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# Facile Method of Controlling Monomer Sequence Distributions in Random Copolymers\*\*

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Over the past few decades, multiple synthetic routes have been developed that facilitate the formation of copolymers comprising A and B units with ordered sequence distributions, including alternating (...ABAB...), diblock (...AABB...), triblock (...AABB...BBAA...), etc.<sup>[1]</sup> The solution and interfacial behaviors of such copolymers have been studied extensively using both experimental and theoretical approaches and are now relatively well-understood.<sup>[2,3]</sup> While copolymers with random sequences of A and B units can also be synthesized, controlling the degree of monomer randomness along the macromolecule still remains a formidable challenge.<sup>[4]</sup> In this report, we present a simple methodology facilitating the formation of A-B random copolymers with tunable sequence distributions. We demonstrate that varying the degree of blockiness in the sequence distribution of A and B monomers has a profound impact on the partition of random copolymers at interfaces.

Random copolymers (RCPs) are long chain molecules made of covalently bound monomers comprising at least two different chemical moieties (say, A and B). In addition to the

overall molecular weight, RCPs are characterized by their composition and monomer sequence distribution. The ability of A-B RCPs to act as “homopolymers with tunable composition”, ranging between A and B homopolymers, has recently attracted considerable attention in controlling polymer miscibility<sup>[5,6]</sup> and various interfacial phenomena.<sup>[7]</sup> This includes compatibilization of two mutually-immiscible homopolymers<sup>[8–10]</sup> or tailoring polymer adsorption at solid/polymer melt interfaces.<sup>[11]</sup> In the aforementioned applications, the sequence distribution of A and B has not been considered. However, in most RCPs the monomer sequence distribution is not perfectly random; that is the position of any monomeric unit in the chain is not completely independent of the chemical nature of adjacent units. Recent theoretical work identified the importance of the monomer sequence distribution in RCPs in determining their unique interfacial and bulk behavior.

The search for understanding the principles of assembly of RCPs has recently experienced notable breakthroughs. In particular, computer simulations and sophisticated theoretical approaches revealed that for certain protein functions, such as chemical recognition, exact control of the monomer sequence distribution may not be required. Chakraborty and co-workers proposed that in order for recognition between a protein-like macromolecule and a surface chemical target to occur, exact matching between the monomer sequence distribution and the surface heterogeneities is not necessary; rather only statistical matching of distributions between the chain and the substrate is needed. Chakraborty and co-workers predicted that RCPs with disordered but tunable monomer sequence distributions should exhibit adsorption behavior that can discriminate between various surface chemical motifs.<sup>[12–14]</sup> In addition, various reports have appeared that predicted the influence of the randomness in RCPs on their critical and self-assembling behavior.<sup>[15,16]</sup> Thus, while it is clear from the theoretical work that the monomer sequence distribution may be important in governing the physico-chemical characteristics of RCPs, the amount of systematic experimental work on this topic is very limited.<sup>[17]</sup> The primary reason for this stems from the inability to control the monomer sequence distribution in RCPs via conventional polymer synthesis methods. Additionally, characterizing the monomer sequence distribution in RCPs remains a formidable experimental challenge because most analytical tools employed to characterize copolymers with ordered monomer sequences (block, alternating, blocky) are not applicable here.

