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Synthesis and Phase Behavior of Block-Random Copolymers of Styrene and Hydrogenated Isoprene

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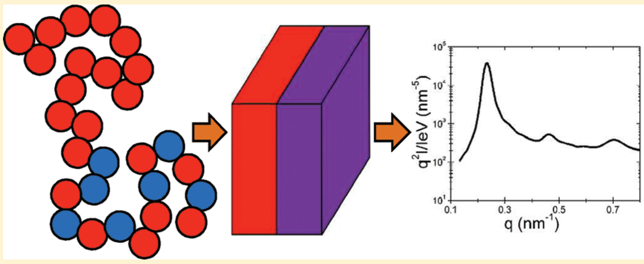
S *Supporting Information*

ABSTRACT: "Block-random" copolymers—wherein one or more blocks is itself a random copolymer—present a useful and convenient variation on the typical block copolymer architecture, as the interblock interactions and physical properties can be tuned continuously through the random block's composition. However, typical living or controlled polymerizations produce compositional gradients along the "random" block, which can in turn influence the phase behavior. Organolithium initiation in a cyclohexane/triethylamine mixture is shown herein to yield narrow-distribution copolymers of styrene and isoprene of any desired composition, with no measurable down-chain gradient. These random copolymers (S*r*I) are also successfully incorporated into well-defined symmetric block copolymers (I-S*r*I diblocks). Isoprene-selective hydrogenation yields thermally stable hI-S*r*hI diblocks, which self-assemble into well-defined lamellar morphologies with sharply defined order−disorder transitions, whose temperatures T_{ODT} scale predictably with diblock molecular weight. The use of S*r*hI in lieu of a styrene homopolymer block allows the diblock molecular weight and domain period to be substantially increased for a given value of T_{ODT}. The measured interaction energy density between hI and S*r*hI is consistent with the mean-field "copolymer equation", providing a first step toward the design of styrene−isoprene block-random copolymers of desired molecular weight and T_{ODT}.



INTRODUCTION

When monomers are simultaneously copolymerized by a "living" mechanism, a composition gradient along the chain typically results, since the reactivity ratios are generally different from unity. Living polymerizations which proceed with random monomer addition (no gradient) are often sought because they permit the synthesis of well-defined polymers of tunable composition (hence tunable properties) which are effectively homogeneous on length scales larger than the monomer size.[1] Such chemistries also permit the synthesis of "block-random" copolymers, such as diblock copolymers represented generally by the structure $(A_xB_{1-x})-(A_yB_{1-y})$, where each of the two blocks is a random copolymer of monomers A and B, simply with different fractions of A (x and y). Since x and y can be varied continuously, the effective interaction parameter between the blocks can be varied continuously as well, allowing the order−disorder transition temperature (T_{ODT}) to be tuned independently of molecular weight using only two monomers, via the difference[2] between x and y. Moreover, physical properties, such as the block glass transition temperatures, can be tuned through the absolute magnitudes of x and y. This flexibility makes block-random copolymers a versatile platform for the exploration of polymer phase behavior and structure−property relationships.

Some success has been obtained in synthesizing block-random copolymers by controlled radical methods, in cases where the reactivity ratios are intrinsically close to unity;[3,4] gradient-free statistical copolymer blocks can also be prepared when the monomer composition is at the azeotropic point.[5] But in radical polymerizations, the reactivity ratios are usually insensitive to the polymerization environment (solvent composition), permitting little variation in the monomer sequencing. Anionic polymerizations, by contrast, are typically very sensitive to solvent, additives, cation type, etc., permitting the reactivity ratios to be tuned significantly.[6] For example, in alkyllithium-initiated copolymerizations of styrene and butadiene (SB) in cyclohexane, the reactivity ratios[6] (at 25 °C) are reported as $r_S = 0.04$ and $r_B = 15.5$; in a living polymerization, such reactivity ratio values yield an architecture resembling a block copolymer, as butadiene is preferentially added in the initial stages of the polymerization, and only when nearly all the butadiene is consumed does a significant fraction of styrene begin to be incorporated into the chain. By contrast, in tetrahydrofuran (at −78 °C), the reactivity ratios[6] are $r_S = 11.0$ and $r_B = 0.04$, producing essentially the inverse of the gradient obtained in cyclohexane. To achieve SB copolymers free from any down-chain composition gradient, Halasa and co-workers[7,8] have shown that adding *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) to copolymerizations in hexane, in a molar ratio of at least 2:1 TMEDA:Li, effectively randomizes the monomer sequence (both reactivity ratios ≈1.4) while maintaining the living character of the polymerization.[8]

Received: April 20, 2011
Published: May 09, 2011

Such random SB copolymers have been successfully incorporated as blocks in well-defined block-random copolymers.[9]

