Synthesis of ABA Type Thermoplastic Elastomers Based on Polyacrylates

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*Received September 29, 1997
Revised Manuscript Received November 19, 1998*

Triblock copolymers of ABA type with an elastomeric central B block and rigid end A blocks or starlike copolymers of $(AB)_n$ type with rigid end blocks based on styrene and dienes are well-known commercially available polymers.[1,2] Synthesis of ABA type triblock copolymer can be achieved by three routes: (1) sequential monomer addition, (2) synthesis of AB diblock followed by linking reaction, and (3) successive polymerization of monomers starting from a difunctional initiator. Block copolymerization of dienes and styrene can be initiated from either dienyl or styrenyl anionic species. ABA type thermoplastic elastomers based on dienes and styrene can be synthesized in a controlled manner following the above three routes. In recent years, special attention has been focused on the synthesis of poly(methacrylate-*b*-dienes-*b*-methacrylate) triblock copolymers, since poly(methyl methacrylate) rich in syndiotactic content has a higher glass transition temperature than atactic polystyrene,[3−5] which allows the increase in upper service temperature of the resulting thermoplastic elastomers. Poly(methacrylate-*b*-dienes-*b*-methacrylate) triblock copolymers of high purity with over 50% trans 1,4 microstructure of the dienes block have been synthesized successfully using 1,3-diisopropenylbenzene-based bifunctional initiator.[6]

Synthesis of ABA triblock copolymer with B block of low glass transition temperature polyacrylate and end block of polystyrene is not possible under anionic polymerization utilizing sequential addition of monomers, since the alkyl acrylate enolate lithium anions are not sufficiently basic to reinitiate a second addition of styrene monomer to obtain linear ABA triblock copolymer. Therefore, such types of triblock copolymers architecture can be synthesized by employing a linking reaction with the macroanions of AB diblock chains. Nearly a decade ago Teyssie et al. demonstrated for the first time a "living" and controlled polymerization of (meth)acrylate with styrene and dienes to develop AB diblock copolymer,[7,8] $(AB)_n$ starlike polymer.[9,10] This was achieved using conventional anionic initiator modified with different ligands able to control the electronic and (mainly) steric environment of the growing ion pair. The possibility of closely controlling the molecular architecture (i.e., number mean molecular weight with low molecular dispersity) and obtaining high-purity diblock copolymers of *tert*-butyl acrylate with styrene, dienes, 2- and 4-vinylpyridines by using a molar excess of LiCl versus the initiator has already been demonstrated.[11,12]

In this preliminary communication, we wish to demonstrate the synthesis of an ABA type triblock copolymer by a linking reaction of the AB type diblock copolymer. Our goal was to synthesize kilogram quantities of such a product on a routine basis. We have designed industrially acceptable methods that utilize a readily available cost-effective linking reagent for the living polymer macroanions. To demonstrate this approach, we have selected A block as either polystyrene or poly(2-vinylpyridine) (2VP) or polydienes rich in 1,4 microstructure (subsequently converted to polyethylene by hydrogenation) and B block as poly(*tert*-butyl acrylate) (tBuA). The central B block of poly(*tert*-butyl acrylate) can easily be converted quantitatively to any poly(alkyl acrylate) by transesterification. Block copolymerization of tBuA with styrene or 2VP was carried out in THF at −78 °C using an initiator system (RLi) as schematically represented in Scheme 1. The living macroanions of P(St-*b*-tBuA) were linked with a stoichiometric amount of high-purity terephthaloyl chloride. After the addition of terephthaloyl chloride the colorless solution of macroanions of P(St-*b*-tBuA) turns to light yellow in 5−6 min. The color darkened as the reaction progressed. The linking reaction was carried out at −35 °C for 2 h to achieve over 90% linking reaction. Size exclusion chromatography (SEC) analysis of the polymer obtained at each monomer dose was carried out with a Varian SEC apparatus (Varian 9050 UV and Varian RI-4 detectors) equipped with three TSK gel columns G6000HXL, G4000 HXL, and G2000 HXL with THF as the eluent at a flow rate of 1 mL/min at 30 °C. Standard polystyrenes were used for the calibration, and the number- and weight-average molecular weights of the polystyrene block and final triblock copolymers were accordingly calculated. Figure 1 illustrates size exclusion chromatography profiles of the product at each step, clearly demonstrating the effectiveness of this approach to synthesize linear triblock copolymers of P(St-*b*-tBuA-*b*-St). Block copolymerization initiated by *tert*-butyl dimethylsiloxy propyllithium[14,15]

