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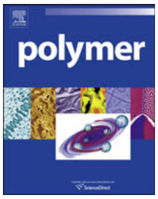

Diamino telechelic polybutadienes for solventless styrene–butadiene–styrene (SBS) triblock copolymer formation

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ABSTRACT

High molecular weight, high functionality diamino telechelic polybutadienes (TPBs) were synthesized by ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene (COD) in the presence of a chain transfer agent, 1,8-dicyano-4-octene, followed by lithium aluminum hydride reduction. Melt coupling of diamino TPB with anhydride-terminated polystyrene (PS-anh) resulted in the formation of styrene–butadiene–styrene (SBS) triblock copolymers; *ca.* 80% maximum conversion of PS-anh was achieved within 30 s. The results from SAXS, TEM, and rheological measurements of the coupling products confirmed the formation of SBS triblock copolymers having lamellar morphology. A fluorescent-labeled PS-anh was used to study the coupling kinetics by diluting the reactants by the addition of non-functional PS.

1. Introduction

Block copolymers (BCPs), *e.g.* poly(styrene-*b*-isoprene-*b*-styrene) (SIS) and poly(styrene-*b*-butadiene-*b*-styrene) (SBS), are difficult to melt process, and usually exhibit yield stresses and high viscosity at temperatures below their order–disorder transition (ODT) [1]. Processing at high temperature, *e.g.* above the ODT, can significantly lower the viscosity, but this may lead to complications from crosslinking or thermal degradation of the copolymers [2]. An alternate strategy for approaching this problem is to use a fast coupling reaction between two functional homopolymers of lower viscosity at a lower temperature to prepare BCPs *in situ* [3]. SBS triblock copolymer is mainly synthesized by sequential anionic polymerization of styrene and butadiene. Melt coupling of a monofunctional polystyrene (*e.g.*, anhydride-terminated polystyrene, PS-anh) and a difunctional polybutadiene [*e.g.*, diamino telechelic polybutadiene (diamino TPB)] should also be able to produce SBS copolymers, and provides a preparative route that is an alternative to sequential anionic polymerization. Additionally, reactive melt blending of homopolymers eliminates the use of solvents and permits creation of a "library" of BCP compositions by coupling a relatively few number of premade functional blocks.

The quality, especially the functionality, of diamino TPBs is critical for complete coupling. Until now, few reports are available concerning the synthesis of diamino polybutadienes. In addition, only low molecular weight diamino polybutadienes (typically <3000 kg/mol) have been reported. The synthesis of high molecular weight, high functionality diamino TPBs has not yet been achieved. Converting hydroxyl-terminated polybutadienes (HTPBs) to diamino TPBs is a usual way to synthesize low molecular weight amine-terminated polybutadienes [4]. To achieve this outcome, primary hydroxyl groups are first treated with alkyl or aryl sulfonyl chloride to form sulfonate terminated polybutadiene. This sulfonate is reacted with ammonia or primary amine providing primary amine or secondary amine-terminated polybutadienes. Aminolysis of HTPB under high temperature and high pressure is also a suitable route to transfer secondary alcohol to amine-terminated polybutadienes, but this has proved difficult to achieve for the analogous transformation of primary alcohol to amine [5]. 4,4′-Azobis(amidinopropane) dihydrochloride was studied as an initiator for butadiene polymerization in an ethanol–water medium [6]. High functionality diamino TPBs ($f_n \sim 2.0$) were achieved by lithium aluminum hydride ($LiAlH_4$) reduction of the amidino end groups. Ring-opening metathesis polymerization (ROMP) was successful in preparing low molecular weight diamino polybutadienes using a Boc protected diamine (BocNHR) as a chain transfer agent. The deprotection efficiency decreased with the increase of molecular weight due to the poor solubility of polybutadienes in the reaction medium [7]. Deprotection by trifluoroacetic acid (TFA) was also tried, however, even when the concentration of TFA was reduced to 2 equiv (relative to the

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number of moles of BocNHR), crosslinking of the polybutadienes was still observed [8].

Here we report the synthesis of high molecular weight, high functionality diamino TPBs by ROMP of 1,5-dicyclooctadiene (COD) and a method to prepare SBS triblock copolymer by fast coupling reaction between two functional homopolymers: PS-anh and diamino TPB. Coupling kinetics and the properties and phase behavior of the coupling products are also discussed.

2. Experimental

2.1. Materials

5-Hexenenitrile, 1-pyrenemethanol, styrene, 4-vinylbenzyl chloride, sodium azide, trifluoroacetic acid (TFA), di-*tert*-butyl dicarbonate [$(Boc)_2O$], Grubbs generation II catalyst (G2), tetrabutylammonium iodide (TBAI), CCl_4 and lithium aluminum hydride (LAH) were purchased from Aldrich. 4-Methylphthalic anhydride was generously provided by Avecia. *N*-Bromosuccimide (NBS) was purified by recrystallization in ethanol. THF and CH_2Cl_2 were purified by passage through an alumina column.

2.2. Instrumentation

2.2.1. Small angle X-ray scattering (SAXS) measurement

SAXS measurement was performed at the Institute of Technology (IT) Characterization Facility at the University of Minnesota. Copper Kα radiation of $\lambda = 1.54$ Å was generated by a Rigaku Ultrex 18 kW rotating anode using a 0.2×2 mm^2 microfocus cathode and monochromatized by total reflecting Franks mirrors and a nickel foil filter. Two-dimensional diffraction patterns were collected with a Bruker Hi-Star multi-wire area detector located 6 m from the sample.