It would be desirable to achieve similar random copolymerizations of styrene and isoprene (SI) to expand the accessible range of polymer properties. In particular, hydrogenated high-vinyl polyisoprene has an exceptionally low cohesive energy density,[10] lower than that for hydrogenated high-vinyl polybutadiene, meaning that a broad range of solubility parameters (>2 MPa$^{1/2}$, as shown herein) could be accessed in random copolymers containing styrene and hydrogenated vinyl isoprene (hI) units. This increased range of solubility parameters translates directly into an increased range of the interblock Flory−Huggins interaction parameter χ in block-random copolymers. The reactivity ratios for SI in hydrocarbon and ether solvents are qualitatively similar to those for SB,[6] but despite the seemingly minor difference between butadiene and isoprene, TMEDA is not an effective randomizer for SI copolymerizations.[8] The addition of substoichiometric amounts of potassium alkoxides to alkyllithium-initiated SB copolymerizations in hydrocarbon media has been shown to produce gradient-free styrene-*ran*-butadiene (S*r*B) copolymers at a suitable K:Li ratio,[11,12] and while this approach has also been applied to SI copolymerizations,[2,13] it has not been shown that the resulting SI copolymers are gradient-free. Over half a century ago, Kelley and Tobolsky[14] showed that triethylamine (TEA) is an excellent randomizer for equimolar SI copolymerizations (∼60 wt % S). Later, Annighöfer and Gronski[15] used a TEA/benzene mixture (20/80 v/v) to synthesize S-S*r*I-I triblock copolymers with styrene-*ran*-isoprene (S*r*I) midblocks (∼50 wt % S); they reported reactivity ratios $r_I = 1.0$ and $r_S = 0.8$, implying that effectively random copolymers could be synthesized at essentially any S:I ratio with this approach.

Here, we show that alkyllithium-initiated polymerizations in TEA/hydrocarbon mixtures can indeed produce narrow-distribution SI copolymers with no significant composition gradient over the full range of S:I ratios; that this approach can also be used to synthesize diblock copolymers, whose isoprene units can be hydrogenated selectively; and that near-symmetric "block-random" copolymers of this type self-assemble into well-ordered lamellar structures with sharply defined order−disorder transitions, whose temperatures are consistent with dilution of the repulsive S−hI interactions through copolymerization.

EXPERIMENTAL SECTION

Synthesis. Polymers were synthesized at a final solids concentration of ∼15 wt %, in a 50/50 vol mixture of cyclohexane and triethylamine (TEA) unless otherwise noted. Glass reactors were flamed out under vacuum and rinsed with *tert*-butyllithium and subsequently with cyclohexane prior to charging with initiator (*tert*-, *sec*-, or *n*-butyllithium) in a nitrogen-filled glovebox. A 50/50 vol mixture of cyclohexane/TEA, or pure cyclohexane for polymerizations not employing TEA, was stirred over diphenylhexyllithium (adduct of *sec*-butyllithium and 1,1-diphenylethylene), degassed via freeze−pump−thaw (FPT) cycles, and vacuum transferred directly into the reactor. For statistical copolymerizations, styrene and isoprene monomers were mixed, stirred over dibutylmagnesium, degassed via FPT cycles, and vacuum transferred into the reactor. Isoprene monomer for homopolyisoprene blocks was handled analogously but stirred over *n*-butyllithium. TMEDA was stirred over *sec*-butyllithium, degassed, vacuum transferred, and diluted in cyclohexane; for polymerizations incorporating TMEDA, aliquots of this solution were charged to the reactor in the glovebox, along with the initiator. Statistical copolymerizations, including the random blocks in block-random copolymers, were run at 30 °C, while isoprene homopolymerizations were performed at 60 °C except where noted. In block copolymerizations, an aliquot of the reaction mixture was collected immediately prior to the second monomer charge to permit characterization of the first (homopolyisoprene) block.

Polymers were catalytically hydrogenated using a homogeneous Ni−Al catalyst to selectively saturate the isoprene units while retaining the styrene aromaticity.[16,17] Saturations were performed in a 2 L Parr batch reactor with 7−10 g/L polymer in cyclohexane. The catalyst was prepared by mixing triethylaluminum (1 M in hexanes, 10 mL) with nickel 2-ethylhexanoate (0.1 M in cyclohexane, 30 mL) in a dry round-bottom vessel previously purged with N_2. The catalyst was injected directly into the reactor followed by N_2 and H_2 purges before a final charge of H_2 was added. Hydrogenations were conducted at 80 °C and 400−500 psi H_2. Catalyst deactivation typically mandated multiple catalyst charges to achieve complete saturation. The extent of hydrogenation was monitored with ^{1}H NMR on samples taken from the reactor, and upon completion (>99% of the isoprene units saturated, corresponding to the detectability limit), the catalyst was removed by vigorous stirring with aqueous citric acid (16 wt %) until the catalyst color disappeared. Polymers were recovered by precipitating into methanol.

