

# Synthesis of Diblock and Triblock Copolymers from Butyl Acrylate and Styrene by Reverse Iodine Transfer Polymerization

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Received 14 February 2010; accepted 9 May 2010

DOI 10.1002/app.32759

Published online 7 September 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Well-defined **AB** and **BA** diblock copolymers were obtained by a one-pot two-step sequential block copolymerization by reverse iodine transfer polymerization (RITP), **A** being a poly(styrene) block and **B** a poly(butyl acrylate) block. High monomer conversions during the formation of the first block avoided the purification steps before growing the second block. In a third sequential step, the diblock copolymers were further extended to synthesize **ABA** and **BAB** triblock copolymers. Furthermore, the synthesis of **ABA** and **BAB** copolymers in only two steps by RITP was investigated starting with the for-

mation of the central block using 2,5-di(2-ethylhexanoylperoxy)-2,5-dimethylhexane as a difunctional initiator and then resuming the polymerization to grow the external blocks in a second step. The obtained copolymers were analyzed by size exclusion chromatography, transmission electron microscopy, and differential scanning calorimetry. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2476–2484, 2011

**Key words:** reverse iodine transfer polymerization (RITP); radical polymerization; block copolymers; polystyrene; poly(butyl acrylate)

## INTRODUCTION

In recent years, controlled radical polymerizations (CRPs) have provided novel routes to synthesize well-defined low-polydispersity polymers with diverse architectures such as block,<sup>1</sup> graft,<sup>1,2</sup> or gradient<sup>1,3</sup> copolymers. The most well-known CRP techniques are nitroxide-mediated polymerization (NMP),<sup>4</sup> atom transfer radical polymerization (ATRP),<sup>5</sup> reversible addition-fragmentation chain transfer polymerization (RAFT),<sup>6</sup> and iodine transfer polymerization (ITP).<sup>7</sup> A new CRP technique, called reverse iodine transfer polymerization (RITP), that relies on the use of molecular iodine (I<sub>2</sub>) was recently developed,<sup>8,9</sup> and patented<sup>10</sup> by Lacroix-Desmazes et al. (Scheme 1).

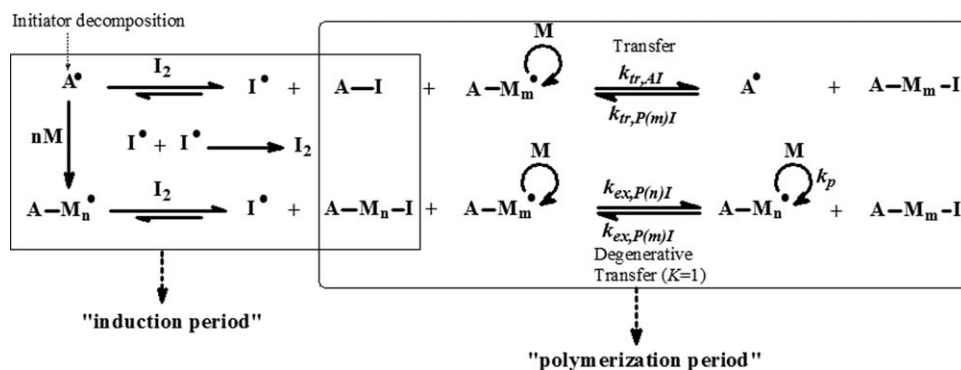
The simplicity of the technique comes from the fact that the chain transfer agents (CTAs) are synthe-

sized *in situ* at the beginning of the polymerization, which is an enormous advantage of RITP over other techniques. Equally important, the I<sub>2</sub> (or a precursor such as NaI<sup>11,12</sup>) is low cost when compared with thiocarbonyl derivatives, organometallic complexes, or nitroxide derivatives. Moreover, controlled polymerization of styrene and (meth)acrylic monomers has been carried out successfully by RITP in homogeneous<sup>8,9,13</sup> and heterogeneous<sup>14,15</sup> systems demonstrating the versatility of the process. The growing interest to synthesize poly(styrene)-poly(acrylate) block copolymers is due to their potential use as impact modifiers and/or as thermoplastic elastomers. The immiscibility of blocks allows phase separation of domains at the nanometric scale. Thus, because of the significant difference of their glass transition temperatures ( $T_{g, PBuA} = -54^{\circ}\text{C}$ ,  $T_{g, PS} = 100^{\circ}\text{C}$ )<sup>16</sup> and depending on the appropriate structure arrangement of the blocks (e.g., ABA vs. BAB) and the overall composition of the copolymer, they could offer interesting mechanical properties.

The successful synthesis of such block copolymers by a degenerative transfer process (RAFT, ITP, or RITP) depends strongly on the order in which the monomers are polymerized to form the blocks. Factors like stability of macroradicals formed (i.e.,

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Contract grant sponsor: French-Mexican PCP program 2007–2010.



**Scheme 1** Simplified mechanism of Reverse Iodine Transfer Polymerization (RITP) ( $A^\bullet$ : radical from the initiator;  $I_2$ : molecular iodine;  $M$ : monomer unit;  $n$ : mean number degree of polymerization;  $k_p$  = propagation rate constant;  $k_{tr}$  = transfer rate constant;  $k_{ex}$  = degenerative chain transfer rate constant).

ability as leaving group), relative reactivity of the monomers (i.e., reactivity ratio), and the stability of the corresponding dormant chain-ends (i.e., degradation issues) represent the most important issues. We report herein the appropriate conditions to efficiently synthesize AB and BA copolymers by RITP in homogeneous systems (bulk or solution) (A: poly(styrene), B: poly(butyl acrylate)). The diblock copolymers are further extended to synthesize ABA and BAB triblock copolymers, the former being especially attractive due to potential applications as thermoplastic elastomers. The same ABA copolymer has been successfully synthesized in a two steps polymerization by other CRP techniques: it was prepared by RAFT using a trithiocarbonate as CTA,<sup>17</sup> it was synthesized by NMP with a difunctional alkoxyamine as initiator,<sup>18</sup> and it was also obtained by ATRP using a difunctional alkyl halide initiator.<sup>19</sup> RITP is a competitive alternative to prepare the same copolymers as it provides a good control over the macromolecular parameters and molecular iodine is a cheap compound readily available from many commercial sources. In this article, we introduce the use of a difunctional initiator to simplify the synthesis of triblock copolymers by RITP in only two steps: a novel process based on the use of 2,5-di(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox 141) as the initiator is proposed to produce an ABA copolymer with promising results. To our knowledge, this is the first report on the synthesis of triblock copolymers, in either three or two steps, by the RITP process.