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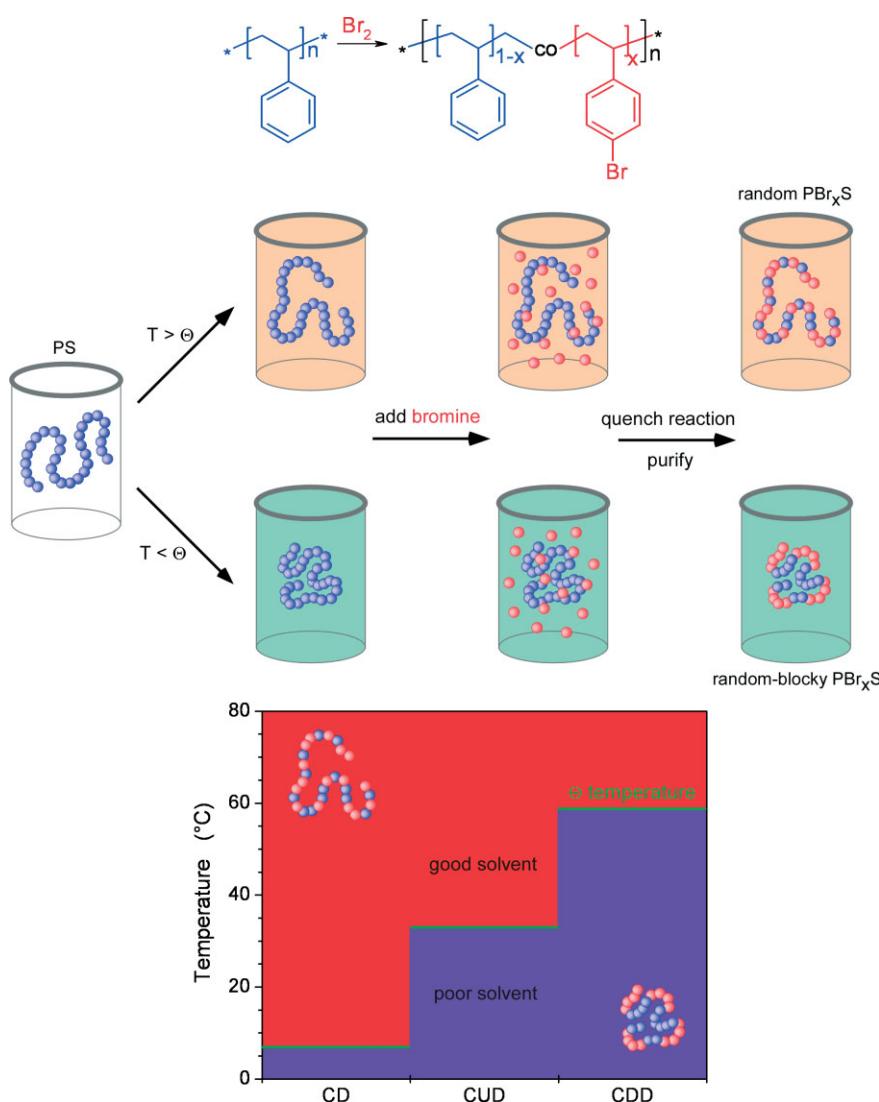
Fresh impetus to examine and design model systems with differing degrees of randomness/blockiness of copolymers has emerged from the biological significance of sequence distribution on functional properties of proteins. The most significant impediment to the experimental realization of such model systems has been the ability to synthesize an ensemble of such structures with large differences in comonomer properties and more importantly to obtain detailed quantitative characterization of such systems. Here we present a simple mechanism for generation and characterization of such structures. Specifically, we show that RCPs with tunable monomer sequence distributions (not monomer sequence in individual chains) can be synthesized by performing simple chemical reaction on a parent homopolymer chain under varying solution conditions. We provide evidence that the monomer sequence distribution in RCPs has a profound impact on the partition of these macromolecules at interfaces. RCPs with tunable monomer sequence distributions will find application in many advanced materials and structures. These include the development of efficient and inexpensive adhesion promoters with tailored characteristics,<sup>[5,6,7]</sup> generation of polymeric particles with tailororable sizes and rheological characteristics,<sup>[18]</sup> which could then be used as solution viscosity regulators or as thin film stabilizers.<sup>[19,20]</sup> A variant of the method described below can also be utilized in fabricating selective adsorption probes that can be used, for instance, as a stationary chromatography phase in interaction chromatography for chemical identification of macromolecular targets.

Our synthetic scheme is based on computer simulations of Khokhlov and co-workers, who have shown that random copolymers with tunable monomer sequence distributions can be prepared by selectively “coloring” certain monomers of a parent A homopolymer with another species, say B.<sup>[21]</sup> In their simulations, a dense globular conformation of a homopolymer chain was constructed by initializing a strong interaction between A units. Once the chain was collapsed, the A units located on the surface of the globule were instantaneously “colored” to become B moieties. Finally, the strong attraction between monomer units was relieved resulting in RCPs with an average B sequence length of 3.173, a value, which was much larger than 1.984 obtained for RCPs with completely random monomer sequence distributions.<sup>[22]</sup> Here we demonstrate how the above process can be realized experimentally by carrying out bromination of polystyrene in different solvents.

More than 20 years ago, Kambour and co-workers reported that poly(styrene-*co*-4-bromostyrene) copolymers ( $\text{PBr}_x\text{S}$ ) can be synthesized by brominating polystyrene (PS),<sup>[23]</sup> where the mole fraction of 4-bromostyrene (4-BrS) in  $\text{PBr}_x\text{S}$  ( $x$ ) can range smoothly from 0 to 1.0 %. Kambour et al showed that solvents with small permanent dipole moments are capable of polarizing the  $\text{Br}_2$  molecule, thus enabling the electrophilic substitution/addition of bromine in the *para* position of the phenyl ring of PS without the use of a catalyst. We have identified a family of alkyl chloride solvents for PS, which facilitate the aforementioned reaction and whose theta tempera-