2.2.2. Rheological measurement

Rheological measurements were performed on an Advanced Rheometric Expansion System (ARES, Rheometric Scientific) using 8 mm parallel plates. The sample was dried and pressed into a disk with a thickness of 1 mm. Temperature-dependent dynamic moduli were collected at 2% strain amplitude at a frequency of 2 rad/s. Frequency-dependent moduli were determined at varying temperatures with 2% strain amplitude.

2.2.3. Differential scanning calorimetry (DSC)

DSC measurement was performed on a TA Q1000 DSC instrument (TA Instruments, Inc.). The heat flow was collected at temperatures range from -100 °C to 280 °C at a heating rate of 20 °C/min.

2.2.4. Gel permeation chromatography (GPC)

Molecular weight and molecular weight distribution were measured on a Waters 590 SEC equipped with three Phenomenex Phenogel columns (5 µm bead size), an internal refractive index detector (Water 410), an external UV detector (Spectroflow 757, Kratos Analytical Instruments), and an external fluorescence detector (F-1050, Hitachi), using THF as eluent at room temperature. The instrument was calibrated with polystyrene standards. The molecular weight of polybutadiene was calculated using universal calibration.

2.2.5. Transmission electron microscopy (TEM)

TEM measurement was performed at the IT Characterization Facility. TEM images were recorded on a JEOL 1210 microscope operating at 120 keV. Thin films ($\sim$70 nm) of SBS copolymer were microtomed using a Reichet Jung ultra-microtome with a diamond knife at -150 °C. The sample was stained with OsO_4 at room temperature for 45 min.

2.3. Experimental procedures

2.3.1. Reactive coupling in the melt

Melt coupling of PS-anh and diamino telechelic polybutadiene (NH_2–PB–NH_2) was performed in a Mini-Max mixer (CS-183MMX, Custom Scientific Instruments) at 120–180 °C and 340 rpm under a nitrogen atmosphere [9]. Three steel balls (3.8 mm diameter) were added into the mixer to enhance the mixing efficiency. PS-anh and NH_2–PB–NH_2 with a molar ratio of 2:1 (equal amount of amine and anhydride functional groups) were used. Samples ($\sim$10 mg) were removed at different time intervals (30, 60, 90, 120, 180, 240, 300 and 600 s), quenched in liquid nitrogen, and then dissolved in THF containing large excess propylamine to quench the unreacted anhydride. The conversion of PS-anh was determined by GPC using either a UV or fluorescence detector.

2.3.2. Synthesis of 1,8-dicyano-4-octene (**2b**)

To a solution of 5-hexenenitrile (565 mg, 5.95 mmol) in CH_2Cl_2 (8 mL), the second generation Grubbs catalyst (75 mg, 1.5 mol%, Grubbs II) was added [10]. The reaction mixture was stirred at 40 °C for 6 h under a nitrogen atmosphere. The crude product was purified by medium pressure liquid chromatography (MPLC) (6:1 hexane:ethyl acetate) to give 266 mg (1.64 mmol, 55.2%) of 1,8-dicyano-4-octene (**2b**): ^{1}H NMR (500 MHz, $CDCl_3$): 5.45 (2H, br t, –CH=, $J = 5.0$ Hz), 2.34 (4H, t, NCCH_2–, $J = 7.0$ Hz), 2.19 (4H, t, –CH_2CH=, $J = 7.0$ Hz), and 1.74 (4H, pentet, –CH_2CH$_2$CN).

2.3.3. Synthesis of 1-((4-vinylbenzyloxy)methyl)pyrene (**6**)

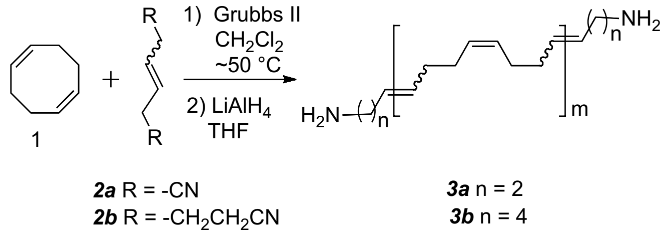
To a solution of 1-pyrenemethanol (232 mg, 1.0 mmol) in THF (10 mL), NaH (160 mg, 60% in mineral oil, 4.0 mmol) was added. After 30 min 4-vinylbenzyl chloride (0.6 g, 4.0 mmol) and TABI (20 mg) were added and the reaction mixture was refluxed for 16 h [11]. The reaction was quenched by addition of 6 M HCl. The mixture was extracted with CH_2Cl_2 and the organic layer was washed with saturated NaCl. CH_2Cl_2 was removed under vacuum. The crude product was purified by MPLC (30:1 hexane:ethyl acetate) to give 160 mg (46%) of 1-((4-vinylbenzyloxy)methyl)pyrene (**6**). ^{1}H NMR (500 MHz, $CDCl_3$): 8.26 (1H, d, pyrene–C*H*–, $J = 9.5$ Hz), 8.11 (1H, d, pyrene–C*H*–, $J = 7.0$ Hz), 8.09 (1H, d, pyrene–C*H*–, $J = 6.5$ Hz), 8.05 (1H, d, pyrene–C*H*–, $J = 7.5$ Hz), 8.03 (1H, d, pyrene–C*H*–, $J = 9.5$ Hz), 7.96 (2H, s, pyrene–C*H*–), 7.94 (1H, d, pyrene–C*H*–, $J = 7.5$ Hz), 7.95 (1H, t, pyrene–C*H*–, $J = 7.5$ Hz), 7.36 (2H, d, Ar-C*H*–, $J = 8.0$ Hz), 7.31 (2H, d, Ar-C*H*–, $J = 8.0$ Hz), 6.68 (1H, dd, =C*H*–, $J = 11.0$, 17.5 Hz), 5.71 (1H, d, =CH_aH$_b$, $J = 17.5$ Hz), 5.21 (1H, d, =CH$_a$$H_b$, $J = 11.0$ Hz), 5.16 (2H, s, Ar-CH_2–), and 4.57 (2H, s, pyrene–CH_2–); ^{13}C NMR (125 MHz, $CDCl_3$): 131.43, 131.38, 130.96, 129.54, 128.30, 127.83, 127.54, 127.20, 126.45, 126.05, 125.36, 125.07, 124.86, 124.62, 123.58, 113.98, 72.04, and 70.74.