## EXPERIMENTAL

### Materials

*n*-Butyl acrylate (99%), styrene (99%), and butyl acetate (99%) from Aldrich were purified by vacuum distillation before use. 2,2'-Azobis(isobutyronitrile) (AIBN, Fluka, 98%) was recrystallized from ethanol. 2,5-Di(2-ethylhexanoylperoxy)-2,5-dimethylhexane

(Trigonox 141, Akzo, 90%) and iodine ( $I_2$ , Aldrich, 99.8%) were used as received.

### Synthesis

#### Synthesis of homopolymers

In a typical RITP procedure (Run 5a in Table I), 2.0864 g (20.0336 mmol) of styrene, 0.0358 g (0.2182 mmol) of AIBN, and 0.0286 g (0.1126 mmol) of  $I_2$  ( $[AIBN]/[I_2] = 1.93$ ) were introduced in a Schlenk flask. Three freeze-thaw-pump cycles were completed and the flask was placed in an oil bath at 70°C. The polymerization was conducted in the dark, with magnetic stirring and under argon atmosphere, for 15 h.  $^1H$  NMR analysis on a crude sample was used to determine monomer conversion, whereas molecular weight was determined by size exclusion chromatography (SEC). Conversion = 94%,  $M_{n,Theo} = 8900 \text{ g mol}^{-1}$ ,  $M_{n,SEC} = 9200 \text{ g mol}^{-1}$ , and  $M_w/M_n = 1.3$ .

#### Synthesis of block copolymers

In a typical procedure for block copolymerization (Run 5b in Table I), in the Schlenk flask containing the crude sample of run 5a were added 1.9956 g (15.5699 mmol) of butyl acrylate and 0.0114 g (0.0695 mmol) of AIBN ( $[AIBN]/[macro-CTA] = 0.3$ ). Three freeze-thaw-pump cycles were carried out, and then the flask was placed in an oil bath at 70°C. The polymerization was conducted in the dark, with magnetic stirring and under argon atmosphere for 15 h to prepare a poly(styrene)-*b*-poly(butyl acrylate-*co*-styrene) copolymer: styrene conversion = 99%, butyl acrylate conversion = 76%,  $M_{n,Theo} = 16200 \text{ g mol}^{-1}$ ,  $M_{n,SEC} = 16050 \text{ g mol}^{-1}$ , and  $M_w/M_n = 1.4$ .

### Analysis

#### Size exclusion chromatography

SEC was used to characterize the crude samples dissolved in THF with a Spectra Physics Instruments SP8810 pump having two 300 mm columns mixed-C

**TABLE I**  
**Homopolymerizations and Block Copolymerizations of Butyl Acrylate and Styrene by RITP Using AIBN as Initiator**

Run <sup>a</sup>	Control agent	Monomer	Polymer obtained	Mass ratio (Monomer/ macro-CTA)	T (°C)	Time (h)	Conversion <sup>d</sup> (%)	$M_{n,Theo}$ (g mol <sup>-1</sup> )	$M_{n,SEC}$ <sup>g</sup> (g mol <sup>-1</sup> )	$M_w/M_n$
1a	I <sub>2</sub>	BuA	PBuA	–	70	15	98	8000 <sup>e</sup>	13200	1.7
1b <sup>b</sup>	1a	S	PBuA- <i>b</i> -P(S- <i>co</i> -BuA)	1	70	15	42	18850 <sup>f</sup>	11450	1.9
2b	2a <sup>h</sup>	S	PBuA- <i>b</i> -P(S- <i>co</i> -BuA)	3	70	15	69	33250 <sup>f</sup>	28400	1.4
2c	2b	BuA	PBuA- <i>b</i> -P(S- <i>co</i> -BuA)- <i>b</i> -P(BuA- <i>co</i> -S)	1	70	15	78	50200 <sup>f</sup>	44800	1.6
3a	I <sub>2</sub>	S	PS	–	70	15	97	9250 <sup>e</sup>	11400	1.4
3b	3a	BuA	PS- <i>b</i> -P(BuA- <i>co</i> -S)	6	85	3	75	62450 <sup>f</sup>	19850	2.5
4b	4a <sup>h</sup>	BuA	PS- <i>b</i> -P(BuA- <i>co</i> -S)	3	85	2	87	32300 <sup>f</sup>	25300	1.7
5b <sup>b</sup>	5a <sup>h</sup>	BuA	PS- <i>b</i> -P(BuA- <i>co</i> -S)	1	85	2	76	16200 <sup>f</sup>	16050	1.4
6b <sup>b,c</sup>	6a <sup>h</sup>	BuA	PS- <i>b</i> -P(BuA- <i>co</i> -S)	6 = (2 × 3)	85	(2 × 3)	97	42300 <sup>f</sup>	31100	2.6
6c	6b	S	PS- <i>b</i> -P(BuA- <i>co</i> -S)- <i>b</i> -P(S- <i>co</i> -BuA)	<1	70	15	69	38700 <sup>f</sup>	34200	2.6

<sup>a</sup> Styrene = S; poly(styrene) = PS; butyl acrylate = BuA; poly(butyl acrylate) = PBuA. Homopolymerizations: molar ratio [AIBN]/[I<sub>2</sub>] = 1.9; Copolymerizations: molar ratio [AIBN]/[macro-CTA] = 0.3.