Characterization. Gel permeation chromatography (GPC) was conducted at 35 °C using two 30 cm Polymer Laboratories PLgel Mixed-C columns and a Waters 410 refractive index detector. THF was used as the mobile phase, and the system was calibrated with narrow-distribution polystyrene standards. The apparent "polystyrene-equivalent" molecular weights obtained by GPC were converted to the true values by correcting for the differences in hydrodynamic volume[18] between polystyrene and homopolyisoprene or S*r*I (see Supporting Information for details). Composition of the polymer aliquots was determined using ^{1}H NMR conducted at 500 MHz on either a Varian INOVA or Bruker AVANCE, using the areas of the styrene aromatic protons and the various isoprene olefinic protons corresponding to different modes of addition (1,4/3,4/1,2). Small-angle X-ray scattering (SAXS) patterns were collected with an Anton-Paar compact Kratky camera fitted with a hot stage, a PANalytical PW3830 X-ray generator with a long-fine-focus Cu tube producing Cu Kα radiation ($\lambda = 0.154\,18$ nm), and an MBraun OED-50 M position-sensitive detector. Data were corrected for detector sensitivity and positional linearity, empty beam scattering, sample thickness and transmittance, placed on an absolute intensity scale via a polyethylene standard, and desmeared for slit length.[19] Absolute SAXS intensities (I/I_eV) are plotted against the magnitude of the momentum transfer vector $q = (4\pi/\lambda)\sin\theta$, where θ is half the scattering angle; calibration was via silver behenate.[20] Intensities were multiplied by q^2 to approximately correct for the form factor of lamellae.[21]

RESULTS

Polymerization in Cyclohexane. Statistical copolymerization of styrene and isoprene in cyclohexane was performed using *sec*-butyllithium as initiator; aliquots were taken throughout the polymerization and assayed for cumulative styrene content in the polymer by ^{1}H NMR. In neat cyclohexane a strong gradient is expected from the reported reactivity ratios,[22] $r_S = 0.046$ and $r_I = 16.6$ (at 40 °C), yielding an architecture approaching that of a diblock copolymer, where the first block is isoprene-rich and the second is styrene-rich. This gradient is confirmed in Figure 1, where the cumulative styrene content in the polymer is plotted against the ratio of the aliquot's number-average molecular weight (M_n) to the final M_n, where the "polystyrene-equivalent" M_n values are used. Since the copolymer composition changes with conversion during this polymerization, the factor relating the hydrodynamic volume of the copolymer chain to that of polystyrene[18] also changes; thus, the apparent M_n/M_n(final) is not precisely equal to the monomer conversion, but the strong gradient is nonetheless quite clear in Figure 1. Final molecular weight and microstructure for this polymer (SI-CH), and all other SI statistical copolymers, are displayed in Table 1.

For polymerization in cyclohexane with the polar modifier TMEDA, a concentration of 4:1 TMEDA:Li was chosen; polymerizations were initiated with either *tert*- or *n*-butyllithium, yielding SI-TMEDA-1 and SI-TMEDA-2, respectively. The resulting polymers do exhibit the expected increase in vinyl content in the presence of TMEDA, but they also show a strong down-chain composition gradient, in the opposite direction as for the polymer synthesized in pure cyclohexane. In effect, the preferentially incorporated monomer shifts from isoprene to styrene with addition of the TMEDA. While it is possible that a lower level of TMEDA could randomize SI copolymerizations, the TMEDA level would likely need to be adjusted for different monomer feed ratios, temperatures, and Li concentrations. A reaction system that can robustly produce random copolymers over a broad range of compositions, temperatures, and molecular weights—as adding TMEDA to hexane or cyclohexane does for SB statistical copolymerizations—would be far more desirable.

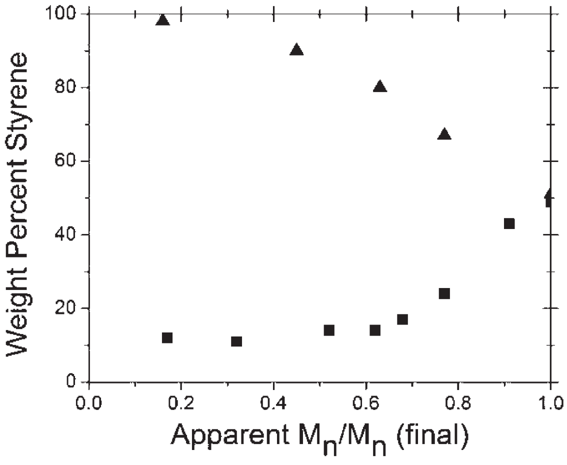


Figure 1. Cumulative styrene content in the polymer during two statistical copolymerizations of styrene and isoprene at 30 °C, both showing pronounced down-chain composition gradients: (■) SI-CH, synthesized in cyclohexane, and (▲) SI-TMEDA-2, synthesized in cyclohexane with 4:1 TMEDA:Li added. Abscissa is apparent conversion: M_n/M_n(final), where M_n is the polystyrene-equivalent value. Final conversion is a few percent short of 100% here, so the final styrene content does not quite reach 50 wt % in either case.

