Selectively Epoxidized Polyisoprene−Polybutadiene Block Copolymers

Robert B. Grubbs, Margaret E. Broz, Jennifer M. Dean, and Frank S. Bates*

Department of Chemical Engineering and Material Science, University of Minnesota, Minneapolis, Minnesota 55455

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Thermodynamic interactions between the two blocks of a block copolymer are generally understood in terms of three parameters: degree of polymerization (N), block volume fraction (f_i), and Flory−Huggins interaction parameter (χ).[1] The χ parameter represents the enthalpic interaction between the two dissimilar components of the copolymer and can be approximated in terms of the solubility parameters (δ_i) of the two blocks as

$$\chi_{12} \approx (V/k_BT)(\delta_1 - \delta_2)^2 \qquad (1)$$

where V is molar volume, k_B is the Boltzmann constant, and δ_i can be calculated from group contributions or determined experimentally.[2]

The phase behaviors of many copolymer systems have been examined in detail and have been found to agree with those predicted by theory.[3−6] In these systems, N and f_i are both adjustable through polymerization stoichiometry, while χ is predetermined by the choice of monomer pair. Recently, two examples of chemically modified polyisoprene−polystyrene (PI−PS) block copolymers with adjustable χ parameters have been described, where χ varies with the extent of PI modification.[7,8]

To extend this concept to allow the use of a polydiene (PD) block as the constant block, the introduction of a chemoselective modification technique is necessary. As PDs have lower solubility parameters than PS, the large solubility difference between PD and modified PD blocks should allow access to a greater range of χ parameters.

Living anionic polymerization of dienes permits control over repeat unit microstructure and therefore degree of double-bond substitution.[4,5,9] A two-step polymerization sequence allows the preparation of poly(1,4-isoprene)-*b*-poly(1,2-butadiene) (1,4PI-1,2PB: **BI**).[5] As alkene reactivity depends on degree of substitution, differentiation between the triply substituted and singly substituted double bonds of **BI** should allow the preparation of functional block copolymers through selective transformation of one block.[10] Specifically, the chemoselectivity of epoxidation for more-substituted olefins should facilitate the preparation of reactive epoxidized copolymers from diene block copolymers. As 1,4PI and 1,2PB do not phase separate,[5] selective epoxidation of 1,4PI double bonds should allow the preparation of a series of block copolymers exhibiting a wide range of χ values.

PDs have been epoxidized with most standard reagents for alkene epoxidation.[11−13] High selectivity for backbone double bonds in PI has been observed with all systems, but the peracid systems often lead to significant extents of undesirable side reactions.[11] Selective conversion of PB backbone double bonds has been achieved with *t*BuOOH/metal systems, though these methods are sensitive to oxygen and moisture.[13]

As dimethyldioxirane (DMD) can be used as a mild alkene epoxidation reagent and has demonstrated chemoselectivity similar to that of peracids,[14] it was examined as a complementary means toward preparation of selectively epoxidized polydienes.

Treatment of symmetric copolymer **BI** (I block: 94% 1,4-addition; B block: 83% 1,2-addition; $M_n \approx 21\,000$) with DMD (generated in situ from acetone and OXONE (potassium monopersulfate)) yielded poly(epoxy-1,4-isoprene-*r*-isoprene)-*b*-1,2PB (**BIx*n***; ***n*** = percentage of isoprene repeat units epoxidized) copolymers, in which PI double bonds were selectively epoxidized (Scheme 1).[15] For example, treatment of copolymer **BI** with 1.5 equiv of OXONE per PI double bond yielded epoxidized copolymer **BIx87** in which 87% of the I repeat units were epoxidized while no 1,2-butadiene (1,2B) repeat units and fewer than half of 1,4-butadiene (1,4B) repeat units were epoxidized (total PB epoxidation ≈ 7% by ^{1}H NMR).[16] Epoxidized **BIx*n*** copolymers retain the narrow molecular weight distribution ($M_w/M_n < 1.05$ vs PS standards) of the parent **BI** copolymer (Figure 1).

The value of ***n*** could be controlled by varying the amount of OXONE used (Table 1). Up to 1.75 I equiv could be used without significant 1,2BD epoxidation. The epoxidation proceeds in a controllable manner if the final concentration of OXONE in the aqueous phase ($[\text{OXONE}]_{H_2O}$) is kept below 0.16 M. At higher OXONE concentrations, epoxidation extents are lower than expected, presumably due to loss of DMD through side reactions with OXONE.[14] Efficient epoxidation is contingent upon vigorous mixing of the organic and aqueous phases, as attempts at larger-scale reactions required the use of mechanical stirring to achieve high extents of epoxidation (Table 1: entries 2, 3).

While the two blocks of the parent **BI** polymer are fully miscible,[5] small-angle X-ray scattering (SAXS) analysis indicates **BIx** copolymers exhibit ordered lamellar morphologies over a range of epoxide contents at 25 °C (Figure 2). As ***n*** is decreased from 96 to 75, the principal microdomain spacing (d^*) decreases from 23.6 to 22.0 nm (Table 1). Higher-order reflections disappear for ***n*** < 60, thus preventing definitive morphology identification, but a strong first-order peak remains for ***n*** as low as 46.