<sup>b</sup> Butyl acetate (50 wt % according to monomer) was used as solvent when monomer was not sufficient to dissolve the macro-CTA.

<sup>c</sup> Three shot additions of BuA.

<sup>d</sup> Determined by <sup>1</sup>H-NMR in CDCl<sub>3</sub>.

<sup>e</sup> Calculated by  $M_{n,Theo} = (\text{mass of monomer}) \times (\text{fractional conversion}) / (2 \times (\text{moles of I}_2)) + M_{\text{chain ends}}$ .

<sup>f</sup> Calculated by  $M_{n,Theo} = (\text{mass of monomer}) \times (\text{fractional conversion}) / (\text{moles of macro-CTA}) + M_{\text{macro-CTA}}$ .

<sup>g</sup> Polystyrene calibration.

<sup>h</sup> **2a:** PBuA, conv. = 86%,  $M_{n,Theo} = 7100 \text{ g mol}^{-1}$ ,  $M_{n,SEC} = 9700 \text{ g mol}^{-1}$  and  $M_w/M_n = 2.0$ ; **4a:** PS, conv. = 91%,  $M_{n,Theo} = 8800 \text{ g mol}^{-1}$ ,  $M_{n,SEC} = 8950 \text{ g mol}^{-1}$  and  $M_w/M_n = 1.3$ ; **5a:** PS, conv. = 94%,  $M_{n,Theo} = 8900 \text{ g mol}^{-1}$ ,  $M_{n,SEC} = 9200 \text{ g mol}^{-1}$  and  $M_w/M_n = 1.3$ ; **6a:** PS, conv. = 98%,  $M_{n,Theo} = 8100 \text{ g mol}^{-1}$ ,  $M_{n,SEC} = 7650 \text{ g mol}^{-1}$  and  $M_w/M_n = 1.3$ .

PL-gel 5 μm from Polymer Laboratoires (2 × 10<sup>2</sup>–2 × 10<sup>6</sup> g mol<sup>-1</sup> molecular weight range), at T = 30°C and at THF flow rate of 1.0 mL min<sup>-1</sup>, equipped with a Shodex Rise-61 refractometer detector and a Milton Roy ultra-violet spectrometer detector. Calibration was performed with poly(styrene) standards.

#### Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) analyses were performed at room temperature with a Bruker 400 MHz spectrometer using deuterated chloroform (CDCl<sub>3</sub>) as solvent.

#### Transmission electron microscopy

Transmission electron microscopy (TEM) analyses were performed on a TITAN 80–300 kV. Samples were prepared by ultramicrotomy technique and stained with ruthenium tetroxide (RuO<sub>4</sub>) vapors.

#### Differential scanning calorimetry

Differential scanning calorimetry (DSC) analyses were performed with a Q1000 from TA Instruments. The samples were heated at 10°C min<sup>-1</sup> from –80 to +120°C.

## RESULTS AND DISCUSSION

### Controlled butyl acrylate and styrene polymerizations by RITP: Formation of first blocks

It is well-known that molecular iodine acts as a strong inhibitor in free radical polymerizations. RITP process takes advantage of this characteristic of iodine to generate *in situ* the iodinated CTAs. A series of experiments was performed to check the efficiency of RITP process in bulk conditions and to produce the first block of the targeted block copolymers. A summary of results is shown in Table I. Results corresponding to butyl acrylate bulk polymerizations (runs 1a and 2a) show a close correlation between theoretical and experimental molecular weights: run 2a for example presented a theoretical molecular weight of 7100 g mol<sup>-1</sup> and an experimental molecular weight of 9700 g mol<sup>-1</sup>. Polydispersity indexes ( $M_w/M_n$ ) around 1.8 are in a good agreement with values reported for ITP of acrylates.<sup>8</sup> Similarly, results corresponding to styrene bulk polymerizations (runs 3a to 6a) also show a good correlation between theoretical and experimental molecular weights: run 4a for instance presented a theoretical molecular weight of 8800 g mol<sup>-1</sup> and an experimental molecular weight of 8950 g mol<sup>-1</sup>. Polydispersity indexes around 1.3 in all cases indicates a rather fast interchange of iodine atom