tures,  $\theta$ , for PS (temperatures below which the PS coil collapses and above which it expands) are experimentally accessible.<sup>[24]</sup> Due to their structural resemblance, 1-chlorodecane (CD,  $\theta=6.6^\circ\text{C}$ ), 1-chloroundecane (CUD,  $\theta=32.8^\circ\text{C}$ ), and 1-chlorododecane (CDD,  $\theta=58.6^\circ\text{C}$ ) have very similar dipole moments.<sup>[25–27]</sup> Hence, at a given temperature the kinetics of bromination is expected to be similar for all three solvents. Depending on the solvent and the solution temperature, the PS coil can either be expanded ( $T > \theta$ ), unperturbed ( $T = \theta$ ), or collapsed ( $T < \theta$ ). Because of the temperature- and solvent-dependent conformational changes of PS, bromination is expected to produce  $\text{PBr}_x\text{S}$  with different sequence distributions of 4-BrS. For example, at  $32.8^\circ\text{C}$  PS adopts a swollen coil conformation in CD, Gaussian coil in CUD, and a collapsed conformation when dissolved in CDD. Small angle neutron scattering experiments performed on deuterium-labeled PS (dPS) revealed the radii of gyration of dPS ( $M_n=33\text{ kDa}$ ) to be 5.62 nm (in CD), 5.12 nm (in CUD), and 4.95 nm (in CDD) at  $32^\circ\text{C}$ . Thus, while the  $\text{PBr}_x\text{S}$  copolymers synthesized in CD will have a random distribution of the 4-BrS segments, copolymers formed in CDD are expected to have more random-blocky character. Figure 1 depicts a schematic representation of the experimental “coloring” scheme for PS in good and poor solvents.

A series of  $\text{PBr}_x\text{S}$  copolymers with tunable 4-BrS contents was prepared by brominating PS ( $M_n=30\text{ kDa}$ ) in CD, CUD, and CDD at various temperatures. In the following, we refer to the samples as  $\text{PBr}_x\text{S-SOLtt}$ , where  $x$  denotes the mole fraction of 4-BrS, SOL stands for solvent (CD, CUD, or CDD) and  $tt$  denotes the bromination temperature in  $^\circ\text{C}$ . In order to prevent any aggregation of the parent PS during bromination, the concentration of PS in the solution was kept at 1 %, which is much below the overlap concentration,  $c^*$ , of the solution (estimated to be 4 %). For selected samples, we also monitored the turbidity of the solution throughout the reaction. Absence of any measurable change in turbidity of the solution during the course of bromination ensured that the polymer remained completely dispersed in the solvent at all times. The mole fraction of 4-BrS in the copolymer,  $x$ , was established using elemental analysis and confirmed with  $^{13}\text{C-NMR}$ . While  $^{13}\text{C-NMR}$  experiments confirmed that the bromination occurred exclusively in the *para* position of the phenyl ring of PS (cf. Fig. 2a),<sup>[28]</sup> they did not reveal any key differences in the co-monomer sequencing of the supposed random and random-blocky copolymers. Size exclusion chromatography (SEC) experiments on polymers before and after bromination established that bromination increased the molecular weight of the parent PS, but did not affect the distribution of the molecular weight (i.e., no chain scission or branching took place). Differential scanning calorimetry (DSC) established the presence of a single glass transition temperature ( $T_g$ ) revealing that, on average, all PS chains underwent bromination (cf. Fig. 2b). The same conclusions were reached from independent experiments using interaction chromatography, which revealed that no unbrominated PS was present in the solution.<sup>[29]</sup>



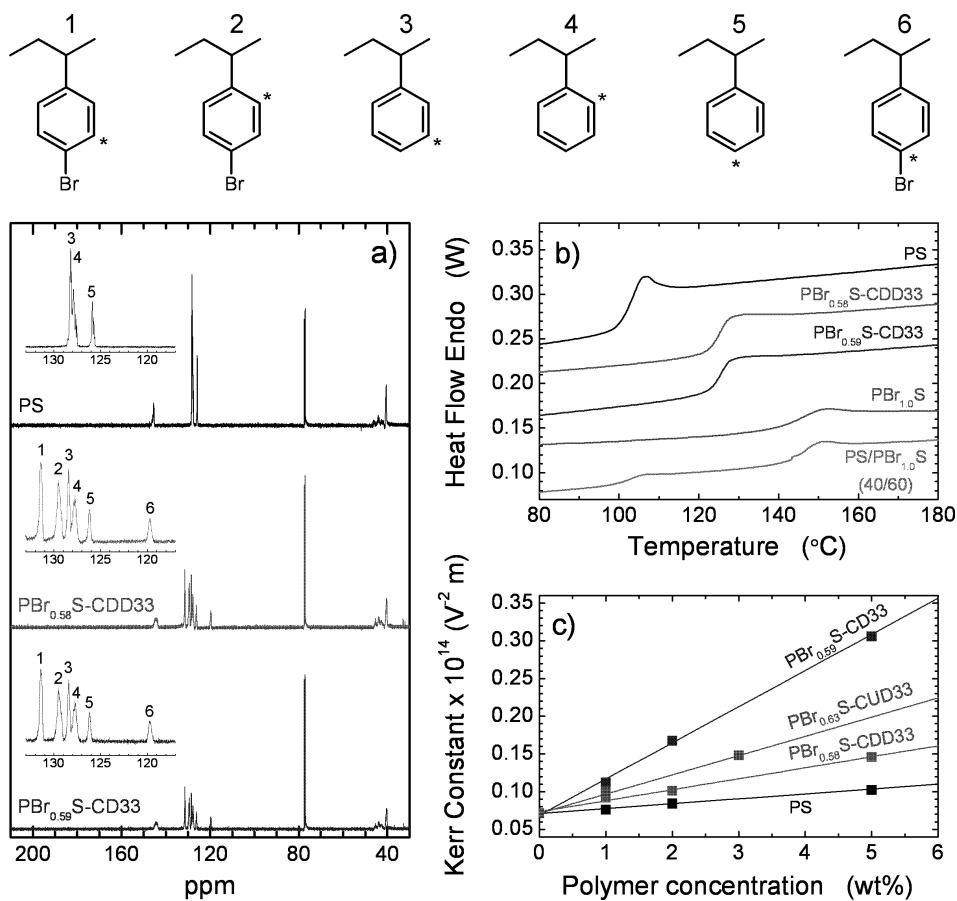
**Figure 1.** (top) Bromination of polystyrene leading to the formation of poly(styrene-*co*-4-bromostyrene). (middle) Parent polystyrene (PS) homopolymer dissolved at room temperature  $T$  in either a good solvent ( $T > \Theta$ ), or a poor solvent ( $T < \Theta$ ), where PS adopts an expanded or collapsed conformation, respectively. Bromine added to the solution under dark conditions is allowed to react with PS for a specific amount of time; the reaction between styrene repeat units and bromine results in 4-bromostyrene. The reaction is terminated and the resultant poly(styrene-*co*-4-bromostyrene) ( $\text{PBr}_x\text{S}$ ) copolymer is purified. (bottom) Depending on the solvent quality,  $\text{PBr}_x\text{S}$  copolymers with random or random-blocky monomer sequence distributions are generated.