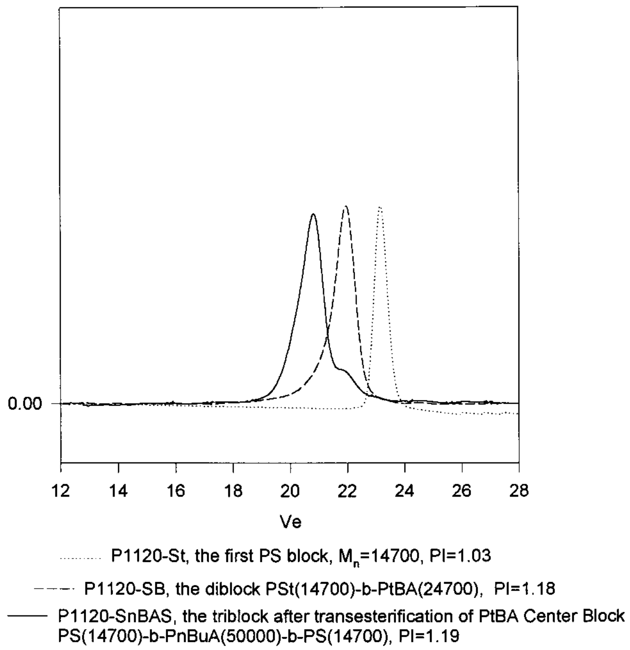

Figure 1. Sequential SEC chromatograms in the synthesis of the triblock copolymer poly(styrene-*b*-*n*-butyl acrylate-*b*-styrene).