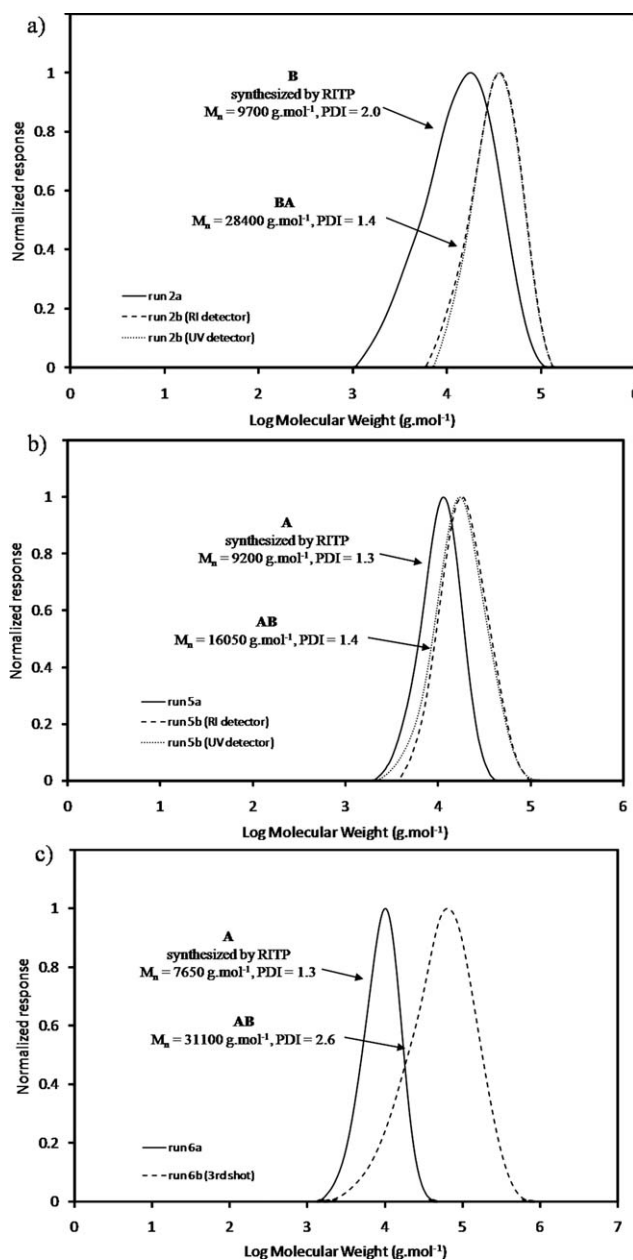
between dormant and active chains as anticipated by the higher exchange constant value  $C_{ex,PS-I} = 3.6$  reported by Goto and Fukuda<sup>20</sup> for ITP of styrene in comparison with  $C_{ex,PMeA-I} = 2.2$  reported by Lacroix-Desmazes<sup>8</sup> for methyl acrylate. Conversions higher than 90% attainable for both monomers are advantageous to avoid purification steps and continue directly with the formation of the second block as small amount of residual monomer should not drastically modify the properties of the second block.

### Synthesis of AB and BA diblock copolymers

Sequential step block copolymerization of different monomers by CRP is not always efficient, depending on several factors previously mentioned. The syntheses of diblock copolymers poly(styrene)-*b*-poly(butyl acrylate-*co*-styrene) (AB) by addition of butyl acrylate and poly(butyl acrylate)-*b*-poly(styrene-*co*-butyl acrylate) (BA) by addition of styrene starting from homopolymers as macro-CTAs are presented in Table I. Butyl acetate was used as solvent when the amount of the second monomer was not sufficient to dissolve the macro-CTA.

As shown in Table I, the BA copolymer is not synthesized in a controlled manner in the conditions of run 1b: the molecular weight did not increase and the molecular weight distribution got wider, indicating that it remained some residual macro-CTA and that homopoly(styrene) chains were formed in competition with diblock copolymer chains. Poly(styrene) propagating radicals ( $PS^*$ ) are not reactive enough toward dormant chains (PBuA-I) (low reaction rate of transfer  $R_{tr} = k_{tr}[PS^*][PBuA-I]$ ) and the backward reaction of poly(butyl acrylate) propagating radicals (PBuA $^*$ ) with PS-I (rate of the backward transfer reaction  $R_{-tr} = k_{-tr}[PBuA^*][PS-I]$ ,  $k_{tr} \ll k_{-tr}$ ) is favored in comparison to propagation ( $R_p$ ) although the cross-propagation rate constant between PBuA $^*$  and styrene is high ( $k_{p,BuA} = 40,400 M^{-1} s^{-1}$  at 70°C<sup>21</sup> and  $r_{BuA} = 0.16$ ,<sup>22</sup> so  $k_{p,BuA,Sty} = 252,500 M^{-1} s^{-1}$ ). A possible strategy to improve the results is to increase [styrene] and/or to decrease [PBuA-I] (i.e., a high molecular weight PBuA-I is beneficial). To favor the formation of the diblock copolymer, the amount of styrene was increased to enlarge the ratio  $R_p/R_{-tr}$  (run 2b), resulting in the controlled synthesis of the BA copolymer: a close correlation between theoretical and experimental molecular weights ( $M_{n,Theo} = 33,250 g mol^{-1}$ ,  $M_{n,SEC} = 28,400 g mol^{-1}$ ) as well as a rather low polydispersity index (1.4) are observed.

Figure 1(a) shows the SEC analysis for the BA block copolymer with two detectors (refractive index and UV) in comparison with the B macro-CTA. The BA copolymer shows a monomodal distribution and



**Figure 1** SEC analysis for: (a) block copolymerization of styrene from a poly(butyl acrylate)-I precursor; (b) block copolymerization of butyl acrylate from a poly(styrene)-I precursor; (c) block copolymerization of butyl acrylate (in three shots) from a poly(styrene)-I precursor (homopolymers A and B: —: trace from refractive index detector, diblock copolymers AB and BA: - - -: trace from refractive index detector, ●●●●●: trace from UV detector).

presents a clear shift toward higher molecular weights compared with B, confirming that most of the poly(butyl acrylate) (PBuA) chains are living and take part in the formation of the BA copolymer.

The preparation of AB copolymer rich in the B elastomeric component is important if mechanical properties of the final ABA copolymer are required (e.g., thermoplastic elastomers). However, when an excess of butyl acrylate over the poly(styrene) (PS)