In order to establish the degree of blockiness of 4-BrS in  $\text{PBr}_x\text{S}$ -SOLtt, we utilized an electro-optical Kerr effect measurement in order to determine the molar Kerr constant,  $mK$ , which bears information about both the monomer stereoregularity and PS/4-BrS sequencing in  $\text{PBr}_x\text{S}$ .<sup>[30,31]</sup> Guided by the experiments of Tonelli et al.,<sup>[30,31]</sup> we anticipated that for  $\text{PBr}_x\text{S}$  copolymers with similar 4-BrS distributions but increasing 4-BrS content, the  $mK$ s would increase with increasing 4-BrS content; and for  $\text{PBr}_x\text{S}$  with the same 4-BrS composition but different sequence distribution, the  $mK$  would decrease with increasing blocky character of the monomer sequence distribution. In Figure 2c we plot the measured Kerr

constant for PS,  $\text{PBr}_{0.58}\text{S-CDD33}$ ,  $\text{PBr}_{0.63}\text{S-CUD33}$ , and  $\text{PBr}_{0.59}\text{S-CD33}$  as a function of polymer concentration in 1,4-dioxane. As expected, the Kerr constant of  $\text{PBr}_{0.58}\text{S-CDD33}$  is consistently lower than that of  $\text{PBr}_{0.63}\text{S-CUD33}$  and  $\text{PBr}_{0.59}\text{S-CD33}$ . Given the fact that all polymers have roughly an equal amount of 4-BrS units, this result indicates that the blockiness in  $\text{PBr}_x\text{S}$  increases with decreasing solvent quality. In order to demonstrate the capability of the preparation method for synthesizing  $\text{PBr}_x\text{S}$  with tunable composition and monomer sequence distribution, additional  $\text{PBr}_x\text{S}$  specimens were prepared with varying 4-BrS content at various bromination temperatures. In Table 1 we list the Kerr constant of 1% (w/w) solution in 1,4-dioxane for three sets of the copolymer compositions. The data illustrates that for each composition, the Kerr constant is much smaller for samples brominated under poor solvent conditions relative to the polymers brominated in good solvents. Moreover, the Kerr constants increase with increasing the 4-BrS content in the copolymer. These trends, which are in qualitative agreement with the prediction of the earlier theoretical work of Tonelli and co-workers,<sup>[30,31]</sup> confirm that Kerr effect measurements provide a very convenient tool for monitoring both the chemical composition and monomer sequence distribution in random copolymers.

To gain a more quantitative insight into the results of the electrical birefringence measurements, we calculated Kerr constants using the rotational isomeric state model (RIS) and matrix multiplication methods of Flory<sup>[32]</sup> for a few selected periodic sequences having the same degree of bromination