Polymerization in Triethylamine/Cyclohexane. Statistical copolymers of styrene and isoprene with targets of 20, 50, and 80 wt % styrene, denoted S*r*I-0.20, S*r*I-0.50, and S*r*I-0.80, were synthesized in a 50/50 vol mixture of triethylamine (TEA) and cyclohexane at 30 °C. Homopolystyrene is not soluble in pure TEA; the 50/50 mixture allows SI copolymerizations to remain homogeneous for any copolymer composition. At a polymerization temperature of 30 °C, we find a homopolyisoprene microstructure of 4% 1,2-, 49% 3,4-, and 47% 1,4-addition, consistent with that reported by Tobolsky and Rogers[23] for isoprene polymerization in TEA at 30 °C initiated by Li metal (3% 1,2-, 45% 3,4-, 52% 1,4-). Our measurements show that the isoprene microstructure depends weakly on both polymerization temperature (1,4-content increases from 47% to 53% upon raising the polymerization temperature from 30 to 60 °C) and comonomer content (at 30 °C, 1,4-content increases from 47% to 51% on going from homopolyisoprene to S*r*I-0.50).

Styrene contents in the polymers are plotted in Figure 2. From this plot it is evident that polymerization in 50/50 cyclohexane/TEA yields a consistently flat composition profile; since there is no significant down-chain gradient in this case, the apparent M_n/M_n(final) is indeed equal to the monomer conversion. Note that S*r*I-0.50 was initiated with *tert*-butyllithium, whereas S*r*I-0.20 and S*r*I-0.80 were initiated with *n*-butyllithium; the GPC results confirm a narrow molecular weight distribution, $M_w/M_n < 1.1$, for all three copolymers. While the choice of butyllithium isomer

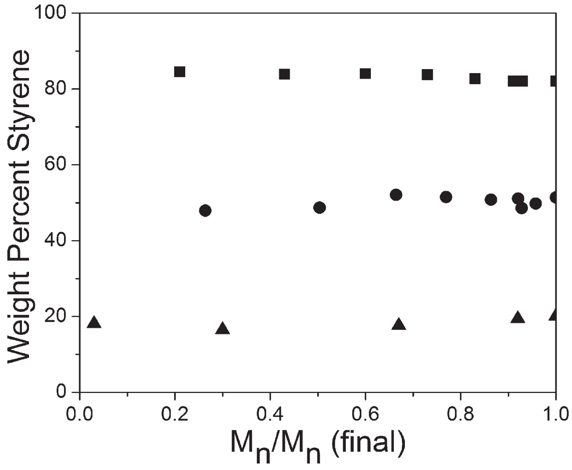


Figure 2. Cumulative styrene contents in the polymer during three statistical copolymerizations of styrene and isoprene in 50/50 TEA/cyclohexane, showing no significant down-chain composition gradient: (▲) S*r*I-0.20, (●) S*r*I-0.50, and (■) S*r*I-0.80.

Table 1. Molecular Characteristics of Statistical SI Copolymers

polymer	solvent system (initiator)	apparent M_n (kg/mol)[a]	M_w/M_n	wt % styrene	% vinyl[b] 3,4 (1,2)
SI-CH	cyclohexane (*t*-BuLi)	63.1	1.06	49	7 (0)
SI-TMEDA-1	cyclohexane with 4:1 TMEDA:Li (*t*-BuLi)	48.2	1.25	50	61 (13)
SI-TMEDA-2	cyclohexane with 4:1 TMEDA:Li (*n*-BuLi)	41.3	1.20	52	63 (13)
S*r*I-0.20	cyclohexane/TEA, 50/50 vol (*n*-BuLi)	53.9	1.06	20	47 (3)
S*r*I-0.50	cyclohexane/TEA, 50/50 vol (*t*-BuLi)	54.2	1.05	50	46 (3)
S*r*I-0.80	cyclohexane/TEA, 50/50 vol (*n*-BuLi)	68.4	1.05	82	[45 (3)][c]

[a] Determined by GPC in THF using RI detection, calibrated against PS homopolymer standards ("polystyrene-equivalent" molecular weight). [b] Percent of the isoprene units enchained as 3,4 (1,2), determined by ^{1}H NMR. [c] Extrapolated from the values for S*r*I-0.20 and S*r*I-0.50; extensive overlap of the olefinic resonances in the ^{1}H NMR spectrum for S*r*I-0.80 does not permit a direct determination of its isoprene microstructure.

Table 2. Molecular Characteristics of I-S*r*I Block-Random Copolymers

polymer	block	true M_n (kg/mol)[a]	M_w/M_n	wt % styrene	% vinyl[b] 3,4 (1,2)
I-S*r*I-31	I	15.2	1.05		44 (3)
	S*r*I	15.4		50	
	diblock	30.6	1.07	25	45 (2)
I-S*r*I-34	I	16.9	1.05		45 (2)
	S*r*I	16.7		51	
	diblock	33.6	1.08	25	45 (2)
I-S*r*I-39	I	19.7	1.06		43 (4)
	S*r*I	19.3		54	
	diblock	39.0	1.08	27	45 (2)
I-S*r*I-65	I	30.9	1.06		43 (3)
	S*r*I	33.7		51	
	diblock	64.6	1.07	26	46 (2)