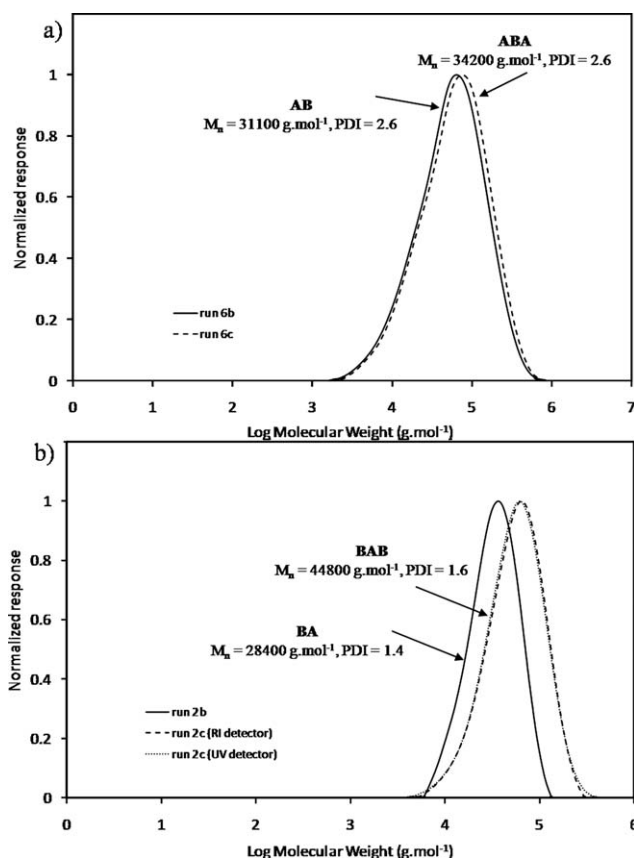


macro-CTA was used in runs 3b (mass ratio butyl acrylate/PS = 6) and 4b (mass ratio butyl acrylate/PS = 3), a bad control of the polymerization was observed: the presence of a bimodal molecular weight distribution in SEC analysis suggests the presence of diblock copolymer chains together with the existence of undesirable PBuA homopolymer chains. The formation of PBuA homopolymer is related to the high homopropagation rate constant of butyl acrylate ( $k_{p,BuA} = 40400 \text{ M}^{-1} \text{ s}^{-1}$  at  $70^\circ\text{C}$ )<sup>21</sup> so that  $R_{tr} = k_{tr}[PBuA^*][PS-I]$  is too low compared to  $R_p$ . The block copolymerization is also disfavored by the rather low cross-propagation rate constant between  $PS^\bullet$  and butyl acrylate ( $k_{p,S} = 498 \text{ M}^{-1} \text{ s}^{-1}$  at  $70^\circ\text{C}$ )<sup>21</sup> and  $r_S = 0.70$ ,<sup>22</sup> so  $k_{p,Sty,BuA} = 711 \text{ M}^{-1} \text{ s}^{-1}$ ; i.e.,  $k_{p,Sty,BuA} \ll k_{p,BuA}$ . A possible strategy for obtaining improved results is to decrease [butyl acrylate] and/or to increase [PS-I] (i.e., a low molecular weight PS-I is beneficial). To favor the block copolymerization, the amount of butyl acrylate monomer was decreased to increase the ratio  $R_{tr}/R_p$ , resulting in a controlled synthesis of the AB copolymer (run 5b): an excellent correlation between theoretical and experimental molecular weights ( $M_{n,Theo} = 16,200 \text{ g mol}^{-1}$ ,  $M_{n,SEC} = 16,050 \text{ g mol}^{-1}$ ) as well as a good 1.4 polydispersity index are observed.

Figure 1(b) shows the SEC analysis for this AB copolymer where the shift of the starting PS curve toward higher molecular weights is visible and the two curves (refractive index and UV detectors) of the diblock copolymer overlap well, indicating the presence of PS in all the detected chains.

Following this strategy of using a low instantaneous concentration of butyl acrylate to reduce  $R_p$  over  $R_{tr}$ , a one-pot controlled synthesis of AB copolymer rich in B component was carried out by growing the second block of PBuA in three-shot additions of butyl acrylate monomer (run 6b), resulting in a better control of the molecular weight compared to a single-shot experiment (run 3b). In the first shot of butyl acrylate in run 6b, the control of the polymerization was actually very satisfactory, whereas in the second and the third shot additions of butyl acrylate, a slight decrease in the control of the polymerization (deviation of the molecular weights and larger polydispersity index) was gradually observed which might be ascribed to an increase of the proportion of dead chains, presumably due to a large overall ratio  $[AIBN]/[\text{macro-CTA}] = 0.9$ , this ratio being 0.3 for each of the three shot additions of butyl acrylate.

Figure 1(c) shows the SEC analysis for this AB copolymer (run 6b) where a shift of the starting poly(styrene) curve toward higher molecular weights is clearly observed. Thus, an AB copolymer ( $M_{n,Theo} = 42,300 \text{ g mol}^{-1}$ ,  $M_{n,SEC} = 31,100 \text{ g mol}^{-1}$  and  $M_w/M_n = 2.6$ ) containing 87 wt % of PBuA (determined by  $^1\text{H NMR}$ ) was produced.



**Figure 2** SEC analysis for: (a) block copolymerization of styrene from a poly(styrene)-*b*-poly(butyl acrylate-*co*-styrene)-I precursor; (b) block copolymerization of butyl acrylate from a poly(butyl acrylate)-*b*-poly(styrene-*co*-butyl acrylate)-I precursor (diblock copolymers AB and BA: —: trace from refractive index detector; triblock copolymers ABA and BAB: - - -: trace from refractive index detector, ●●●●●: trace from UV detector).

### Synthesis of ABA and BAB triblock copolymers in three steps

An ABA copolymer was synthesized using the crude AB copolymer from run 6b as the macro-CTA and styrene as the monomer. Results are shown in Table I (run 6c), presenting a good correlation between theoretical and experimental molecular weights ( $M_{n,Theo} = 38,700 \text{ g mol}^{-1}$ ,  $M_{n,SEC} = 34,200 \text{ g mol}^{-1}$ ). Figure 2(a) shows the SEC analysis for this ABA copolymer having a symmetrical distribution slightly shifted toward higher molecular weights compared with the trace of the parent AB copolymer. This is a modest increase in the molecular weight of this triblock copolymer in comparison with the molecular weight of the macro-CTA ( $31,100 \text{ g mol}^{-1}$ ) but in agreement with our targeted structure involving short PS blocks (the feasibility of the reactivation of PBuA-I by  $PS^\bullet$  was previously demonstrated more clearly in Figure 1(a) where a higher shift was targeted). A transparent and elastomeric material was obtained with a weight composition PS/PBuA = 21/79 as determined by  $^1\text{H NMR}$ .