10.1021/ma971428u CCC: $18.00

Scheme 1

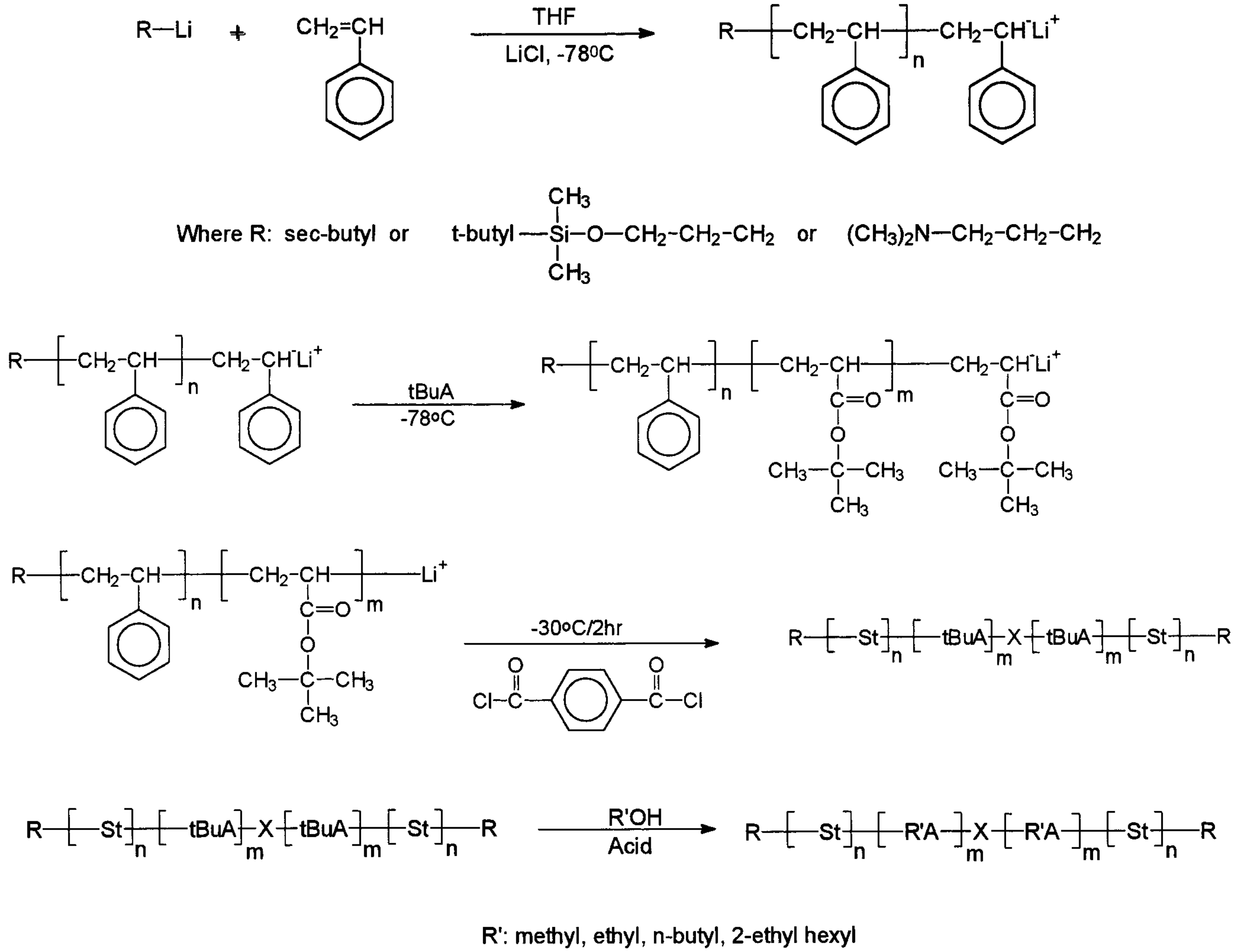

Table 1[a]

sample no.	type of central block-R′	M_n of PSt	M_n of central block	M_w/M_n (final)
P1118-StMeASt	methyl acrylate	13 000/13 000	32 000	1.09
P1120-StMeASt	methyl acrylate	15 000/15 000	33 600	1.18
P1118-StEtASt	ethyl acrylate	13 000/13 000	37 500	1.09
P1120-StEtASt	ethyl acrylate	15 000/15 000	39 000	1.18
P1118-StnBASt	*n*-butyl acrylate	13 000/13 000	48 000	1.09
P1120-StnBASt	*n*-butyl acrylate	15 000/15 000	50 000	1.18
P1118-StEHASt	2-ethyl hexyl acrylate	13 000/13 000	69 000	1.09
P1120-StEHASt	2-ethyl hexyl acrylate	15 000/15 000	72 000	1.18

[a] All triblock copolymers contain less than 5–8% of uncoupled diblock copolymer as determined from SEC profile.

or (dimethylamino)propyllithium initiator[16] produced the α,ω-dihydroxy ABA triblock copolymer (after hydrolysis of *tert*-butyl dimethylsiloxy moiety) or α,ω-dimethylamino ABA triblock copolymer, respectively.

The obtained linear ABA type triblock copoloymers with B block of tBuA could easily be converted into other acrylates such as poly(ethyl acrylate) (T_g −27 °C) and poly(*n*-butyl acrylate) (T_g −45 °C) or into 2-ethylhexyl acrylate (T_g −58 °C) by refluxing the product in the corresponding alcohol catalyzed by *p*-toluenesulfonic acid or HCl. The tranesterification reaction was quantitative without chain degradation or broadening of molecular weight distribution as evidenced by their SEC profile before and after the tranesterification reaction. Still more interestingly, the center poly-tBuA block of these triblock copolymers can also be converted into poly(acrylic acid) developing the hydrogel. These results illustrate a new route for the development of different thermoplastic elastomers based on polyacrylates. Table 1 reports the characterization data for some of the products obtained by this method. The molecular weights of the diblock copolymer before and after the linking reaction with terephthaloyl chloride were calculated by their SEC profile with respect to polystyrene standards.[13]

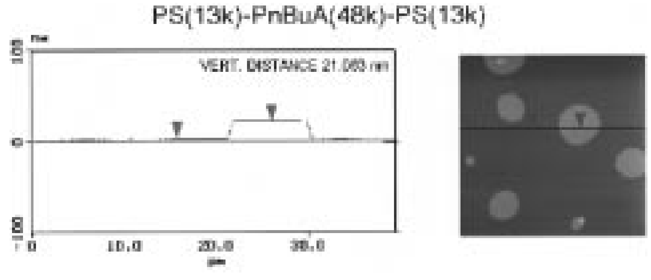

Figure 2. Atomic force topograph (nanoscope dual image screen dump) of poly[styrene(13K)-*b*-*n*-butyl acrylate(48K)-*b*-styrene(13K)] triblock copolymer.

