

Initiation of Anionic Polymerization of *tert*-Butyl 4-Vinylbenzoate by a Living Poly(*tert*-butyl methacrylate) Anion

Jinshan Wang, Philippe Bayard, Robert Jérôme, Philippe Teyssié,* and Sunil K. Varshney

Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6 4000 Liège, Belgium

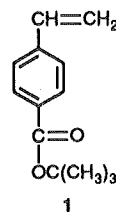
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Introduction. Although a series of monomers are reactive toward anionic species, very few comonomer pairs can be involved in sequential anionic polymerization with formation of well-defined block copolymers irrespective of the addition order of the comonomers. For living block copolymerization to be successful, it is indeed mandatory that the reactivity of the polyanion stemming from the first monomer be higher than that associated with the second one, on the one hand, and the related crossover reaction be very fast, on the other. In agreement with the scale of monomer reactivity,¹ poly(alkyl methacrylate) anions do not initiate polymerization of styrene due to the low relative reactivity of the initiating polyanion.

The purpose of this paper is to show that an appropriate chemical modification of styrene can deeply change the reactivity of the monomer and allows the block copolymerization with living poly(*tert*-butyl methacrylate) (PTBMA) anions in THF. This work actually focuses on the sequential polymerization of *tert*-butyl methacrylate and *tert*-butyl 4-vinylbenzoate (1), which is a purposely modified styrene comonomer.

Experimental Section. Material. *tert*-Butyl methacrylate (TBMA) from Norsolor (France) was first dried by refluxing over CaH₂, distilled under reduced pressure, and stored under inert atmosphere at -20 °C. Just before polymerization, TBMA was treated with a 10% AlEt₃ solution in toluene at 0 °C until a persistent yellow-green was obtained and then was distilled under reduced pressure. *tert*-Butyl 4-vinylbenzoate (1) was prepared as



1

detailed in the scientific literature² and was distilled from fluorenyllithium under vacuum just prior to use. THF was refluxed over a freshly prepared sodium benzophenone complex. The (diphenylmethyl)potassium (Ph₂CHK) initiator was prepared at room temperature by reacting diphenylmethane with potassium naphthalene in THF for 24 h.

Polymerization was carried out in a previously flamed glass reactor under a nitrogen atmosphere. Solvent and initiator were transferred into the reactor using rubber septums and stainless steel capillaries and/or syringes. After the addition of the desired amount of initiator into solvent, the solution was cooled down to -78 °C and reacted with the required amount of TBMA. TBMA polymerization lasted 2 h at -78 °C. Then, an aliquot of the reaction medium was withdrawn for analysis by size-exclusion

chromatography in order to determine the molecular weight of the first block, and *tert*-butyl 4-vinylbenzoate (1) was added into the glass reactor. Copolymerization was allowed to occur for another 40 min at the same temperature. The reaction was stopped by addition of acidified methanol. After solvent evaporation, copolymers were dissolved in benzene and freeze-dried.

Characterization. Size-exclusion chromatography (SEC) was carried out in THF, using a Hewlett-Packard 1037A apparatus equipped with a refractive index detector. Polystyrene standards were used for calibration. It must be mentioned here that the absolute molecular weight of PTBA has been observed to be in close agreement with the value determined by SEC on the basis of a polystyrene calibration.³ ¹H and ¹³C NMR spectra were recorded at 50 °C, at 400 and 100 MHz, respectively, in the FT mode with a Bruker AN 400 superconducting magnet system. Solutions of 20 wt % copolymer in CDCl₃ were prepared and analyzed by ¹³C NMR measurement. Inverse-gated proton decoupling was used in order to perform a quantitative analysis of the high-resolution ¹³C NMR spectra. IR spectra (KBr disk) were obtained on a Perkin-Elmer 197 infrared spectrophotometer. The glass transition temperature (*T*_g) of the polymers was determined by differential scanning calorimetry (DSC) on a Du Pont 9000 instrument.