These results suggest that **Ix** and **B** blocks are strongly segregated and that the strength of this segregation can be controlled by the extent of PI epoxidation. Though **BIx87** cross-links before any order−disorder transition occurs, a value for $\chi_{\text{BIx}n}$ can be estimated from the above SAXS data and eq 1 based on the assumption that $\chi N \approx 10.5$ at the order−disorder transition (ODT).[17] Figure 1 suggests that **BIx*n*** (for $N = 348$) approaches the ODT at ***n*** ≈ 42 and implies that $\chi_{\text{BIx42}} \approx 0.030$.

Molar volumes (V) for **I** and **B** are known,[18] and a value for **Ix** ($V_{\text{Ix}} = 78.8$ cm^3/mol) can be approximated.[2] These values of V can be averaged, weighted by values of N_{Ix}, N_{I}, and N_{B} calculated from ^{1}H NMR data, and used to calculate the value of $V_{\text{BIx}n}$, which can then be substituted into eq 1 to determine $\delta_{\text{Ix}n}$ ($\delta_{\text{Ix42}} = 17.5$ J$^{1/2}$/cm$^{3/2}$).

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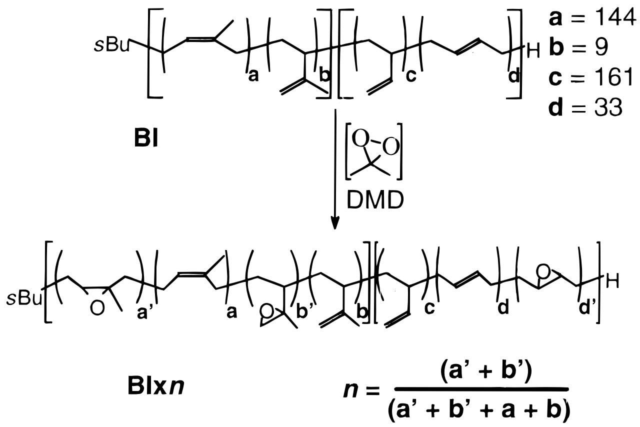
Scheme 1



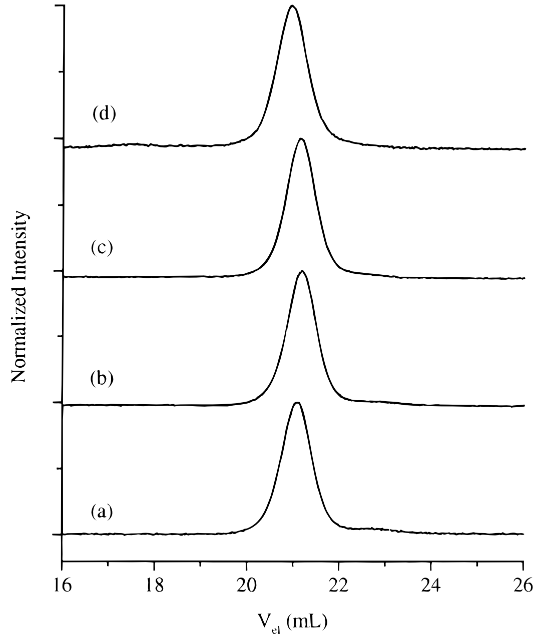


Figure 1. SEC (THF, flow rate = 1.0 mL/min) traces for copolymers **BI** (a), **BIx45** (b), **BIx73** (c), and **BIx87** (d).

Table 1. Preparation of Epoxidized BIx*n* Copolymers[a]

entry	equiv of OXONE	n^b	a'^c	b'^c	d'^c	d^* (nm)
1	1.75	96	138	7	27	23.6
2	1.50[d]	87	132	6	14	23.1
3	1.50[e]	75	116	2	11	22.0
4	1.20	59	85	1	8	20.4
5	0.86	46	66	1	6	18.4
6	0.60	38	54	<1	3	16.8
7	0.30	22	32	0	2	

[a] For all epoxidations, unless noted: scale = 1−2 g of **BI**; t = 18 h; [isoprene repeat units]$_{CH_2Cl_2}$ = 0.18 M, [OXONE]$_{H_2O}$ = 0.165 M, 3.3 equiv of acetone (relative to OXONE), [NaHCO$_3$]$_{H_2O}$ = 0.5 M, T = 0 °C to RT. [b] Percent isoprene repeat units epoxidized. [c] See Scheme 1 for explanation; values determined by ^{1}H NMR. a = 144 − a'; b = 9.2 − b'; c = 161.1; d = 33 − d'. [d] Epoxidation run on a 2 g scale with magnetic stirring and on a 10 g scale with overhead stirring. [e] Epoxidation run on 10 g scale with magnetic stirring.