[a] Determined by GPC in THF using RI detection, corrected for the differences in hydrodynamic volume with composition (homopolystyrene vs homopolyisoprene vs S*r*I); see Supporting Information for details. GPC measurements were conducted on aliquots of the I block and diblock; M_n for the S*r*I block was determined by difference. [b] Percent of the isoprene units enchained as 3,4 (1,2), determined by ^{1}H NMR.

should have no bearing on the chain composition profile, the ability to rapidly initiate is crucial to obtain near-monodisperse polymers; while *n*-butyllithium is somewhat slow to initiate in pure cyclohexane, evidently both isomers initiate sufficiently rapidly in the 50/50 cyclohexane/TEA mixture. Additionally, the conversion vs time data for the polymers in Figure 2 followed first-order kinetics with respect to monomer, with the polymerization rate increasing with styrene content (see Supporting Information); also, the glass transition temperatures, T_g, of the three S*r*I copolymers were adequately described by the Fox equation, as expected for homogeneous copolymers with no specific interactions between the monomers (see Supporting Information).

Block-Random Copolymers. With the ability to polymerize random copolymers of styrene and isoprene (S*r*I) confirmed, four block-random copolymers of homopolyisoprene with S*r*I (I−S*r*I diblocks) were synthesized, as summarized in Table 2. A composition of 50 wt % S for the S*r*I block was targeted; this produces a low glass transition temperature after hydrogenation (T_g = 11 °C, measured on S*r*hI-0.50 by differential scanning calorimetry at 10 °C/min), facilitating equilibration of the microdomain structure while retaining satisfactory X-ray contrast against hI. The isoprene block was synthesized at 60 °C, while the S*r*I block was synthesized at 30 °C; this change of temperature was made principally to adjust polymerization rate, but it also fortuitously compensates the change in isoprene microstructure with styrene content, such that the isoprene microstructure in both blocks is essentially identical (≈53% 1,4).

Figure 3 shows GPC traces for the first (I) block, the I−S*r*I diblock, and the diblock after hydrogenation (hI-S*r*hI), for a representative synthesis (I-S*r*I-31, where the number indicates the approximate total molecular weight in kg/mol). A monomodal and narrow molecular weight distribution is preserved throughout; the slight shift of the diblock peak to lower elution time upon hydrogenation simply reflects the small increase in hydrodynamic volume which accompanies the change from I-S*r*I to hI-S*r*hI. Table 2 shows molecular weight and compositional characteristics for all four block copolymers synthesized; these characteristics were generally quite close to the targets, as expected, though I-S*r*I-39 had an overall styrene content exceeding the target (27 wt % measured vs 25 wt % targeted), reflecting a metering error in the monomer mixture charged for the random block.

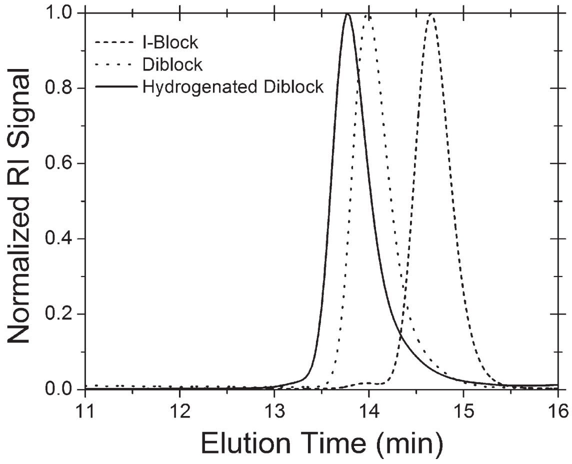


Figure 3. GPC traces taken at various points during the synthesis of the block-random copolymer hI-S*r*hI-31: (---) sample of the I block, removed from the reactor prior to the second monomer charge, showing a small amount of coupled material generated in the aliquot; (— — —) I-S*r*I-31 diblock; (—) diblock following selective hydrogenation of the isoprene units (hI-S*r*hI-31).

Table 3. Interaction Energy Densities from Block-Random Copolymers

polymer	φ_{hI} at 23 °C	T_{ODT} (°C)	X_{expt} (J/cm^3)[a]	f_S at T_{ODT}	X_{corr} (J/cm^3)[b]
hI-S*r*hI-31	0.53	87	0.88	0.44	0.89
hI-S*r*hI-34	0.53	105	0.83	0.45	0.81
hI-S*r*hI-39	0.54	181	0.82	0.48	0.70
hI-S*r*hI-65	0.51	>250			

[a] Calculated according to eq 1. [b] Corrected to 50 wt % S (f_S = 0.44) as $X_{corr} = X_{expt}(0.44/f_S)^2$.

