N</i> -dimethylformamide	yes	yes
Methanol	yes	yes
Water <sup>b</sup> pH:		
> 9	no	solution
9 to 3	no	cloudy suspension
< 3	no	precipitate

<sup>a</sup> Block copolymer contains ca. 41 mol % PtBMA.

<sup>b</sup> As observed with naked eye.

instrumental in promoting water-in-water emulsions.<sup>13</sup> Diblock copolymers of PMAA and PEO are typical bishydrophilic copolymers, the solution behavior of which will be investigated in the near future.

Block copolymers of PtBMA and PEO can be synthesized in a well-controlled way by sequential anionic polymerization of the parent monomers, irrespective of the addition order. The block copolymers can be completely hydrolyzed under neutral conditions with formation of a hydrophilic poly(methacrylic acid-*b*-ethylene oxide) copolymer of well defined molecular weight and composition and of a narrow molecular weight distribution.

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