2.3.4. Synthesis of 4-bromomethylphthalic anhydride (**4**)

To a solution of 4-methylphthalic anhydride (5.0 g, 30 mmol) in CCl_4 (50 mL), NBS (550 mg, 3 mmol) and benzoyl peroxide (3 mg) were added. The reaction mixture was refluxed for 2 h. CCl_4 was evaporated under vacuum. A new peak in the ^{1}H NMR spectrum at δ 4.60 ppm indicated the presence of –CH_2Br. The content of 4-bromomethylphthalic anhydride (**4**, *ca.* 8.8 wt%) in this crude mixture was estimated by ^{1}H NMR spectroscopy. The mixture was used as the ATRP initiator without further purification [12].

2.3.5. Pyrene labeled anhydride-terminated polystyrene (pyrene-PS-anh) by ATRP

To a 50 mL reactor, CuBr (144 mg, 1 mmol), Cu (64 mg, 1 mmol), 2,2′-bipyridyl (dpy, 468 mg, 3 mmol) and 4-bromomethylphthalic anhydride (**4**, 241 mg, 1 mmol, 8.8 wt% in 2.73 g of 4-methylphthalic anhydride) were added [12]. Three freeze–thaw cycles



Scheme 1. Synthesis of diamino TPBs via ROMP.

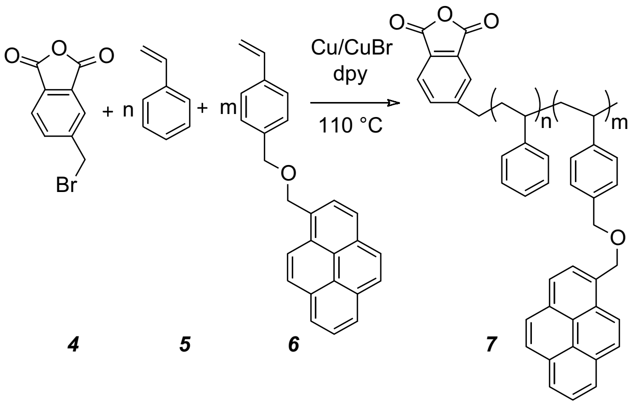
were repeated to remove oxygen. 1-((4-Vinylbenzyloxy)methyl)pyrene (**6**, 348 mg, 1 mmol) in 15 g (144 mmol) of styrene (**5**) was purged with high purity argon for 30 min. Styrene solution was then transferred to the reactor via cannula and stirred for 15 min at ambient temperature. The reactor was then placed in a preheated oil bath at 110 °C. After 24 h *ca.* 85% conversion of styrene was obtained (^1H NMR analysis). The mixture was dissolved in THF and filtered through an activated neutral aluminum oxide (Brockmann I, standard grade, ~150 mesh, 58 Å) column. The solution was concentrated and then precipitated in pentane. The precipitation process was repeated twice to give 11.7 g (78%) of pyrene-PS-anh (**7**).

3. Results and discussion

3.1. Synthesis of diamino telechelic polybutadienes (TPBs)

We examined two dicyanoalkenes (**2a** and **2b**) as the chain transfer agents (CTAs) to prepare diamino TPBs (Scheme 1). A dicyano-terminated TPB was synthesized via ROMP of COD (**1**, purified by hydroboration followed by vacuum distillation, purity > 99.999%) using 1,4-dicyano-2-butene (**2a**) as the CTA [13,14]. The resulting dicyano-terminated TPB (MW up to 200 kg/mol) was then subjected to $LiAlH_4$ reduction in THF. However, the degree of functionality of the reduction product **3a** was determined to be very low even for the low molecular weight polymers ($M_n < 10$ kg/mol) based on the ^{19}F NMR analysis technique that we developed [15]. We assume that this was due to the acidity of the (allylic) protons at the α-position of the nitrile group. To explore this hypothesis, **2a** was used as the model compound for the $LiAlH_4$ reduction. Upon addition of $LiAlH_4$ into a THF solution of **2a**, the solution turned to a dark purple/brown color quickly. After 12 h the reaction mixture was quenched, and no desired 1,6-diamino-3-hexene was observed based on ^1H NMR analysis.

