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Synthesis of ABA Triblock Copolymers via a Tandem Ring-Opening Metathesis Polymerization: Atom Transfer Radical Polymerization Approach

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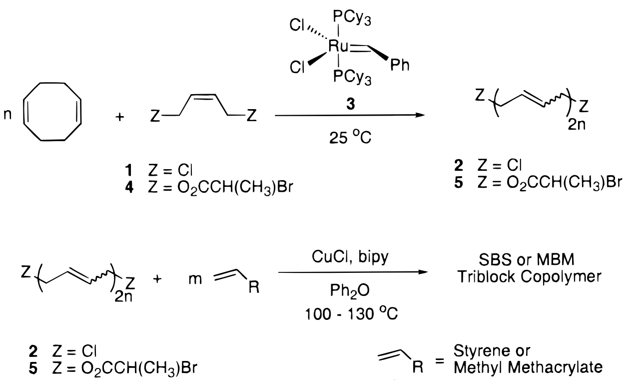
ABSTRACT: The synthesis of poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene) (SBS) and poly(methyl methacrylate)-*b*-poly(butadiene)-*b*-poly(methyl methacrylate) (MBM) triblock copolymers with poly(butadiene) (PBD) segments containing 100% 1,4-microstructure is described. Bis(allyl chloride) and bis(2-bromopropionate) terminated telechelic PBD's were synthesized by the ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene in the presence of the corresponding difunctional chain transfer agents. These telechelic PBDs were subsequently used as difunctional macroinitiators for the heterogeneous atom transfer radical polymerization (ATRP) of styrene and methyl methacrylate to form SBS and MBM triblock copolymers. Triblock structure was confirmed by selective PBD degradation. In addition, the tandem ROMP−ATRP approach was successfully extended to a "one-pot" synthesis.

Recently, great attention has been directed toward the synthesis of ABA triblock copolymers that function as thermoplastic elastomers.[1−4] Thermoplastic elastomers such as poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene) (SBS) triblock copolymers have been known for over three decades and have found many commercial applications.[2] However, since the useful service temperature of these polymers is limited by the glass transition temperature (T_g) of the poly(styrene) segments, there has been an increasing demand for thermoplastic elastomers that retain their function at higher temperatures.[3] Poly(methyl methacrylate)-*b*-poly(butadiene)-*b*-poly(methyl methacrylate) (MBM) triblock copolymers have been considered alternatives, as the PMMA blocks should have a higher T_g than their analogous PS counterparts. Although well-defined MBM triblock copolymers have been synthesized[4] by Jérôme et al. via anionic polymerization methods, the elastomeric properties of these copolymers are limited by a relatively high 1,2-PBD content (>40%) formed during the polymerization.

Ring-opening metathesis polymerization (ROMP) is a well-known technique for the preparation of telechelic PBDs with 100% 1,4-microstructures.[5] For example, the ROMP of 1,5-cyclooctadiene (COD) in the presence of an appropriate chain transfer agent (CTA) has provided routes to telechelic PBDs end-capped with amino, hydroxy, methacrylate, and carboxy functional groups.[6]

The integration of ROMP with other polymerization methods such as atom transfer radical polymerization (ATRP),[7] a controlled radical polymerization process, has permitted the preparation of novel block copolymers. For example, this approach has successfully been used to synthesize poly(styrene)-*b*-poly(norbornene) and poly(methyl acrylate)-*b*-poly(norbornene) diblock copolymers.[8] In these cases, the ROMP of norbornene was terminated with an agent that could also function as an ATRP initiator. While this was found to be an effective route for preparing diblock copolymers, the synthesis of triblock copolymers requires a telechelic polymer[9] with initiating groups on *both* ends.

Scheme 1



This report describes the synthesis and characterization of two new telechelic PBDs prepared by ROMP. The polymers were end-capped with allyl chloride[10] or 2-bromopropionyl ester[11] groups, known ATRP initiators. The utility of these macroinitiators in the ATRP of styrene and methyl methacrylate to prepare SBS and MBM triblock copolymers with 100% 1,4-PBD microstructures was investigated (Scheme 1).