Densities for the various blocks as functions of temperature were computed as follows: for hI, the density and ambient-pressure thermal expansion coefficient data of Graessley et al.[10,24] for hydrogenated polyisoprenes with 93% 1,4-addition (PEP) and 37% 1,4-addition (50SPI[25]) were employed and linearly interpolated by 1,4-content to the value appropriate for hI (53% 1,4-). For polystyrene (S), liquidlike densities were obtained using the correlation of Richardson and Savill[26] (based on data for $T > T_g$) for a narrow-distribution polystyrene homopolymer with M_n = 111 kg/mol. For the random copolymers, the density was computed as the harmonic mean of the hI and S densities, weighted by the hI and S weight fractions (i.e., assuming that the copolymer has the same average density as a coarse physical mixture of the two homopolymers). Since T_g for the S*r*hI block is below room temperature, use of the liquidlike correlation for the S density down to room temperature in this calculation is appropriate. The volume fraction of hI block, φ_{hI}, at room temperature for each diblock is given in Table 3.

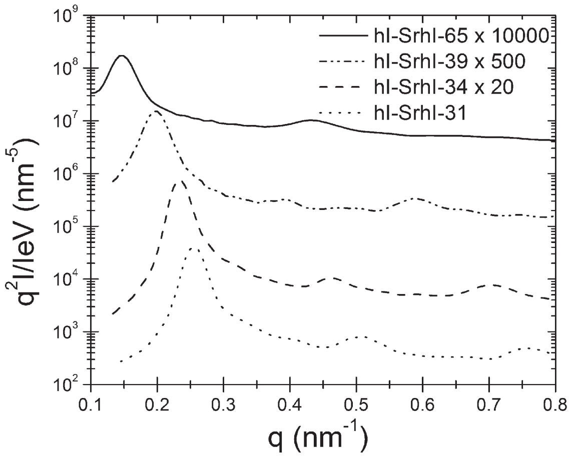


Figure 4. SAXS patterns of hI-S*r*hI block-random copolymers at room temperature. Intensities $q^2(I/I_eV)$ offset by the indicated factors for clarity.

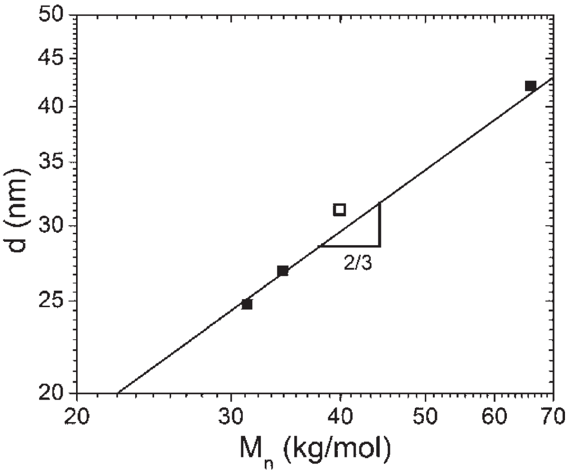


Figure 5. Lamellar *d* spacing at room temperature plotted against molecular weight for hI-S*r*hI block-random copolymers. Open symbol corresponds to hI-S*r*hI-39, which has a slightly higher styrene content in the S*r*I block. Line represents $d = 2.53(M_n)^{2/3}$, where *d* is in nm and M_n in kg/mol.

Room-temperature small-angle X-ray scattering (SAXS) patterns for all four diblocks are shown in Figure 4, on specimens compression-molded at 120 °C. All four diblocks adopt a lamellar microdomain structure, as evidenced by peaks in a q/q^* ratio of 1:2:3..., where q^* is the position of the first-order peak; however, the even orders of reflection are weak in these near-symmetric polymers ($\varphi_{\mathrm{hI}} \approx 1/2$). The lamellar repeat distance, $d = 2\pi/q^*$, is plotted in Figure 5; the lamellar spacings generally follow the anticipated $d \sim M_n^{2/3}$ scaling. Notably, the absolute magnitudes of the *d* values are quite close to (~5% larger than) the *d*-spacings for symmetric block copolymers of polystyrene and high-vinyl polyisoprene,[27] indicating that the differences between the two systems (incorporation of isoprene units into the styrene block, differences in statistical segment length, and increase in segmental interaction parameter upon hydrogenation of the isoprene units) fortuitously cancel out in their effects on *d*.