To reduce the acidity of the allylic protons, 1,8-dicyano-4-octene (**2b**), with 2 more methylene spacers between the cyano group and alkene, was studied under the same conditions. When 10 equiv of $LiAlH_4$ were added to the THF solution of **2b**, the reaction mixture remained colorless, all nitriles were consumed, and a new ^1H resonance was observed at δ 2.7 ppm ($-CH_2NH_2$). The reaction cleanly proceeded to the corresponding diamine (^1H NMR analysis). 1,8-Dicyano-4-octene (**2b**) was then used as the CTA for the synthesis of diamino TPB (**3b**). A series of dicyano-TPBs were synthesized via ROMP and then reduced by $LiAlH_4$ in THF. Functionalities of the reduced TPBs were determined by both the ^{19}F NMR spectroscopy method and reactive coupling with PS-anh followed by GPC analysis; these results are summarized in Table 1. For TPBs with MW lower than 38 kg/mol (entries 1–4, Table 1), the functionalities were high (>1.7), and the data determined by both methods were in reasonable agreement. However, for TPBs with MW about 60 kg/mol and 80 kg/mol (entries 5 and 6), even though different sources and concentration of $LiAlH_4$ were tried, the f_n was always lower and reproducibility was poor. The poor reproducibility may be due to the inhomogeneity of the reduction system. Both the ^{19}F NMR and PS-anh coupling showed low f_n for high MW diamino TPBs.



Scheme 2. Synthesis of pyrene-PS-anh (**7**) via ATRP.

3.2. Pyrene labeled anhydride-terminated polystyrene (pyrene-PS-anh, 7) by ATRP

Styrene (**5**) and 1-((4-vinylbenzyloxy)methyl)pyrene (**6**) have similar structures and are expected to have similar reactivity in atom transfer radical polymerization (ATRP). Copolymerization of **5** and **6** should result in a random copolymer with similar monomer ratio as that in the monomer feed. Polymerization of **5** and **6** with a molar ratio of 144:1 gave *ca.* 78% of purified pyrene-PS-anh (**7**, Scheme 2). Fig. 1 shows the ^1H NMR spectrum of polymer **7**. The resonances of the pyrene group appear between δ 8.0 and 8.3 ppm. The phthalic anhydride moiety gives rise to two broad resonances at δ 7.45 and 7.75 ppm, assigned to the protons *ortho* to each of the anhydride carbonyl groups. Two methylene groups of the unsymmetrical ether linkage within the pyrene moiety appear at δ 4.5 and

Table 1
Functionality of diamino telechelic polybutadienes (**3b**) determined by ^{19}F NMR analysis [15] and by reactive coupling with PS-anh

Entry	$H_2N–PB–NH_2$ (M_n, kg/mol)[a]	$[NH_2]$ by ^{19}F NMR (mmol/g)[b]	f_n by ^{19}F NMR[b,c]	f_n by reactive coupling[d]
1	14.2	0.130	1.9	1.8
2	15.5	0.125	1.9	1.9
3	25.5	0.081	2.1[e]	1.8
4	38.2	0.048	1.7	1.7
5	60	<0.016	<1.0	<1.0
6	80	<0.012	<1.0	<1.0

[a] Calculated using PS standard (universal calibration), PDI ~ 1.6–2.0.
[b] Functionalities were measured in triplicate and the results were reproducible to within 5% except for entries 5 and 6.
[c] # of functional groups on a single chain [$f_n = [NH_2]$ (in mmol/g) × M_n of PB (in kg/mol)].
[d] # of functional groups on a single chain, calculated based on % conversion of PS-anh.
[e] f_n cannot be >2.0; this value is due to the uncertainty in M_n.

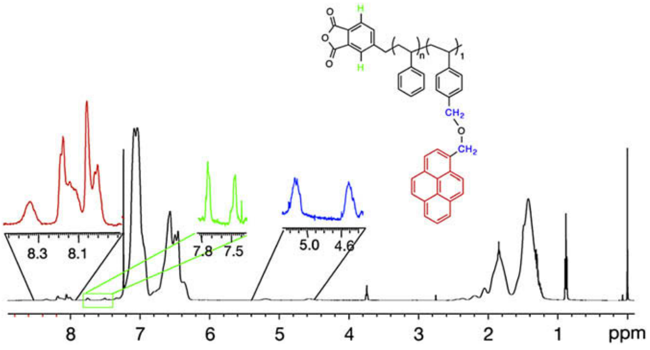


Fig. 1. ^{1}H NMR spectrum of pyrene-PS-anh **7**.

5.2 ppm. The amount of pyrene incorporation was quantified by comparing its peak areas to the areas of polystyrene backbone. A 120:1 ratio of **5** to **6** was measured based on ^{1}H NMR analysis of the resulting polymer, which also supported the hypothesis that the two monomers had similar reactivity. Furthermore, the relative ratios between the resonances for protons residing within the pyrenic vs. terminal phthalic anhydride subunits indicate a ratio of *ca.* 4.6:1 (9H vs. 2H), which is consistent with above 120:1 ratio, assuming every chain carries the initiating anhydride subunit. The molecular weight was determined by GPC equipped with three detectors (UV, RI and fluorescence) using THF as eluent at 25 °C. The number average molecular weight (M_n) was 13.2 kg/mol with a PDI of 1.11 relative to polystyrene standards and $f_n = 1.00 \pm 0.05$, determined by coupling with an excess amount of amine-terminated poly(ethylene glycol) followed by GPC analysis. Since the fluorescence detector has greater sensitivity, PS with only a few percent of pyrene functionality is sufficient for the dilution studies described below [16]. Anhydride-terminated PS without pyrene was also synthesized by ATRP with $M_n = 11.8$ kg/mol, $f_n = 1.00 \pm 0.05$.