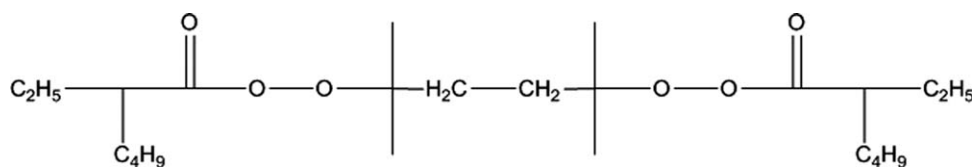


Figure 3 Structure of 2,5-di(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox 141).

The reversed-order BAB copolymer was synthesized successfully by a third sequential block copolymerization of butyl acrylate starting from the crude BA copolymer prepared from run 2b ( $M_{n,SEC} = 28,400 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.4$ ). As shown in Table I (run 2c), the correlation between the theoretical and experimental molecular weights of the final product ( $M_{n,Theo} = 50,200 \text{ g mol}^{-1}$ ,  $M_{n,SEC} = 44,800 \text{ g mol}^{-1}$ ) is relatively good and the polydispersity index (1.6) is also in a good range for ITP. Figure 2(b) shows the SEC analysis for this BAB copolymer synthesized in three steps with monomodal distributions and a perfect overlap of the curves for refractive index and UV detectors. The observed shift toward higher molecular weights in each step [Figs. 1(a) and 2(b)] confirms the effectiveness of the RITP and subsequent ITP processes when the appropriate conditions of monomer to macro-CTA ratio are used. A transparent and flexible material was obtained with a weight composition PS/PBuA = 48/52 as determined by  $^1\text{H}$  NMR.

The knowledge of appropriate conditions for the successful synthesis of ABA and BAB copolymers in three steps allowed us to investigate a more straightforward way to produce such copolymers in only two steps using a difunctional initiator.

### Synthesis of ABA and BAB triblock copolymers in two steps

Synthesis of triblock copolymers by RITP using a difunctional initiator would open the possibility to prepare such copolymers in only two steps. Homopolymerizations of styrene and butyl acrylate were performed by RITP in bulk using the difunctional initiator 2,5-di(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox 141) (Fig. 3).

Monofunctional and difunctional CTAs are formed *in situ* during the polymerization resulting in a difunctional macro-CTA, with its respective amount of monofunctional macro-CTA corresponding to the external fragments coming from the initiator. The theoretical molecular weight of the polymer produced by RITP with a difunctional initiator can be calculated with eq. 1 assuming that all the fragments of the initiator give rise to polymer chains (eq. 1):

$$M_{n,Theo} = (\text{mass of monomer}) \times (\text{fractional conversion}) / ((3/2) \times (\text{moles of } I_2)) \quad (1)$$

RITP of styrene with Trigonox141 (Run 7a in Table II) resulted in the production of narrow poly(styrene) ( $M_w/M_n = 1.3$ ) in high yield (98%) with a rather good control of the molecular weights in

TABLE II  
Homopolymerizations and Block copolymerizations of Butyl Acrylate and Styrene  
by RITP Using Trigonox 141 as Initiator

Run <sup>a</sup>	Control agent	Monomer	Polymer obtained	Mass ratio (Monomer/macro-CTA)	T (°C)	Time (h)	Conversion <sup>b</sup> (%)	$M_{n,Theo}$ (g mol <sup>-1</sup> )	$M_{n,SEC}$ <sup>e</sup> (g mol <sup>-1</sup> )	$M_w/M_n$
7a	I <sub>2</sub>	S	PS	–	70	15	98	10,500 <sup>c</sup>	16,000	1.3
7b	7a	BuA	P(BuA-co-S)-b-PS-b-P (BuA-co-S)	3	85	1	76	51,900 <sup>d</sup>	24,150	2.3
8a	I <sub>2</sub>	BuA	PBuA	–	80	15	93	4900 <sup>c</sup>	47,000	1.9
9a	I <sub>2</sub>	BuA (and 5 wt % S)	P(BuA-co-S)	–	80	15	91	9900 <sup>c</sup>	46,400	1.6
9b	9a	S	P(S-co-BuA)-b-P (BuA-co-S)-b-P (S-co-BuA)	3	70	15	37	97,900 <sup>d</sup>	73,100	1.7

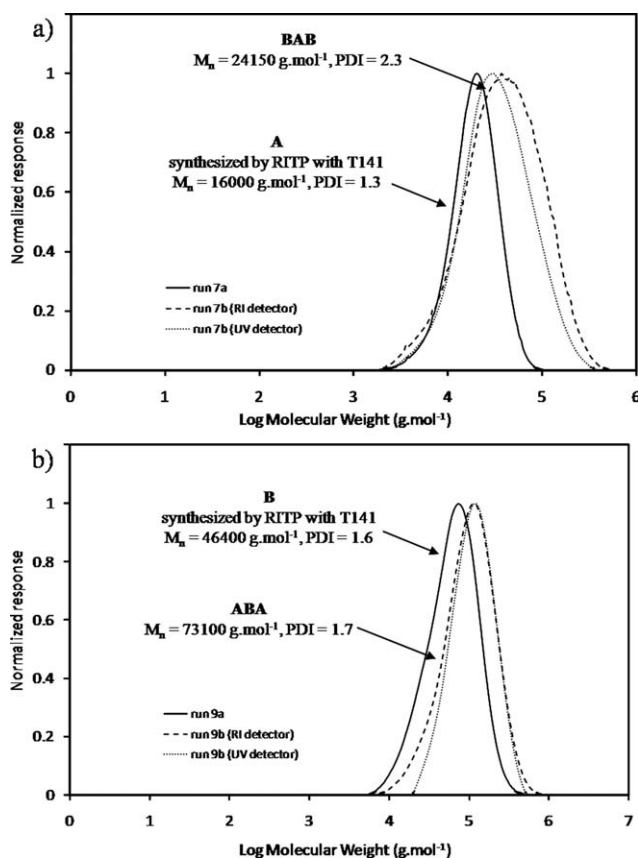
<sup>a</sup> Styrene = S; poly(styrene) = PS; butyl acrylate = BuA; poly(butyl acrylate) = PBuA. Homopolymerizations: molar ratio [T141]/[I<sub>2</sub>] = 1.13 for run 7a, 0.85 for run 8a, and 0.78 for run 9a; Copolymerizations: molar ratio [AIBN]/[macro-CTA] = 0.3.