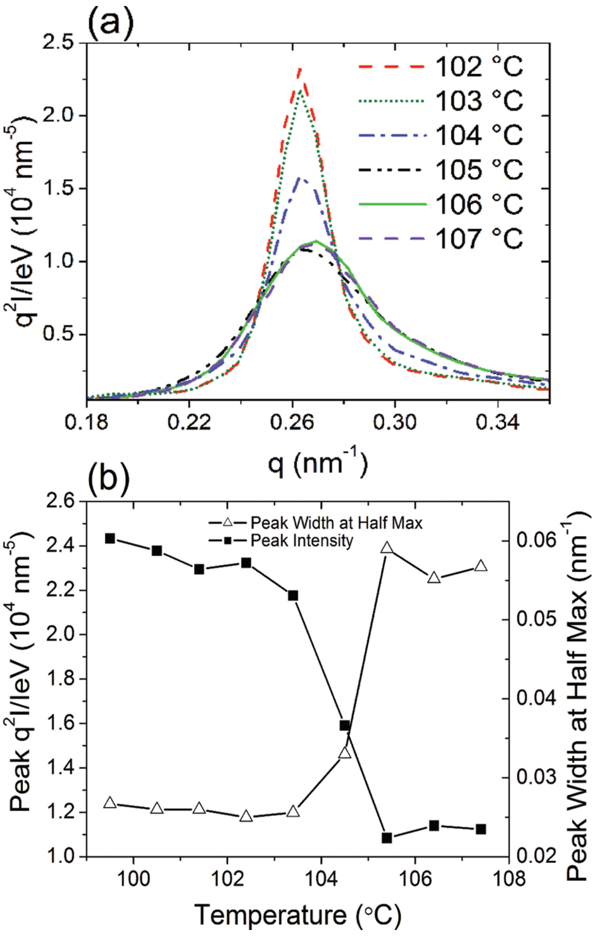


Figure 6. (a) SAXS patterns for hI-S*r*hI-34 near the order−disorder transition temperature, T_{ODT}. (b) SAXS peak intensity (■, left axis) and full width at half-maximum (Δ, right axis) plotted against temperature; T_{ODT} = 105 ± 1 °C.

SAXS patterns were also obtained for all four hydrogenated block-random copolymers at elevated temperatures to determine their order−disorder transition temperatures, T_{ODT}. At T_{ODT}, the peak intensity and breadth undergo a step decrease and a step increase, respectively.[28] No ODT was expected for hI-S*r*hI-65 due to its high molecular weight, and none was observed up to 250 °C. However, ODTs were both expected and observed in the other three block-random copolymers. Successive SAXS patterns at elevated temperatures for hI-S*r*hI-34 are shown in Figure 6, along with corresponding peak intensity and peak breadth data, indicating T_{ODT} = 105 ± 1 °C. Similar experiments on hI-S*r*hI-31 and hI-S*r*hI-39 yielded T_{ODT} values of 87 ± 1 and 181 ± 1 °C.

From these values of T_{ODT}, the interaction energy density between hI and S*r*I can be calculated:[17]

$$X = \chi(N\rho/M)RT = (\chi N)_{\mathrm{ODT}}\rho RT_{\mathrm{ODT}}/M \qquad (1)$$

The first equality in eq 1 shows the direct relationship between *X* and the Flory interaction parameter χ. For the second equality, the value of $(\chi N)_{\mathrm{ODT}}$ which corresponds to the volume fraction of hI (φ_{hI} calculated at T_{ODT}) was taken from the self-consistent-field phase diagram of Matsen and Bates[29] (e.g., $(\chi N)_{\mathrm{ODT}} = 10.6$ at $\varphi_{\mathrm{hI}} = 0.54$). Values of *X* are included in Table 3 and are plotted in Figure 7, where they appear to have an irregular dependence on inverse temperature. This irregularity is due to small variations in styrene content in the S*r*I block across the series, especially in hI-S*r*hI-39. To compensate for this difference, the

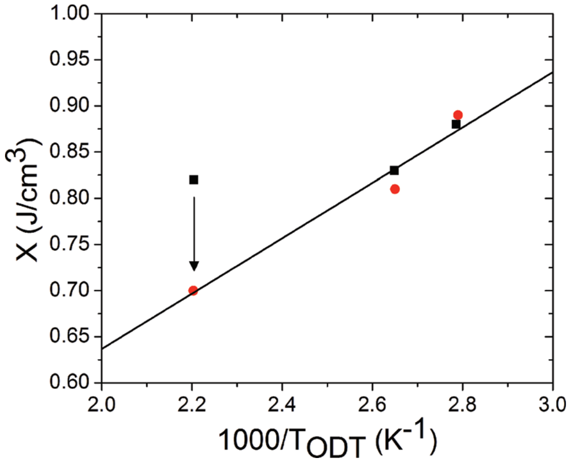


Figure 7. Interaction energy densities X between hI and S*r*hI. (■) Values directly measured from block-random T_{ODT} values, X_{expt}, and (●) values corrected to a common styrene content in the S*r*hI block (50 wt % S, $f_S = 0.44$), X_{corr}.

Table 4. Polymer Solubility Parameters and Mass Densities at 180 °C

polymer	δ (MPa$^{1/2}$)	ρ (g/cm^3)
S	16.29	0.9807
S*r*hI[a]	14.81	0.8628
EP	14.29	0.7663
hI	13.97	0.7702

[a] With $f_S = 0.44$ (50 wt % styrene).

experimental X values (X_{expt}) for these diblocks were scaled by $f_S{}^2$, where f_S is the volume fraction of styrene units in the S*r*I block (values given in Table 3). The $f_S{}^2$ scaling is that predicted from mean-field theory:[30] $\chi_{eff} = f_S{}^2\chi_{hI/S}$, the well-known "copolymer equation". A value of $f_S = 0.44$ (50 wt % S at 180 °C) was chosen for reference; the corrected values, X_{corr}, are also given in Table 3 and plotted in Figure 7. After correction, X is seen to decrease monotonically with $1/T$, as expected. This correction demonstrates that X (hence χ_{eff}) can be sensitively tuned in these systems through adjustment of f_S—and as noted in Figure 2, essentially any value of f_S can be achieved in the S*r*I block. Moreover, the simple mean-field scaling ($X \sim f_S{}^2$) seems to be a satisfactory guideline for tuning the random block composition, a point which we will return to below.