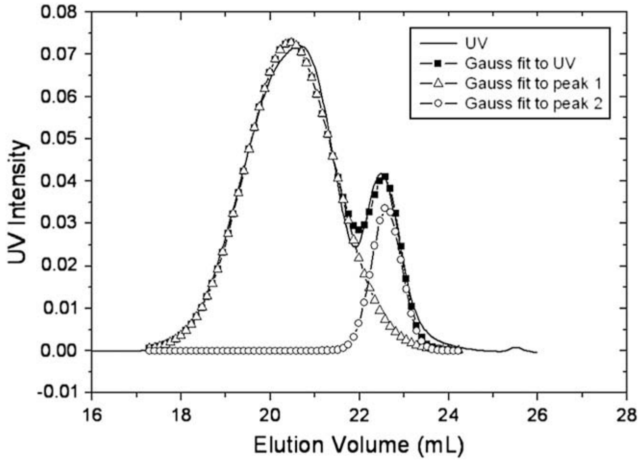
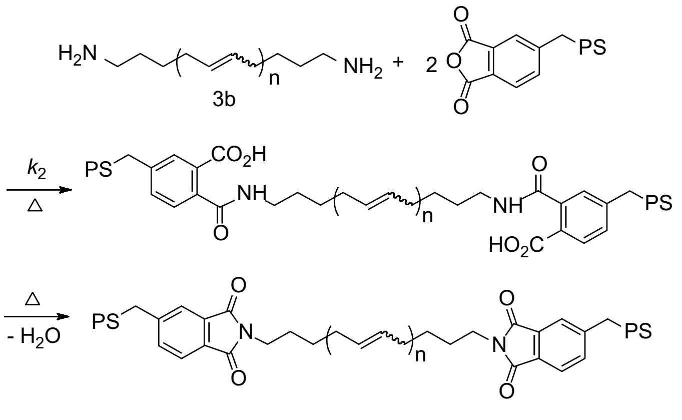


Fig. 2. GPC results for a 30 s reaction aliquot at 180 °C. Peak deconvolution of the UV signal by Gaussian distribution using Origin® software. The conversion of PS-anh was calculated based on the peak areas of the newly formed peak and the remaining PS-anh peak.

3.3. *Reactive coupling in the melt*

Reactive blending of PS-anh and NH_2–PB–NH_2 resulted in the formation of SBS through imide linkage, via the amic acid intermediate (Scheme 3). In each run, typically about 150 mg of PB (~20 μmol of NH_2, $M_n = 15.5$ kg/mol, $f_n \sim 1.9$) and 230 mg of PS (~20 μmol of anhydride, $M_n = 11.8$ kg/mol, $f_n \sim 1.0$) were used. Samples (~10 mg) were taken at different time intervals, and the reaction conversion was determined by gel permeation chromatography (GPC) by peak deconvolution of UV ($\lambda = 254$ nm) curves using 2-peak Gaussian distribution (Fig. 2). Since PB has no absorbance at 254 nm and the UV detector is only sensitive to the PS block (no PB signals were detected), PB does not interfere with the determination of PS-anh conversion. At three different temperatures (120 °C, 150 °C, 180 °C) studied, the reactions reached maximum conversion within 30–60 s, the shortest time that we could remove samples from the mixer (Fig. 3). Increasing reaction time (up to 30 min) did not increase the conversion. The conversion (~67%) at 120 °C was slightly lower than the conversions (~80%) at 150 and 180 °C. We believe that phase separation may have occurred at 120 °C, thereby preventing further reaction.



Scheme 3. Reaction of PS-anh with NH_2–PB–NH_2 **3b**.

The rate of amic acid formation is expected to be much faster than imidization, but the conversion of amic acid to imide does not affect the GPC measurement (Scheme 3). Thus we assume second-order kinetics between amine and anhydride:

$$\frac{-\mathrm{d}[\mathrm{Anh}]}{\mathrm{d}t} = k_2[\mathrm{NH_2}][\mathrm{Anh}] \tag{1}$$

Assuming equal molar concentration for amine and anhydride, and integrating gives:

$$k_2 = \frac{\dfrac{1}{[\mathrm{Anh}]_t} - \dfrac{1}{[\mathrm{Anh}]_0}}{t} \tag{2}$$

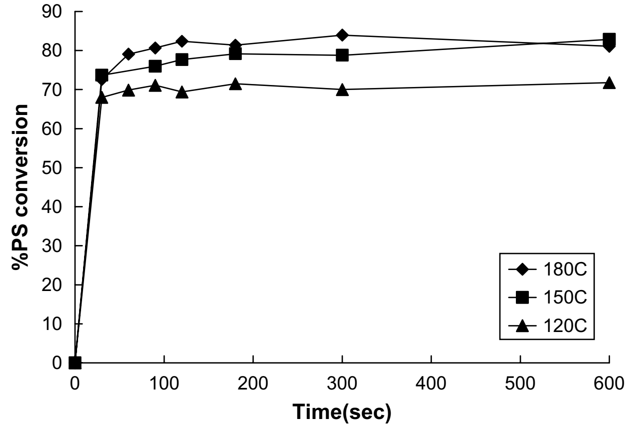


Fig. 3. Conversion of PS-anh (11.8 kg/mol) vs. time of reaction with NH_2–PB–NH_2 (15.5 kg/mol) at three different temperatures. All coupling reactions were essentially complete within 30 s. Results are based on GPC peak deconvolution.