<sup>b</sup> Determined by  $^1\text{H}$ -NMR in CDCl<sub>3</sub>.

<sup>c</sup> Calculated by  $M_{n,Theo} = (\text{mass of monomer}) \times (\text{fractional conversion}) / ((3/2) \times (\text{moles of } I_2)) + M_{\text{chain ends}}$ .

<sup>d</sup> Calculated by  $M_{n,Theo} = (\text{mass of monomer}) \times (\text{fractional conversion}) / (\text{moles of macro-CTA}) + M_{\text{macro-CTA}}$ .

<sup>e</sup> Polystyrene calibration.



**Figure 4** SEC analysis for: (a) block copolymerization of butyl acrylate from a I-poly(styrene)-I precursor; (b) block copolymerization of styrene from a I-poly(butyl acrylate-co-styrene)-I precursor (homopolymers A and B: —: trace from refractive index detector, triblock copolymers BAB and ABA: - - -: trace from refractive index detector, ●●●●●: trace from UV detector).

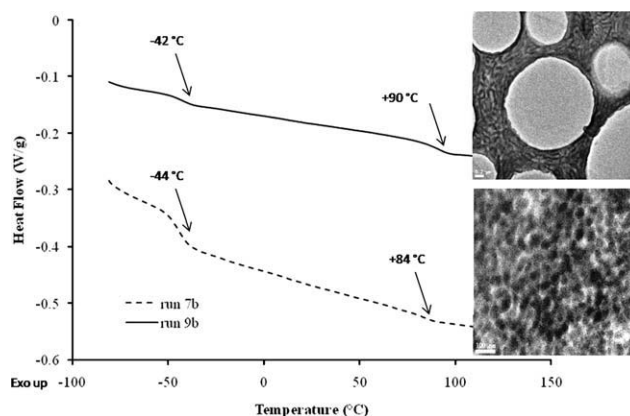
reference to eq. 1 ( $M_{n,Theo} = 10,500 \text{ g mol}^{-1}$ ,  $M_{n,SEC} = 16,000 \text{ g mol}^{-1}$ ).

In the case of RITP of butyl acrylate with Trigonox141 as the initiator (Run 8a in Table II), the polydispersity index of 1.9 is in the expected range for RITP of acrylates but a strong upward deviation of the molecular weight is observed ( $M_{n,Theo} = 4900 \text{ g mol}^{-1}$ ,  $M_{n,SEC} = 47,000 \text{ g mol}^{-1}$ ). In contrast to the case of styrene, this deviation indicates an overall low efficiency of the *in situ* formed transfer agents derived from Trigonox141 in the polymerization of butyl acrylate. In a model study which will be published in detail elsewhere, the efficiencies of the fragments R-C(O)O- ( $\alpha$ ) and -O-R'-O- ( $\beta$ ) of the Trigonox141 initiator (R-C(O)O-O-R'-O-OC(O)-R) were assessed in RITP (where  $M_{n,Theo} = (\text{mass of monomer}) \times (\text{fractional conversion}) / (((2\alpha + \beta)/2) \times (\text{moles of } I_2))$ ):  $\alpha = 0.07$  and  $\beta = 0.14$  for RITP of butyl acrylate instead of  $\alpha = 0.31$  and  $\beta = 0.97$  for RITP of styrene. In run 9a, the addition of 5 wt % of styrene as comonomer was slightly helpful as it results in a lower polydispersity index (1.6) although the deviation of the molecular

weight is still significant ( $M_{n,Theo} = 9900 \text{ g mol}^{-1}$ ,  $M_{n,SEC} = 46,400 \text{ g mol}^{-1}$ ). Thus, the control of the polymerization of butyl acrylate by RITP with Trigonox141 is rather poor. It can be only slightly improved by adding styrene as comonomer. It must be noticed that the high molecular weight of the resulting PBuA is not a drawback in our case since a high molecular weight for the elastomeric block is actually required in thermoplastic elastomers. Furthermore, the polydispersity index of the polymers (between 1.6 and 1.9) indicates that the degenerative chain transfer mechanism between dormant and propagating chains still operates. Indeed, the conventional radical polymerization of butyl acrylate without reversible transfer to alkyl iodide leads to much broader molecular weight distribution ( $PDI > 3$ ). Hence, although the polymerization of butyl acrylate by RITP with Trigonox141 suffers from a bad control of the molecular weight (low overall efficiency of Trigonox141 in RITP, i.e.,  $M_{n,SEC} \gg M_{n,Theo}$ ), the polymer chains are expected to bear an iodine atom at the chain-ends, allowing block copolymerization.

The crude product of run 7a was used as the macro-CTA to synthesize the BAB copolymer (run 7b in Table II). Figure 4(a) shows the SEC analysis of this BAB copolymer showing a monomodal distribution with a shift toward higher molecular weights compared with the parent macro-CTA. The control of the molecular weight is rather poor (possibly because butyl acrylate was added in one single-shot addition) but the final product (31/69 of PS/PBuA weight composition determined by  $^1\text{H NMR}$ ) afforded a nanostructured transparent and flexible film (evidenced by TEM analysis) with two distinctive  $T_g$  at  $-44^\circ\text{C}$  and  $84^\circ\text{C}$  (determined by DSC) shown in Figure 5.