Results and Discussion. Table I reports the characteristic molecular features of diblock copolymers prepared from macroanions of the TBMA type. When the PTBMA precursor is synthesized in THF at -78 °C by using Ph₂CHK as an initiator, the expected molecular weight is actually observed, as well as a very narrow molecular weight distribution. This is in agreement with a previously reported living mechanism.³

Polyanions of the TBMA type have been used as macroinitiators for the *tert*-butyl 4-vinylbenzoate (1) polymerization. Upon the addition of the monomer, the color suddenly changes from light yellow to dark red which is the typical color of living poly(1) associated with a potassium counterion.² To some extent, this suggests that the crossover reaction from PTBMA-K⁺ to 1 occurs. Table I also shows that the overall conversion of the comonomer is nearly quantitative (>96%).

A typical SEC chromatogram of the crude copolymerization product is shown in Figure 1 and compared to the elution curve of the first PTBMA block. No homo-(PTBMA) is observed to contaminate the block copolymer within the limits of the sensitivity of the method.

In order to confirm that preliminary observation, samples reported in Table I have been extracted with hexane, a selective solvent for PTBMA, and found to be free of homopolymer of that type. Moreover, sample 2 is soluble in methanol, a selective solvent of PTBMA, which gives credit to the absence of homopoly (1).

When 100-MHz ¹³C NMR spectra of block copolymers are recorded, furthermore, it is clear that two types of ¹³C resonances at *tert*-butyl ester groups characteristic of the poly(1) and PTBMA^{2,3} [i.e., poly(1)/PTBMA: 28.2/27.7 ppm (-C(CH₃)₃), 80.7/80.5 ppm (-C(CH₃)₃), and 165.5/176.0-177.0 ppm (C=O)] are observed (Figure 2). Similarly, two types of ¹H signals at the *tert*-butyl group (1.57/1.45 ppm for the poly(1)/PTBMA) are also noted. As far as IR spectroscopy is concerned, the C=O stretching vibration is known to be observed at 1710 cm⁻¹ for poly(1)² and at 1722 cm⁻¹ for PTBMA.³ The IR spectrum of diblock copolymers shows an absorption at an intermediate position of 1715 cm⁻¹ (Figure 3), which most probably results from a miscibility of poly(1) and PTBMA segments

Table I
Anionic Polymerization of *tert*-Butyl 4-Vinylbenzoate (1) with Living PTBMA-K⁺ as an Initiator in THF at -78 °C^a

sample	PTBMA			yield ^d	PTBMA- <i>b</i> -poly(1)		
	$\bar{M}_{n,th}^b$	$\bar{M}_{n,SEC}$	\bar{M}_w/\bar{M}_n^c		$\bar{M}_{n,th}^b$	$\bar{M}_{n,NMR}^e$	\bar{M}_w/\bar{M}_n^c
1	8400	9000	1.10	98	16 000	17 000	1.30
2	6100	6700	1.05	100	8 200	8 500	1.10
3	8500	9300	1.05	96	11 000	11 600	1.20

^a Polymerization of TBMA: 2 h. Copolymerization of 1: 40 min. ^b $\bar{M}_{n,th}$ = weight of reacted monomer (g) per mole of initiator. ^c SEC value. ^d In wt %. ^e ¹³C NMR analysis. Calculation based on the relative intensity of the types of *tert*-butyl resonance peaks at 28.2 ppm (poly(1) block) and at 27.7 ppm (PTBMA block).

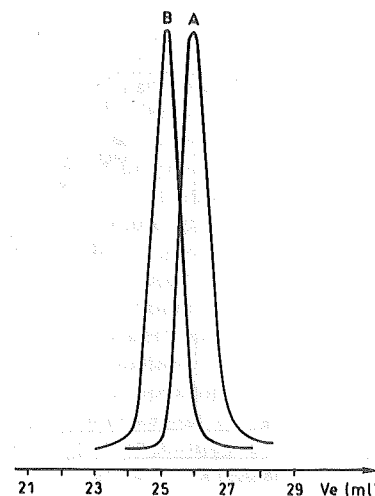


Figure 1. SEC chromatograms of sample 2 (Table I). (A) First PTBMA block: \bar{M}_n , 6700; \bar{M}_w/\bar{M}_n , 1.05. (B) PTBMA-*b*-poly(1) diblock copolymer: \bar{M}_n , 8500; \bar{M}_w/\bar{M}_n , 1.10.