(~60%) and degree of polymerization (=300) as the experimental system. In Table 2 we list  $mK$  ratios for the periodic sequences relative to random comonomer sequences determined by rationing the values of the slopes shown in Figure 2.<sup>[33]</sup> Table 2 also contains the  $mK$  value measured for  $\text{PBr}_{0.58}\text{S-CDD33}$  and  $\text{PBr}_{0.63}\text{S-CUD33}$  normalized by the experimentally determined  $mK$  of  $\text{PBr}_{0.59}\text{S-CD33}$ . Comparison of the  $mK$  ratios for the RIS periodic sequences and the experimental sequences provide clear evidence that  $\text{PBr}_{0.58}\text{S-CDD33}$  and  $\text{PBr}_{0.63}\text{S-CUD33}$  have a more blocky character relative to  $\text{PBr}_{0.59}\text{S-CD33}$ ; the average block length of the 4-BrS units within  $\text{PBr}_{0.58}\text{S-CDD33}$  and  $\text{PBr}_{0.63}\text{S-CUD33}$  is in



**Figure 2.** Characterization of poly(styrene-*co*-4-bromostyrene) (PBr<sub>x</sub>S) copolymers, where *x* is the mole fraction of 4-BrS. a) <sup>13</sup>C-NMR spectra of PS (top), b-PBr<sub>0.58</sub>S (middle), and r-PBr<sub>0.59</sub>S (bottom); the peaks in the spectra mark the resonances of phenyl ring carbons in the *ortho*, *meta*, and *para* positions (shown in the upper panel of the figure) in PS and PBr<sub>x</sub>Ss. The <sup>13</sup>C-NMR data confirm that the bromination occurred exclusively in the *para* position of the phenyl ring of PS, while the aliphatic part of the PS chain and its <sup>13</sup>C-NMR spectrum are not affected by the bromination. The mole fraction of 4-bromostyrene in PBr<sub>x</sub>S can be obtained from the ratios of peaks 1 & 3, 2 & 4, or 6 & 5. b) Differential scanning calorimetry (DSC) from PS, PBr<sub>0.58</sub>S-CDD33, PBr<sub>0.59</sub>S-CD33, PBr<sub>1.0</sub>S, and a mixture of PS and PBr<sub>1.0</sub>S (40/60 m m<sup>-1</sup>). The DSC results provide the *T<sub>g</sub>* of each material and also serve as further evidence that the bromination reaction takes place on all PS chains present in the reaction vessel. c) Kerr constant for PS, PBr<sub>0.58</sub>S-CDD33, and PBr<sub>0.59</sub>S-CD33 as measured on solutions (1–5 wt %) of polymers in 1,4-dioxane (>99 % purity) at 293 K.

the range of 20 and 10 monomers, respectively. The aforementioned experimental scheme differs from that suggested by Khokhlov in that the chemical reaction performed on the parent homopolymer does not take place instantaneously. Yet, the monomer sequence distribution of 4-BrS in PS brominated in CDD exhibits more blocky character relative to that

detected in PS brominated in CD. We reason that as the first 4-BrS segments are formed along the PS chain, they may concentrate inside the collapsed PS globula, thus making it more compact and amendable to producing longer continuous 4-BrS sequences. Recent small-angle neutron scattering experiments suggest that this is indeed the case.<sup>[34]</sup> We note that a

**Table 1.** Kerr constants (in 10<sup>14</sup> V<sup>-2</sup> m) measured on 1 % (w/w) solutions of PBr<sub>x</sub>S in dioxane. PBr<sub>x</sub>S with various mole fractions of 4-BrS (given in parenthesis) were synthesized by carrying out bromination under a variety of solvent/temperature conditions.

Solvent [a]	x=0.24±0.01 [b]			x=0.34±0.03 [b]			x=0.60±0.03 [b]		
	T=26°C	33°C	40°C	T=26°C	33°C	40°C	T=26°C	33°C	40°C
CD ( $\theta=6.6^\circ\text{C}$ )		0.0733 (0.25)					0.129 (0.58)	0.142 (0.59)	
CUD ( $\theta=32.8^\circ\text{C}$ )				0.0444 (0.37)	0.119 (0.35)	0.11 (0.31)		0.123 (0.63)	0.124 (0.63)
CDD ( $\theta=58.6^\circ\text{C}$ )		0.0263 (0.24)					0.098 (0.59)		

[a] CD = 1-chlorodecane, CUD = 1-chloroundecane, CDD = 1-chlorododecane,  $\theta$  = Theta temperature.

[b] Average mole fraction of 4-BrS in PBr<sub>x</sub>S measured by elemental analysis (error < 1 %).

**Table 2.** Normalized molar Kerr constants (mK) for monomer sequence distributions obtained using rotational isomeric state (RIS) model of Flory [28,29] and experimentally measured monomer sequence distributions in PBr<sub>x</sub>S (exp).

Monomer sequence distribution	Method	mK/mK <sub>random</sub>
(PS <sub>2</sub> -b-PBrS <sub>3</sub> ) <sub>60</sub>	RIS	0.773±0.14 [a]
(PS <sub>4</sub> -b-PBrS <sub>6</sub> ) <sub>30</sub>	RIS	0.621±0.14 [a]
(PS <sub>10</sub> -b-PBrS <sub>15</sub> ) <sub>12</sub>	RIS	0.363±0.15 [a]
(PS <sub>20</sub> -b-PBrS <sub>30</sub> ) <sub>6</sub>	RIS	0.216±0.15 [a]
PBr <sub>0.63</sub> S-CDD33	exp	0.533±0.03 [b]
PBr <sub>0.58</sub> S-CDD33	exp	0.304±0.03 [c]

[a] Calculated mK for ordered sequence distributions normalized with mK of a random sequence distribution.