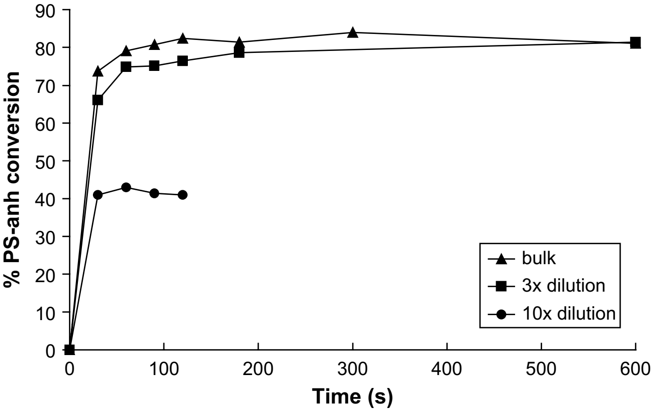


Fig. 4. Conversion of PS-anh vs. time of reaction with NH_2–PB–NH_2 (15.5 kg/mol) at 180 °C. Bulk data from Fig. 3. Dilutions with non-reactive PS (19.7 kg/mol) and pyrene labeled PS-anh (13.2 kg/mol).

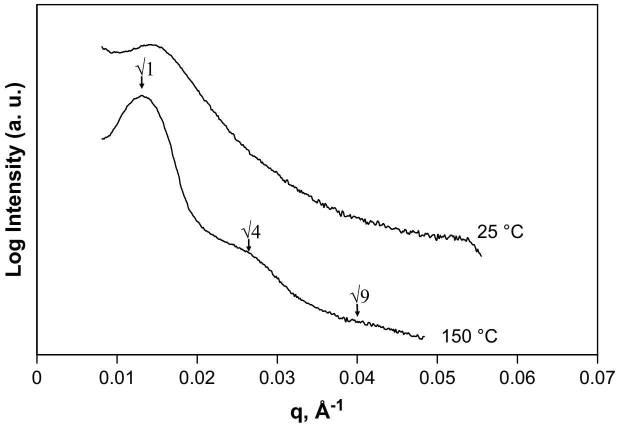


Fig. 5. Small angle X-ray scattering (SAXS) profiles of the coupling product of PS-anh (11.8 K) and NH_2–PB–NH_2 (25.5 K) at 25 °C as quenched and after being annealed 30 min at 150 °C. For clarity, the curve at 25 °C has been vertically shifted.

Using the first data points in Fig. 3 gives $k_2 = 80$, 120 and 120 kg mol^{-1} min^{-1} at 120, 150 and 180 °C, respectively [17]. These values are conservative since the reaction was too fast to measure conversion at short time (<30 s) using our technique.

3.4. Fluorescence labeling and dilution study

To determine the reaction rate constant more accurately, we diluted the number of functional groups by addition of non-functional (unreactive) polystyrene, thereby slowing the reaction and permitting us to monitor the reaction progress. A pyrene labeled anhydride-terminated polystyrene (**7**, pyrene-PS-anh) was used for this coupling study. The non-functional PS was not labeled; the GPC equipped with a fluorescence detector ($\lambda_{ex} = 348$ nm; $\lambda_{em} = 396$ nm) only detected pyrene-PS-anh and its coupled copolymer.

Two dilution experiments were performed at 180 °C. First, a twofold excess of non-functional polystyrene ($M_n = 19.7$ kg/mol) was blended with pyrene-PS-anh ($M_n = 13.2$ kg/mol, PDI = 1.11) and NH_2–PB–NH_2 ($M_n = 15.5$ kg/mol, $f_n = 1.9$; equal moles of NH_2 and anh). The concentrations of both amino and anhydride groups were lowered by a factor of three. The conversion of PS-anh was calculated based on the areas of the deconvoluted GPC peaks, and plotted in Fig. 4. The reaction was still fast with little further conversion after 30–60 s, and the final conversion of the coupling reaction was similar to that of undiluted reactions. In a second experiment the reaction system was diluted by a factor of 10. Using Eq. (2) for 3× (67% initial conversion) and 10× dilution (40% conversion) gives second-order rate constants to be > 250 kg mol^{-1} min^{-1} and >280 kg mol^{-1} min^{-1}, respectively [18].

The amine and anhydride reaction is known to be very fast. For homogeneous coupling of anhydride terminal PS with aliphatic amine terminal PS, Orr et al. reported reaction rates of 1400 kg mol^{-1} min^{-1} [19]. For heterogeneous coupling Jones et al. found reaction rates and total conversion decreased significantly, inversely correlated to the polymer–polymer interaction parameter χ [20]. They argued that functional pairs with high χ have thin interfaces and low volume for functional groups to come into contact resulting in slower reaction. Using their first conversion data point and Eq. (2) we calculated the second-order rate constants shown in Table 2. Indeed k_2 decreases with the increase of χ and our rate constant is in reasonable agreement with that found by Jones et al. for PS–NH_2 with PB-Anh. It is very difficult to compare reaction rates for heterogeneous coupling since they depend on the morphology, *i.e.* the amount of interface available to the functional groups. Jeon et al. used SEM images of several reactive blends to estimate the interfacial area [21]. With this and the thickness of the interface they calculated a volume fraction available for reaction (1–5%), which gave $k_2 = 1000$–4000 kg mol^{-1} min^{-1}.