The ROMP of COD in the presence of the commercially available CTA 1,4-dichloro-*cis*-2-butene **1** (COD/CTA = 5/1) resulted in bis(allyl chloride) functionalized telechelic PBD **2**. Polymerization was performed in neat monomer at ambient temperature and initiated by ruthenium catalyst[5b] **3** ($[\mathrm{M}]_0/[\mathrm{I}]_0 = 2000/1$). After 24 h, the solutions were poured into an excess of methanol to afford telechelic PBD **2** ($M_n = 2400$, PDI = 1.59) in 75% isolated yield. ^{1}H and ^{13}C NMR spectroscopy indicated that the polymer backbone contained a "perfect" 1,4-PBD microstructure.[12] 1,4-Linkages are highly ideal as they display elastomeric properties superior to 1,2-linkages.[1−4] Both ^{1}H and ^{13}C NMR spectroscopy supported an end group functionality ratio (F_n) near 2.0, in accordance with previous results obtained by ROMP using symmetrically disubstituted olefin CTAs.[6a]

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Table 1. Synthesis of SBS and MBM Triblock Copolymers via ATRP of Styrene and Methyl Methacrylate Using Telechelic PBDs 2 and 5 as ATRP Macroinitiators[a]

polymer	$[\mathrm{M}]_0/[\mathrm{I}]_0$[b]	$M_{\mathrm{n,theo}}$[c]	$M_{\mathrm{n,gpc}}$[d]	$M_{\mathrm{n,nmr}}$[e]	PDI	% conv[f]	yield[g]
SBS	20	4200	4800	4300	1.48	88	75
SBS	40	6500	7300	6900	1.45	99	99
SBS	80	10200	10100	12300	1.45	93	93
SBS	120[h]	14900	13800	15900	1.52	97	89
SBS[i]	80[j]	8100	8000	8500	1.63	73	70
SBS[k]	80	10100	10000	10400	1.25	92	90
MBM	20	4400	9400	4700	1.58	86	77
MBM	80	10600	18100	11500	1.54	99	90
MBM	180	20600	28300	23900	1.59	99	88
MBM	360[h]	38700	39600	41700	1.68	99	99

[a] General reaction conditions: initiator/CuCl/bipy = 1/2/6, Ph_2O as solvent, N_2 atmosphere. For SBS synthesis: 130 °C, 7 h, telechelic PBD **2** MW (NMR) = 2400, PDI = 1.59. For MBM synthesis: 100 °C, 2.5 h, telechelic PBD **5** MW (NMR) = 2700, PDI = 1.57. [b] Initial monomer/macroinitiator ratio. $[\mathrm{I}]_0 = 50$ mM for SBS, 25 mM for MBM. [c] Calculated based on monomer conversion and assumes $F_n = 2.0$. [d] Relative to PS (SBS) or PMMA (MBM) standards in THF. [e] Determined by ^{1}H NMR spectroscopy using end group analysis. [f] Determined by GC. [g] Isolated yield. [h] Reaction performed in bulk monomer. [i] "One-pot" synthesis. PBD **2** MW was assumed to be 2400. Air atmosphere. Styrene contained BHT. [j] Ratio was approximated. [k] 4,4′-Diheptylbipyridine was used in lieu of bipy.