[b] Experimental mK of Br<sub>0.63</sub>S-CDD33 normalized by the experimentally measured mK of PBr<sub>0.59</sub>S-CD33. The value corresponds to the ratio of the slopes of Kerr constant versus concentration shown in Figure 2c.

[c] Experimental mK of Br<sub>0.58</sub>S-CDD33 normalized by the experimentally measured mK of PBr<sub>0.59</sub>S-CD33. The value corresponds to the ratio of the slopes of Kerr constant versus concentration shown in Figure 2c.

similar pathway has been proposed by Dickinson and co-workers for the sulfonation of polystyrene.<sup>[35]</sup>

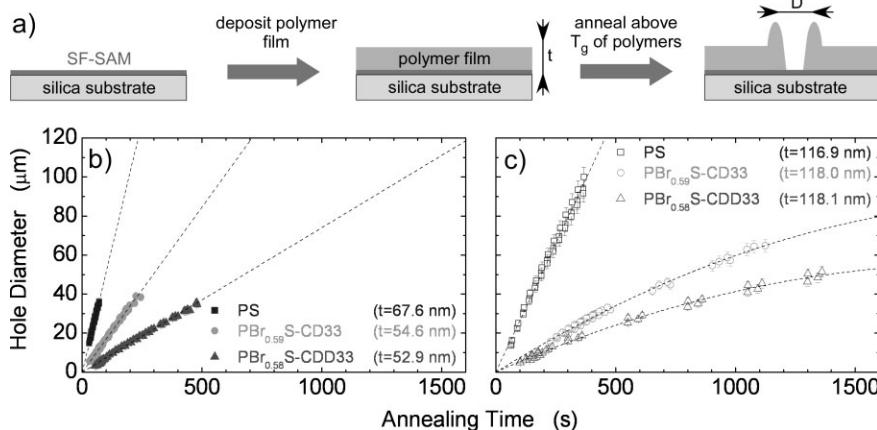
The differences in monomer sequence distribution will significantly influence the partitioning of copolymers at interfaces. Macromolecules with longer consecutive sequences of “colored” monomers that interact preferentially with the substrate are expected to adhere more strongly to the substrate relative to the polymers with random distribution of the “colored” units.<sup>[22,36]</sup> Therefore, mobility of random copolymers on substrates, as reflected by the rate of spreading, is also expected to decrease with increasing degree of blockiness of the “colored” monomers. Here we study dewetting<sup>[37]</sup> of PBr<sub>0.59</sub>S-CD33 and PBr<sub>0.58</sub>S-CDD33 thin films from solid

substrates to confirm the differences in monomer sequence distributions between PBr<sub>0.59</sub>S-CD33 and PBr<sub>0.58</sub>S-CDD33. The effect of the monomer sequence distribution in PBr<sub>x</sub>S is elucidated by depositing films of the same thickness onto substrates having the same surface energy and annealing the specimens at the same  $T - T_g$ , where  $T$  is the annealing temperature and  $T_g$  is the bulk glass transition temperature of the copolymer as measured by DSC.<sup>[38]</sup>

Thin films of PS, PBr<sub>1.0</sub>S (completely brominated sample), PBr<sub>0.59</sub>S-CD33, and PBr<sub>0.58</sub>S-CDD33 were spun-cast on glass substrates, floated onto deionized water, and transferred onto silicon wafers that were previously decorated with a self-assembled monolayer (SAM) made of semifluorinated 1H,1H,2H,2H-perfluorodecyltrichlorosilane (SF).<sup>[39]</sup> After drying, the samples were annealed under a nitrogen atmosphere at  $T - T_g = 35$  °C (cf. Fig. 3a). Dewetting of the copolymer films from the SF-SAM substrates was monitored by optical microscopy. The growth and coalescence of holes in the PS, PBr<sub>1.0</sub>S, and PBr<sub>x</sub>S films of various thicknesses were recorded over a period of several minutes to hours. Our results revealed that PS films (thicknesses ranging from 68 to 117 nm) dewetted completely from the SF-SAM substrates, while films of PBr<sub>1.0</sub>S with comparable thicknesses did not dewet at all. The latter observation suggests that the 4-BrS units interact strongly with the underlying silica substrates through the thin ( $\approx 1$  nm) SF-SAM layer. This result is in accord with previous work by Oslanec and co-workers, who have shown that PBr<sub>1.0</sub>S exhibits an attractive potential ( $\approx -0.07$  kT/monomer unit) towards silica.<sup>[40]</sup> The strong attraction between 4-BrS and silica presumably offsets the unfavorable contacts between PBr<sub>1.0</sub>S and the -CF<sub>3</sub> groups in the SF-SAM. In Figure 3b and c, we plot the dewetting rates for PS (squares), PBr<sub>0.59</sub>S-CD33 (circles) and PBr<sub>0.58</sub>S-CDD33 (triangles) films

of two different thicknesses. PS with the same degree of polymerization as PBr<sub>x</sub>S dewets much faster than PBr<sub>x</sub>S. Concurrently, the dewetting rate of PBr<sub>0.58</sub>S-CDD33 thin films is consistently slower than that measured on PBr<sub>0.59</sub>S-CD33 specimens.