Fig. 4 shows that for the 10× diluted case the reaction stopped after 30 s and the final conversion was *ca.* 40 mol% (Fig. 4). This is much lower than the conversions of undiluted or 3× dilution reactions. Moon et al. also observed ~40% conversion when 8.3% of PMMA-anh was used [16]. One explanation for such low conversion could be that PB forms a droplet morphology in the PS matrix, and the block copolymer present at the interface prevented further conversion [16,21]. It is also possible that unknown side reactions are present. They would be much more significant at lower concentration of the main reactants.

3.5. Characterization of resultant copolymers

The coupling of a 2:1 weight ratio of PS-anh (11.8 K) and NH_2–PB–NH_2 (25.5 K) was also studied. The crude mixture was analyzed

Table 2
Second-order reaction rate constants for coupling of amine and anhydride-terminated polymers at 180 °C

	Anhydride (M_n, kg/mol)	Amine (M_n, kg/mol)	k (kg mol^{-1} min^{-1})	χ	References
Homogeneous	PS-Anh (34.5)[a]	PS–NH_2 (20.9)	1400	0	[19]
Heterogeneous	PMMA-anh (15)[b]	PS–NH_2 (26)	121	0.037	[19]
	PB-anh (25)[b]	PS–NH_2 (18)	250[c]	0.024	[20]
	PS-anh (35)[b]	PEE–NH_2 (18)	25[c]	0.038	[20]
	PDMS-(anh)$_2$ (28)[b]	PEE–NH_2 (18)	10[c]	0.055	[20]
	PDMS-(anh)$_2$ (28)[b]	PS–NH_2 (15)	8[c]	0.18	[20]
	PS-anh (13.2)[b]	NH_2–PB–NH_2 (15.5)	>280[c]	0.024	This work

[a] Succinic anhydride.
[b] Phthalic anhydride.
[c] Calculated from the conversion of the first data point using Eq. (2).

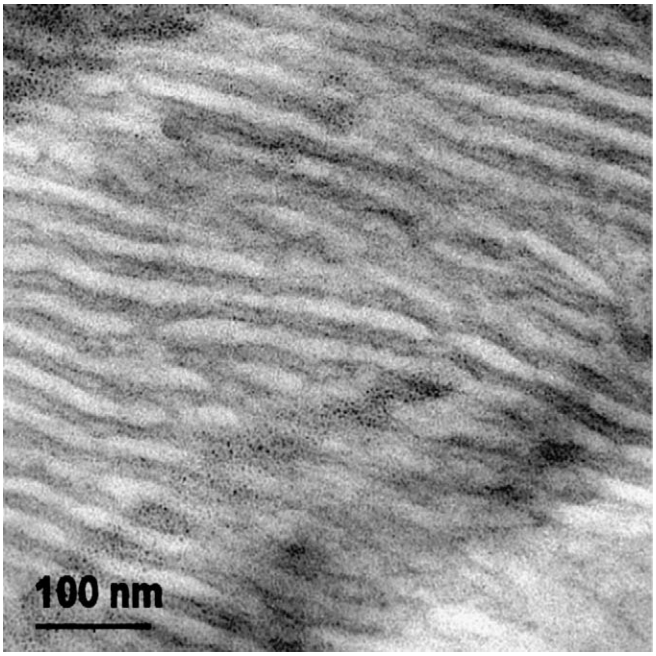


Fig. 6. TEM micrograph of the coupling product of PS-anh (11.8 K) and NH_2–PB–NH_2 (25.5 K) after 30 min annealing at 150 °C. Stained with OsO_4 vapor for 45 min.

by GPC equipped with a UV detector, and ~87% PS-anh was converted to copolymer. *Ca.* 67 wt% of SBS triblock copolymer and 26 wt% of SB diblock copolymer were obtained assuming all PBs had either one or two amino groups and all amino groups reacted with PS-anh. The morphology of the resulting copolymers was studied by small angle X-ray scattering (SAXS). The coupling product was quenched and pressed into a disk with 1 mm thickness. The SAXS profile of the sample at 25 °C showed a broad reflection at $q = 0.014$ Å^{-1}. The sample was then annealed at 150 °C for 30 min. Two evenly spaced broad reflections were observed, indicating formation of lamellar morphology (Fig. 5), and the intensity of the peak near 0.014 Å^{-1} also increased [22]. The lamellar morphology provides evidence of formation of 12–25–12 SBS triblock copolymer. The domain size, d, was calculated to be ~45 nm from the peak position q ($d = 2\pi/q$). However, the peaks in the SAXS pattern were very broad. Lynd and Hillmyer reported the effect of PDI on the morphology of a PEP–PLA diblock copolymer [23]. A lamellar morphology was obtained for their symmetrical diblock copolymers even for broad PDIs of their PLA blocks. They found that the position of the principal spatial frequency decreased with the increase of the PDI of one block. Additionally, the scattered intensity decreased as the PDI increased. The large PDI of the middle polybutadiene block in SBS and the presence of SB diblock copolymers likely contribute to the peak broadening in the X-ray pattern.