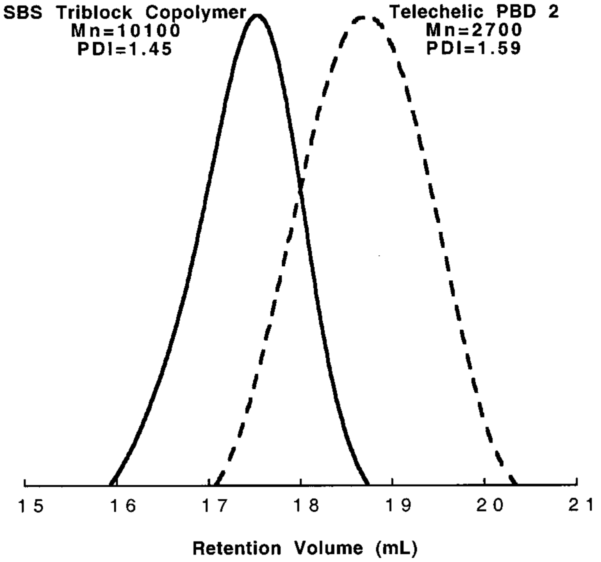

Figure 1. Representative GPC traces of PBD **2** (dotted line) and SBS (solid line) synthesized by ATRP of styrene initiated with **2** (catalyzed with CuCl/bipy). Molecular weights are reported relative to PS standards.

Telechelic PBD **2** was used to initiate the heterogeneous ATRP of styrene in the presence of CuCl/2,2′-bipyridine (bipy) (1/3 molar ratio) at 130 °C.[10] After 7 h, the reaction mixture was diluted with tetrahydrofuran and poured into an excess of methanol to afford SBS triblock copolymer. Table 1 summarizes the polymerization results for a variety of styrene/macroinitiator ratios. Gel permeation chromatography (GPC) indicated the $M_{\mathrm{n,gpc}}$ values of the SBS triblock copolymers agree with the theoretical molecular weights ($M_{\mathrm{n,theo}}$) which were calculated on the basis of monomer conversion and the assumption that each macroinitiator chain contained two allyl chloride end groups. In addition, the MW distributions were unimodal, with no detectable signal attributable to the starting macroinitiators (Figure 1). Lower PDIs could be obtained (1.25 vs 1.45) by employing a more soluble bipy derivative (e.g., 4,4′-diheptyl-2,2′-bipyridine). The SBS triblock copolymers were also characterized by ^{1}H and ^{13}C NMR spectroscopy which indicated that the 1,4-PBD microstructure of the macroinitiator was conserved.[13]

Since GPC and ^{1}H NMR spectroscopy do not allow discrimination between diblock and triblock copolymers of identical MW, a characterization method based on the cleavage of the PBD segment was used to determine block arrangement.[14] Selective PBD degradation of a SBS polymer (M_{n} = 12 300) with OsO_4/H_2O_2 gave PS (T_g = 91 °C) with $M_{\mathrm{n,gpc}}$ = 4900 (PDI = 1.23), as expected for a triblock structure. No PBD was observed in the ^{1}H NMR spectra of these degraded samples, indicating that the degradation was complete.

Radical polymerizations must generally be carried out under inert atmospheres to prevent reaction of oxygen with free radicals and catalyst. However, Matyjaszewski et al. have recently shown[15] that ATRP can be carried out in a closed system under an atmosphere of air and in the presence of radical scavengers when Cu^0 (combined with small amounts of CuX_2) is used in lieu of Cu^I halide salts. The application of this technique toward our system permitted the synthesis of SBS triblock copolymers via a "one-pot" procedure. Telechelic PBD **2** was prepared as above with an assumed MW of 2400 and yield of 75% based on prior results. After terminating the ROMP of COD by the addition of ethyl vinyl ether,[5b] the flask was charged with appropriate amounts of phenyl ether, styrene, bipy, copper powder, and $CuBr_2$ under air, capped, and then heated to 130 °C for 7 h. As shown in Table 1, monomer conversion was lower than the analogous two-step synthesis described above, presumably due to relatively more dilute conditions. However, good agreement between the theoretical and the experimental MW was observed.

Attempts at preparing MBM triblock copolymers using PBD **2** as the macroinitiator for the ATRP of MMA resulted in bimodal distributions in the GPC traces. In these cases, the low-MW peaks were in the MW range of unreacted macroinitiator, suggesting that the high-MW peak corresponded to a mixture of triblock and diblock copolymers. The bimodality was presumably due the initiation rate being slower than propagation. This was supported by a decrease in the low-MW peak area with monomer conversion and the observation of residual allyl chloride resonances in the ^{1}H NMR spectra of the isolated polymers.