To determine the morphology of the polymers, 400 Å thick films were spun cast from chlorobenzene onto Formvar-covered 400 mesh Cu grids and HF stripped silicon wafers. The wafers and the grids were annealed together in a vacuum of 10^{-3} Torr for 24 h at 150 °C. Figure 2 shows the surface topography of the poly(styrene$_{13000}$-*b*-*n*-butyl acrylate$_{48000}$-*b*-styrene$_{13000}$) triblock copolymer. The triblock copolymer film shows the "island" structures which are known to appear when the surface-induced ordering of the polymer layer occurs, and the total film thickness is not an integral of the natural layer spacing.[17,18] The height of the islands, 172 Å, corresponds to the height of the ordered layers within the film. The surface morphology of the diblock copolymer is far from unusual. No contrast appears in friction scans of the surface, indicating that only one of the blocks segregates to the surface.

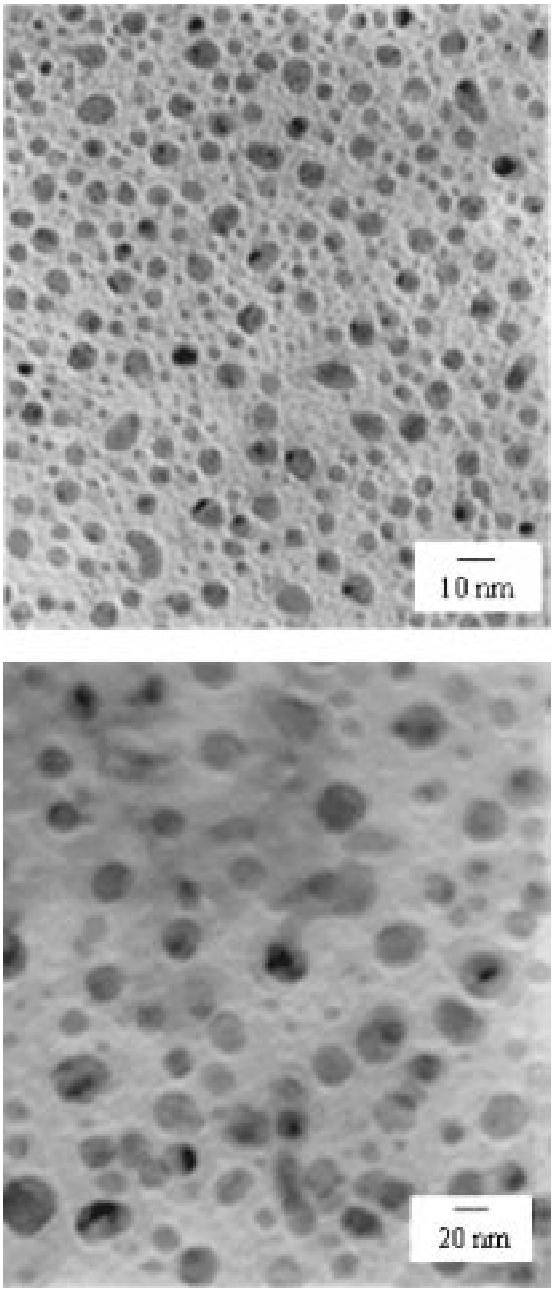

Figure 3. (a, top) Transmission electron micrograph (TEM) of poly[styrene(13K)-*b*-*n*-butyl acrylate(48K)-*b*-styrene(13K)] triblock copolymer. (b, bottom) Transmission electron micrograph (TEM) of poly[styrene(16.4K)-*b*-*n*-butyl acrylate(7.7K)] diblock copolymer.

The microphase structure of the polymers was also studied by TEM (Phillips model operating at 120 kV). The films on Formvar were exposed to gaseous ruthenium tetraoxide vapors which are known to stain preferentially with the polystyrene phase.[19] Figure 3a shows the microphase sepration for the poly(styrene$_{16400}$-*b*-*n*-butyl acrylate$_{7700}$) diblock copolymer and Figure 3b for the poly(styrene$_{13000}$-b-*n*-butyl acrylate$_{48000}$-*b*-styrene$_{13000}$) triblock copolymer. In both cases the polystyrene phase forms spherical inclusions in the poly(*n*-butyl acrylate) matrix with the triblock inclusions being significantly smaller. A more detailed description of these reactions using various initiator systems as well as characterization of different new thermoplastic elastomeric products accessible through this methodology will be the subject of forthcoming articles.

Acknowledgment. We are indebted to Federal Office Regional Development-Quebec (BFDRQ) and Innovatech Grand Montreal-Quebec for their financial support.

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MA971428U