Stability of thin films on substrates is typically discussed in terms of the so-called spreading coefficient,  $S = \gamma_{\text{substrate}} - (\gamma_{\text{film}} + \gamma_{\text{film/substrate}})$ , where  $\gamma_{\text{substrate}}$  and  $\gamma_{\text{film}}$  represent the surface energies of the substrate and the film, respectively, and  $\gamma_{\text{film/substrate}}$  denotes the interfacial energy at the film/substrate interface. Films dewet when  $S < 0$ . Applying the aforementioned equation to our situation suggests that  $\gamma_{\text{PBr0.59S}} + \gamma_{\text{substrate/r-PBr0.59S}} > \gamma_{\text{PBr0.58S}} + \gamma_{\text{substrate/b-PBr0.58S}}$ , because  $\gamma_{\text{substrate}}$  is the same in both cases. Based on water contact angle data collected from r-PBr<sub>0.59</sub>S and b-PBr<sub>0.58</sub>S, which revealed no measur-



**Figure 3.** a) Samples for dewetting studies are formed by covering the silica substrate with a self-assembled monolayer of 1H,1H,2H,2H-perfluorodecyltrichlorosilane (SF-SAM), casting thin polymer films (thickness  $t$ ), and heating to temperature  $T$  such that  $T - T_g = 35$  °C, where  $T_g$  is the bulk glass transition temperature of the polymer. Upon annealing, holes (diameter  $D$ ) develop in the films and grow with increasing time. The time dependence of the hole diameters for PS (squares), PBr<sub>0.59</sub>S-CD33 (circles) and PBr<sub>0.58</sub>S-CDD33 (triangles) measured on films having a thickness of  $t \approx 53-67$  nm (b) and  $t \approx 117-118$  nm (c) are presented. The lines are meant to guide the eye.

able difference in wettability between the two surfaces, it is reasonable to conclude that b-PBr<sub>0.58</sub>S has a higher number of 4-BrS segments at the film/substrate interface relative to r-PBr<sub>0.59</sub>S, which results in  $\gamma_{\text{substrate/r-PB0.59S}} > \gamma_{\text{substrate/b-PB0.58S}}$ . This finding is in accord with the earlier molecular dynamics simulations of Liu and Chakrabarti who studied spreading of “colored” copolymers of Khokhlov and co-workers on solid substrates and showed that copolymers with a blocky character spread at slower rates relative to those with “true” random sequence distribution.<sup>[41]</sup> We note, however, that wettability experiments may not be capable of resolving subtle differences between the surface composition of the copolymer films. Clearly, measurements using more sensitive and localized probes are required to determine the exact values of the surface energies in PBr<sub>0.59</sub>S-CD33 and PBr<sub>0.58</sub>S-CDD33 samples. While more work is needed to explore these effects, the dewetting experiments presented here demonstrate unambiguously that the monomer sequence distribution in copolymers has a profound effect on the interfacial behavior of random copolymers.

In this work we demonstrated that the randomness in the monomer sequence distribution in random copolymers of poly(styrene-co-4-bromostyrene) (PBr<sub>x</sub>S) can be adjusted by “chemically coloring” polystyrene coils with bromine in selective solvents. Specifically, while the distribution of 4-bromostyrene (4-BrS) in PBr<sub>x</sub>S is random when the bromination reaction is performed in good solvents, it results in blocky 4-BrS sequences when carried out in poor solvents for PS. PBr<sub>x</sub>S copolymers provide a very useful platform for further chemical tailoring because the presence of bromine in 4-BrS can be utilized in Suzuki coupling reactions<sup>[42]</sup> of “click chemistry”.<sup>[43]</sup> Kerr constants, as determined in an electrical birefringence experiment, may hold great promise in determining comonomer sequences in random copolymers even in situations, where other conventionally applied techniques (e.g., NMR) fail. While many open questions that pertain to the formation of such polymers and the details of their interfacial behavior still exist, experiments using thin films of PBr<sub>x</sub>S reveal that the monomer sequence distribution greatly affects partitioning of random copolymers at interfaces. Considering that numerous chemical modifications exist for the generation of random copolymers by chemical conversion of homopolymers, the method of adjusting the monomer sequence distribution proposed by Khokhlov and experimentally realized in this work will aid in many technological applications, some of them mentioned earlier.