Within the context of mean-field theory, as in the Flory−Huggins model, X is related to the difference in solubility parameters (δ) of the two blocks as $X = (\Delta\delta)^2$. The measured values of X_{corr} thus allow us to rank S*r*hI in solubility parameter relative to other polymers, particularly the saturated hydrocarbon polymers studied extensively by Graessley and co-workers.[10,24] We choose as the reference polymer hydrogenated low-vinyl polyisoprene (93% 1,4-addition), usually referred to as poly(ethylene-*alt*-propylene) or PEP; we set $\delta_{EP} = 14.29$ J/cm^3 = 14.29 MPa$^{1/2}$, calculated at 180 °C using molar attraction constants (F_i) from the method of Hoftyzer and van Krevelen[31] via $\delta = \Sigma F_i/V$, where V is the repeat unit molar volume (cm^3/mol). The solubility parameter decreases with increasing temperature simply due to the increase in molar volume (reduction in density);[32] the experimental mass density of PEP[24] extrapolated to 180 °C was thus used to calculate V. The solubility parameter for our hydrogenated mixed-microstructure polyisoprene (hI) was again determined by linear interpolation of the values for hydrogenated polyisoprenes having 93% (PEP[24]) and 37% (50SPI[25]) 1,4-addition, yielding $\delta_{hI} = 13.97$ MPa$^{1/2}$ at 180 °C. This value and the measured $X_{corr} = 0.70$ J/cm^3 at 180 °C yield $\delta_{SrhI} = 14.81$ MPa$^{1/2}$, for $f_S = 0.44$ (50 wt % S). These values of δ, along with mass densities ρ at 180 °C, computed from literature data as outlined above, are compiled in Table 4; though 180 °C was chosen here, the procedure and references above could be used to generate the δ and ρ values at any temperature. Interestingly, the value of δ_{SrhI} determined here is close to that for polyethylene,[24] suggesting potential miscibility between polyethylene and S*r*I, an idea we plan to test in future work.

We can further test the validity of the mean-field model through its prediction for δ_{SrhI}, which is simply that it should be the volume-fraction-weighted ($f_S = 0.44$) linear combination of δ_{hI} and δ_S, where δ_S is the solubility parameter of homopolystyrene. To compute δ_S, we use the data of Lai[33] for two asymmetric PS−PEP diblocks; the procedure of eq 1 yields $X_{S/EP}$ = 4.57 J/cm^3 at 121 °C, decreasing to 3.52 J/cm^3 at 249 °C, or 4.01 J/cm^3 at 180 °C assuming a linear dependence on $1/T$; this yields $\delta_S = 16.29$ MPa$^{1/2}$. With this value, the mean-field prediction at $f_S = 0.44$ is $\delta_{SrhI} = 14.99$ MPa$^{1/2}$, in reasonable agreement with our measured value of 14.81 MPa$^{1/2}$. While this simple single-point test is no substitute for a thorough examination of interactions between S*r*hI copolymers covering the full range $0 \le f_S \le 1$, which often reveals quantitative deviations from the copolymer equation,[32] it does suggest that this simple mean-field scaling is a useful guide for tuning the S*r*hI composition to achieve a desired interaction parameter for a particular block-random copolymer.

■ CONCLUSIONS

The use of a 50/50 cyclohexane/triethylamine mixture allows for the anionic copolymerization of styrene and isoprene with no substantial down-chain compositional gradient: a truly random styrene−isoprene copolymer (S*r*I) of targeted molecular weight and narrow molecular weight distribution. S*r*I blocks were also incorporated into well-defined symmetric diblock copolymers with homopolyisoprene (I) by sequential monomer addition. The thermooxidatively stable isoprene-saturated derivatives, hI-S*r*hI, self-assemble into lamellar melts with a d spacing that follows the usual $M^{2/3}$ scaling. However, the block-random architecture effectively dilutes the unfavorable contacts between the two blocks in the homogeneous phase, reducing the effective χ and allowing for accessible order−disorder transitions at greatly elevated molecular weights and d spacings. At 50 wt % styrene in the random copolymer block (volume fraction f_S = 0.44), the interaction energy density ($X = (\Delta\delta)^2$) against hI is reduced by a factor of ≈8 from X between hI and homopolystyrene, allowing M to be increased by a similar factor at a given order−disorder transition temperature T_{ODT}; this factor is comparable to that predicted by mean-field theory ($f_S{}^{-2} \approx 5$).

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Detailed procedures for determining the true molecular weights of the I and S*r*I blocks, including refractive index increments; polymerization reaction kinetics in 50/50 cyclohexane/TEA at 30 °C for various S:I ratios; and comparison of the glass transition temperatures of S*r*I copolymers with the Fox equation. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

This work was generously supported by the National Science Foundation, Polymers Program (DMR-1003942).

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