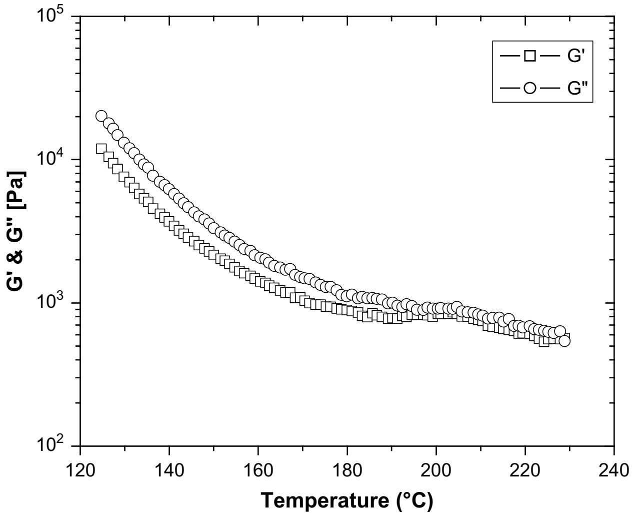


Fig. 7. Temperature-dependent dynamic storage (G') and loss (G'') moduli for the coupling product of PS-anh ($M_n = 11.8$ K) and NH_2–PB–NH_2 ($M_n = 25.5$ K) at 2% strain amplitude and a frequency of 2 rad/s, heated at 5 °C/min.

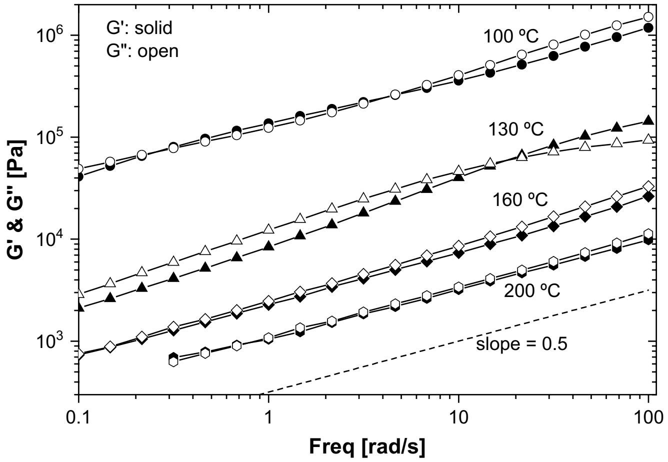


Fig. 8. Storage (G', solid) and loss (G'', open) moduli of the SBS copolymer from Fig. 7 at varying temperatures.

In order to confirm that we have lamellar morphology of the coupling products, the sample from the SAXS measurement was microtomed to ~70 nm thin films at −150 °C and imaged by TEM. A representative TEM image is shown in Fig. 6; it confirms the SAXS results and the lamellar morphology.

Dynamic moduli are shown in Fig. 7 as a function of temperature. There was no terminal drop in moduli at temperatures below 225 °C, which indicates that the order–disorder transition (ODT) temperature of the reactively formed SBS is higher than 225 °C. Fig. 8 shows the frequency-dependent moduli at 2% strain at several temperatures (100–200 °C). Both G' and G'' exhibited similar dependence on frequency, proportional to $\omega^{1/2}$, and were nearly equal to each other which is typical behavior for lamellar morphology [24]. Since no typical terminal viscoelastic behavior was observed, the ODT is >200 °C.

The resulting coupling product was also studied by differential scanning calorimetry (DSC). The melting peak, which started at approximately −9 °C in the heating curve with the peak position at 26 °C, of *trans*-PB (~65% *trans*- for PB block based on ^{1}H NMR analysis) was observed. The PS block has a T_g of ~81 °C, while the T_g of the PB block was not observed in the temperature range that we studied (greater than −100 °C). The temperature was raised to 280 °C in order to identify the ODT. However, it is typically difficult to determine an ODT by DSC. Moreover, the PB blocks crosslinked at high temperatures even with addition of Irganox 1010 as the antioxidant.

4. Conclusions

For the first time high molecular weight, high functionality diamino telechelic polybutadienes (**3b**, diamino TPBs, M_n up to 38 kg/mol, $f_n > 1.7$), have been synthesized. This was achieved by ring-opening metathesis polymerization (ROMP) of high purity 1,5-cyclooctadiene (COD) in the presence of 1,8-dicyano-4-octene as the chain transfer agent followed by lithium aluminum hydride reduction to the diamine. The fluorescently labeled pyrene-PS-anh **7** was synthesized by copolymerization of 1-[(4-vinylbenzyloxy)methyl]pyrene (**6**) and styrene using bromomethylphthalic anhydride as the initiator via ATRP. The melt coupling of a diamino TPB with PS-anh resulted in the formation of a styrene–butadiene–styrene (SBS) triblock copolymer, the lamellar morphology of which was confirmed by SAXS and TEM measurements. This coupling strategy, an alternative to anionic polymerization for the synthesis of SBS, should allow for processing at a lower temperature than that conventionally used with preformed SBS. Rapid conversion of PS-anh was achieved within 30 s even at 120 °C. The reaction rate constant estimated from the first data point at 30 s was greater than 280 kg mol^{-1} min^{-1} and is consistent with previous reports.

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[17] Anhydride bulk concentration is 84.7 mmol/kg for PS-anh ($M_n = 11.8$ kg/mol). The initial concentration of PS-anh, $[\text{Anh}]_0 = 50$ mmol/kg (=84.7 mmol/kg × wt% of PS), was used for the calculation using Eq. (2).
[18] Anhydride bulk concentration is 75.8 mmol/kg for PS-anh ($M_n = 13.2$ kg/mol). The initial concentration of PS-anh, $[\text{Anh}]_0 = 48$ mmol/kg (=75.8 mmol/kg × wt% of PS), for the non-diluted sample was used for the calculation using Eq. (2).
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