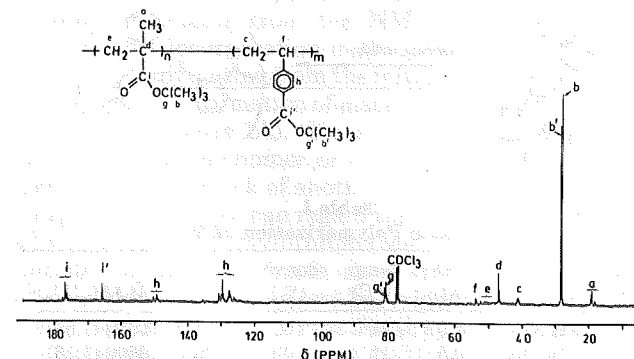


Figure 2. 100-MHz ¹³C NMR spectrum of a PTBMA-*b*-poly(1) diblock copolymer (sample 1, Table I).

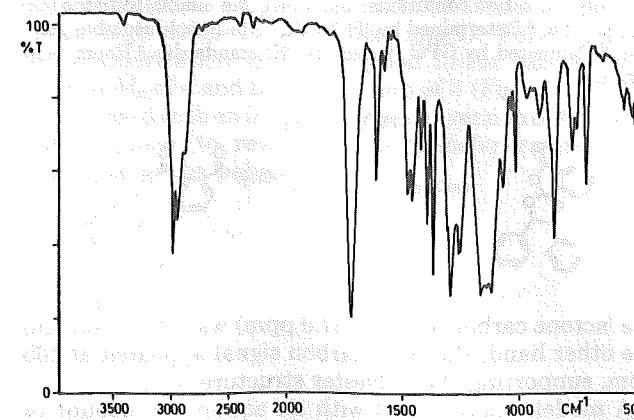


Figure 3. IR spectrum of sample 1 (Table I).

in related block copolymers since only a single *T*_g was detected for such a type of block copolymer by means of DSC. Moreover, the absorption at 1608 cm⁻¹ is characteristic of the aromatic ring of poly(1). Thus, ¹H NMR, ¹³C NMR, and IR spectroscopies all confirm that poly(1)

and TBMA are associated as a result of the sequential polymerization of TBMA and 1.

Finally, the molecular weight of block copolymers has been calculated from the molecular weight of PTBMA and the relative intensities of two types of ¹³C resonances at the *tert*-butyl group associated with the methacrylate (27.7 ppm) and styrene (28.2 ppm) subunits, respectively. Experimental \bar{M}_n is found to be close to theoretical values (Table I).

In conclusion, all together solubility in selective solvents, SEC, and ¹H and ¹³C NMR prove the formation of copolymer when the anionic polymerization of *tert*-butyl 4-vinylbenzoate is initiated with living TBMA macroanions in THF and in the presence of a potassium counterion.

However, we still note that in each case the \bar{M}_w/\bar{M}_n of the resulting block copolymer is higher than one of the PTBMA precursors. This we believe might result from a sluggish crossover reaction from the PTBMA macroanion to 1.

Although the anionic polymerization of styrene cannot be initiated by living PTBMA-K⁺, the para substitution of the aromatic ring by an electron-withdrawing ester group is very effective in increasing the styrene reactivity to the point where it is polymerized in a living manner by PTBMA-K⁺ in THF at -78 °C. It is worth recalling that Nakahama et al. have previously reported that living poly(1) actually initiates the anionic polymerization of methyl methacrylate (MMA) but not styrene, in THF with a K counterion.² Since the reactivity of TBMA toward anions is very similar to that of MMA,¹ living poly(1) should be able to initiate the block copolymerization of TBMA in THF as well. Accordingly, a para-ester-substituted styrene, e.g., *tert*-butyl 4-vinylbenzoate, is expected to display a reactivity very similar to that of alkyl methacrylates, thus definitely higher than that of styrene.

Since the cross propagation of living anionic polymerization of alkyl methacrylate (A) and *tert*-butyl 4-vinylbenzoate (B) has proved to be feasible, synthesis of well-defined AB (BA), ABA, and BAB di- and triblock copolymers could be performed whatever the addition order of the comonomers: that situation opens the way to produce interesting new materials including polyelectrolytes obtained by easy hydrolysis of the *tert*-butyl esters. This will be the subject of a forthcoming paper.

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* To whom all correspondence should be addressed.