On the basis of group additivity arguments,[2] $\delta_{\mathrm{Ix}n}$ can be separated into contributions from isoprene repeat units (δ_{I} = 16.6 J$^{1/2}$/cm$^{3/2}$)[19] and epoxyisoprene repeat units (δ_{Ix}) by the relationship

$$\delta_{\mathrm{Ix}n}{}^2 = (n/100)\delta_{\mathrm{Ix}}{}^2 + (1 - n/100)\delta_{\mathrm{I}}{}^2 \qquad (2)$$

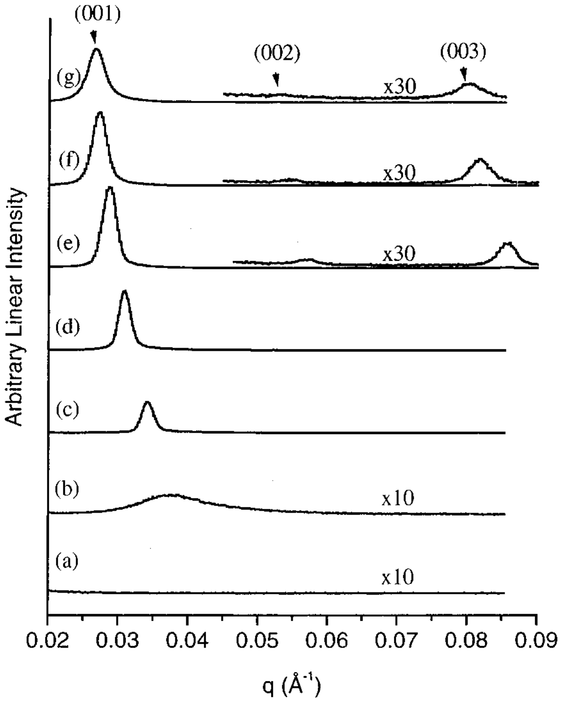


Figure 2. SAXS spectra of copolymers **BIx22** (a), **BIx38** (b), **BIx46** (c), **BIx59** (d), **BIx75** (e), **BIx87** (f), and **BIx96** (g) at 25 °C. Higher q^* peaks are magnified by the amount specified. Spectra are shifted vertically for clarity.

From eq 2 and the above value of δ_{Ix42}, δ_{Ix} is calculated to be 18.7 J$^{1/2}$/cm$^{3/2}$, a value somewhat higher than that calculated solely by additivity of cohesive energies of the constituents of the Ix repeat unit (17.5 J$^{1/2}$/cm$^{3/2}$). The calculated value of δ_{Ix} is somewhat lower than that of the more polar PEO ($\delta_{\mathrm{PEO}} \approx 20$ J$^{1/2}$/cm$^{3/2}$),[19] close to that of PS ($\delta_{\mathrm{PS}} \approx 18.6$ J$^{1/2}$/cm$^{3/2}$),[19] and well above those of PI and PBD. Thus, for the parent **BI** copolymer examined (N = 348), χN for the resulting **BIx*n*** copolymers can be varied from 0.14 to 44 by altering ***n***, enabling access to a range of segregation regimes from a single parent copolymer.

The tunable thermodynamic interactions of these block copolymers will be used to examine phase-separation processes in blends with epoxy resins.[20] The potential reactivity of the copolymer epoxy groups will also be exploited in epoxy blends and for the preparation of blocks with new functionalities resulting from modification of the epoxy block.

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Supporting Information Available: ^{1}H NMR spectra of copolymers **BI** and **BIX*n***. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) For a typical epoxidation, a two-phase mixture of **BI** (2.1 g, 14.4 mmol PI equiv) dissolved in CH_2Cl_2 (80 mL) and acetone (5.3 mL) and aqueous $NaHCO_3$ (5.44 g in 90 mL of H_2O) was cooled to 0 °C, stirred vigorously with a magnetic stirbar, and treated dropwise with a solution of OXONE (13.3 g, 21.6 mmol) in H_2O (45 mL). The ice bath was removed, and the reaction mixture was allowed to stir for 18 h. Larger quantities of **BIx*n*** were prepared with the aid of an overhead stirrer. The organic phase was separated, washed with H_2O, precipitated into MeOH, and dried to a clear tacky solid, **BIx*n***. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.8−0.9 (m, 6H init $\mathrm{C}H_3$), 1.15 ($\mathrm{C}H_2$), 1.29 (Ix $\mathrm{C}H_3$), 1.63, 1.70 ($-\mathrm{CH}{=}\mathrm{C}(\mathrm{C}H_3)-$), 2.11 ($={\mathrm{CH}}-\mathrm{C}H_2-$), 2.60 (3,4Ix $-\mathrm{OC}H_2-$), 2.72 (1,4Ix CH), 2.82, 2.91 (1,4Bx CH), 4.67, 4.75 (3,4I $\mathrm{C}H_2$), 4.93 (1,2B $\mathrm{C}H_2$), 5.18 (1,4I CH), 5.31 (1,2B $\mathrm{C}H_2$), 5.30−5.60 (1,4B CH).

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