The problem of inefficient initiation was overcome by the incorporation of 2-bromopropionate, a known[11] MMA initiator, into the CTA used during the ROMP of COD. The ROMP of COD in the presence of CTA **4** was performed in a similar manner as above and resulted in bis(2-bromopropionate) functionalized telechelic PBD **5** (M_{n} = 5500, PDI = 1.57) in 80% yield. ^{1}H and ^{13}C NMR spectroscopy indicated the presence of only 1,4-PBD linkages in the polymer backbone[12] and supported

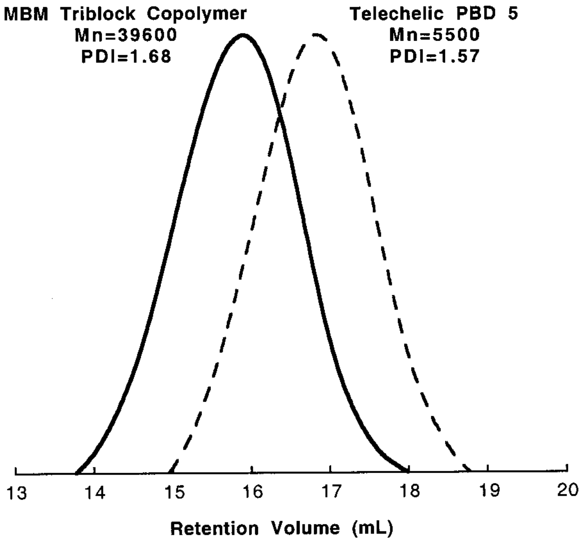

Figure 2. Representative GPC traces of PBD **5** (dotted line) and MBM (solid line) synthesized by ATRP of MMA initiated with **5** (catalyzed with CuCl/bipy). Molecular weights are reported relative to PMMA standards.

a F_n near 2.0. Telechelic PBD **5** was used as a macroinitiator for the heterogeneous ATRP of MMA to produce MBM triblock copolymers. The polymerizations were run under similar conditions as for the synthesis of SBS (CuCl/bipy catalyst system) using a variety of MMA/macroinitiator ratios (Table 1). The ^{1}H NMR spectra of the MBM triblocks revealed no change in the PBD microstructure relative to the PBD **5** macroinitiator.[13] GPC data (Figure 2) indicated that the MBM triblock copolymer MW distributions were unimodal and low (ca. 1.6). Selective PBD degradation[14] suggested a triblock structure[16] and provides evidence that discrepancies between the $M_{\mathrm{n,gpc}}$ of the MBM triblock copolymers and the theoretical $M_{\mathrm{n,theo}}$ were due to differences in the hydrodynamic volumes of MBM and the PMMA standards used for GPC calibration. To the best of our knowledge, this is the first report of a well-defined MBM triblock copolymer containing a 100% 1,4-PBD microstructure.

The thermal properties of the SBS and MBM triblock copolymers synthesized in this work were analyzed using differential scanning calorimetry (DSC). The T_g of the PBD segments appeared at −108 °C, indicating a high 1,4-microstructure. Unfortunately, the phase transition of the PS or PMMA segments occurred over a very broad temperature range, preventing an accurate determination of the T_g.[17] This behavior has been previously observed with other low molecular weight SBS triblock copolymers and may result from high compatibility between the PBD and PS microphases.[18]

In conclusion, we report the synthesis of telechelic PBDs with allyl chloride or 2-bromopropionate end groups by the ROMP of COD in the presence of an appropriate CTA. These polymers serve as bifunctional macroinitiators for the ATRP of styrene or MMA to form well-defined SBS and MBM triblock copolymers with 100% 1,4-PBD microstructures. Future studies will focus on the preparation of analogous triblock copolymers with higher MW PBD segments and the study of their respective thermal and mechanical properties.

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