The crude product of run 9a was used to prepare the ABA copolymer using an excess of styrene and stopping the reaction at low conversion (37%) (run 9b in Table II). A high molecular weight product was obtained with a rather good agreement between



**Figure 5** DSC and TEM analyses ( $\text{RuO}_4$  staining) for run 7b (scale = 100 nm) and run 9b (scale = 200 nm).



theoretical and experimental molecular weights ( $M_{n,\text{Theo}} = 97,900 \text{ g mol}^{-1}$ ,  $M_{n,\text{SEC}} = 73,100 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.7$ ). Figure 4(b) shows the SEC analysis of this ABA copolymer showing a monomodal distribution with a shift toward higher molecular weights compared with the parent macro-CTA. However, the tail observed with the refractive index detector in the low molecular weight region indicates that it remained some residual macro-CTA. Furthermore, the deviation of the experimental molecular weight  $M_{n,\text{SEC}}$  versus  $M_{n,\text{Theo}}$  ( $M_{n,\text{SEC}} < M_{n,\text{Theo}}$ ) reveals the formation of new homopoly(styrene) chains. The TEM analysis confirms the presence of some block copolymers, proving that some macro-CTA chains were efficiently reactivated, although a significant amount of homopoly(styrene) is also clearly visible (Fig. 5). The 62/38 weight composition of PS/PBuA (determined by  $^1\text{H NMR}$ ) gives glassy properties to this nanostructured transparent (hazy) material which shows two  $T_g$  at  $-42^\circ\text{C}$  and  $90^\circ\text{C}$  (Fig. 5). The TEM analyses given in Figure 5 suggest that the BAB copolymer 7b contains a lower amount of homopolymer than the ABA copolymer 9b; this is in agreement with the fact that PS-I is more easily reactivated by PBuA $^*$  than PBuA-I by PS $^*$ .

Although the synthesis of the ABA triblock copolymer with the appropriate molecular weight of each block and the right composition for thermoplastic elastomer applications is not so easy at this stage either with AIBN or with Trigonox 141, these novel experiments of RITP with Trigonox 141 as industrially available difunctional initiator are extremely promising to produce nanostructured multiblock copolymers in a very straightforward manner. A systematic model study to evaluate in detail the efficiency of Trigonox 141 in RITP, concomitantly leading to a mixture of diblock and triblock copolymers, is underway and will be reported elsewhere.

ABA copolymers could be prepared by RAFT<sup>17</sup> with for instance *S,S*-di(1-phenylethyl)trithiocarbonate by polymerizing styrene first and then butyl acrylate but it requires the rather tedious synthesis of trithiocarbonates as control agents whereas RITP is based on the *in situ* facile synthesis of the transfer agents. Furthermore, the somewhat fragile trithiocarbonate linkage is in the middle of the copolymer chain and could be damaged during polymer processing. NMP<sup>18</sup> can also be used for instance with a difunctional SG1 alkoxyamine (SG1: *N-tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide) by polymerizing butyl acrylate first in the presence of a slight excess of free SG1 nitroxide (5 mol % SG1 per alkoxyamine function)<sup>23</sup> and then styrene but the ABA triblock copolymers were contaminated with homopolystyrene due to thermal polymerization of styrene at  $T = 120^\circ\text{C}$  whereas RITP can be per-

formed in milder conditions of temperature (e.g.,  $T = 70^\circ\text{C}$  for RITP of styrene in the present study). ATRP<sup>19</sup> has also been used for instance with 2,6-dibromoheptanedioate initiator to prepare ABA copolymers by polymerizing butyl acrylate first and then styrene but it requires halogen exchange (CuCl vs. bromo initiator) as well as the addition of a small amount of deactivator Cu<sup>II</sup> (10 mol % of Cu<sup>II</sup> vs. Cu<sup>I</sup>) to increase the rate of crosspropagation relative to the rate of homopropagation and to minimize the coupling of radicals in the early stages of the polymerization. Thus, the resulting ATRP reaction mixture contains many additives (ligand, metal catalysts) and is more complex than in the case of RITP. In summary, although RAFT, NMP, and ATRP are very competitive controlled polymerization techniques to prepare such multiblock copolymers, the control of the polymerization is obtained at the expense of the practical simplicity in comparison with RITP. A compromise should be found between the final properties of the copolymer (related to the level of control) and the facility of polymerization, and RITP is in good place.

## CONCLUSIONS

Appropriate conditions to successfully synthesize diblock copolymers of styrene and butyl acrylate by RITP in bulk or solution were established. To obtain a well-controlled poly(styrene)-*b*-poly(butyl acrylate) copolymer in a sequential block copolymerization starting from RITP of styrene, it was necessary to use a low ratio of [butyl acrylate]/[PS-I] (i.e., multiple shots or continuous addition of butyl acrylate and/or a low molecular weight PS-I were beneficial). In contrast, to effectively synthesize poly(butyl acrylate)-*b*-poly(styrene) starting from RITP of butyl acrylate, it was preferable to use a high ratio of [styrene]/[PBuA-I] (i.e., large amount of styrene in one single shot addition and/or a high molecular weight PBuA-I were preferable). This knowledge was further adapted to produce either poly(styrene)-*b*-poly(butyl acrylate)-*b*-poly(styrene) or poly(butyl acrylate)-*b*-poly(styrene)-*b*-poly(butyl acrylate) triblock copolymers in three steps. Complementarily, the commercially available difunctional initiator 2,5-di(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox 141) was used for the first time in RITP of styrene and butyl acrylate to synthesize difunctional macro-CTAs and further produce triblock copolymers in only two steps.

Support for this work has been provided by the CONACyT, Mexico (CB-01637) and the CNRS, France. We were also granted by the French-Mexican PCP program to favor the cooperation between the two countries.



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