## Experimental

The bromination reactions were carried out in the following manner. A 1.0% (w/w) solution of PS (30 kDa, Pressure Chemical Company) in either CD or CDD (TCI America) was placed into a controlled temperature cell, which was subjected to a temperature cycle. Specifically, the cell was ramped to 70 °C (well above the theta temperature of both solvents) and maintained for 60 min. Afterwards the cell temperature was lowered to the bromination temperature at a rate of 0.3 °C min<sup>-1</sup> and maintained for 60 min. After completing the equilibration, a three-fold stoichiometric excess of bromine (Aldrich

Chemical Company) was added to the solution under dark conditions. The reaction was allowed to proceed for varying times (determined by trial and error) depending upon the extent of bromination desired. The reaction was terminated by adding a few drops of 1-pentene. The samples were then purified by dissolution into tetrahydrofuran and subsequently precipitated into methanol. The purification step was repeated 5 times to eliminate any residual reactants and/or solvent. The polymer was then dried at 60 °C under 30 inches of vacuum in order to remove the all remaining traces of methanol. The concentration of bromine in the sample was established by elemental analysis (Atlantic Microlabs, Norcross, GA).

Pulsed field NMR experiments were performed on a Bruker AVANCE 500 MHz Spectrometer with an Oxford Narrow Bore Magnet. The NMR probe was tuned to the <sup>13</sup>C frequency, which is at 125.75 MHz for the 500 MHz spectrometer. All quantitative measurements were done using a single frequency 5 mm <sup>13</sup>C dedicated probe (Ge NMR adopted for Bruker shims). NMR experiments revealed that the bromination occurred exclusively in the para position of the phenyl ring of PS and confirmed the results of the elemental analysis concerning the molar content of 4-BrS in the sample.

The Kerr effect measurements were carried out using the nulled-pulse method, which utilizes a rectangular-shaped electric pulse to the electrodes of the Kerr cell. The duration of the pulse is adjusted so that it is sufficiently long to obtain an equilibrium orientation of the molecules at a given strength of electric field, yet it is sufficiently short to prevent or minimize any effects due to electrolysis and/or electrode polarization. Measurements of the Kerr effect were made on polymer solutions (1–5% w/w) in 1,4-dioxane (>99% purity) at 293 K.

Glass transition temperature ( $T_g$ ) measurements were performed on a TA Instruments Q100 DSC. Dynamic heating and cooling scans were carried out at a rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere, over a temperature range of 60 to 200 °C. Indium and octane were employed as calibration standards. The  $T_g$  values reported in this work correspond to the midpoint of the heat capacity transition observed on second heating scans.

Small Angle Neutron Scattering (SANS) measurements were performed on the 30 m SANS beamline (NG3) at the cold neutron research facility at National Institute of Standards and Technology, Gaithersburg, MD. Neutrons with wavelength ( $\lambda$ ) of 6 Å and  $\Delta\lambda/\lambda$  of 0.15 were used with sample to detector distances of 1.3, 4, and 13 m to result in a  $q$  (magnitude of the scattering wavevector) range of 0.003 to 0.35 Å<sup>-1</sup>. The two-dimensional SANS data were reduced to one-dimensional intensity versus  $q$  after correcting for parasitic background and empty-cell scattering and placed on an absolute intensity scale. Finally, a  $q$ -independent incoherent scattering correction was subtracted and the coherent scattered intensity from at least three solution concentrations analyzed using both a Guinier analysis and Zimm analysis.

Dewetting studies were carried out on 1-inch silicon wafers (University Wafers). After pre-cleaning using a standard RCA clean, the wafers were subjected to ultraviolet/ozone treatment for 30 min. Following the cleaning, the surfaces of the silicon wafers were covered with a self-assembled monolayer of 1H,1H,2H,2H-Perfluorodecyltrichlorosilane (SF-SAM, Gelest) through a 10 minute vapor deposition. The wafers were subsequently rinsed with toluene to remove any physisorbed SF molecules. Contact angle measurements were conducted using a Ramé-Hart contact angle goniometer on several positions across the specimens to insure that the sample surfaces were very homogeneous; the advancing and receding contact angles measured with deionized water were 114 and 110°, respectively. Thin polymer films were spun coated onto glass slides and floated onto the surface of deionized water. The films were then transferred from the water bath onto the SF-SAM-covered silicon wafers. The samples were allowed to dry overnight and their thicknesses were measured by ellipsometry before performing dewetting experiments. After drying, the samples were annealed in a hot stage (FP82HT, Mettler Toledo) and the dewetting was monitored with an optical microscope (BX60M Olympus) equipped with a 20× long working distance objective and a SPOT RF Color digital camera (Diagnostic Instruments, Inc.). All experiments were carried out under a nitrogen purge with

the temperature set at  $T = T_g + 35^\circ\text{C}$ . Sequential images were taken during the dewetting process at a rate of one image every 10 s. Post image processing was conducted using Scion Image software (Scion Corporation). The threshold density option was used to determine the area of the dewetting holes in order to calculate the diameter of each hole.

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