Determining the Polydispersity in Chemical Composition and Monomer Sequence Distribution in Random Copolymers Prepared by Postpolymerization Modification of Homopolymers

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Supporting Information

ABSTRACT: We report on establishing the polydispersity in chemical composition (PCC) and polydispersity in monomer sequence distribution (PMSD) in random copolymers of poly(styrene-co-4-bromostyrene) (PBr_xS), where x = (0.385 ± 0.035) is the mole fraction of the 4-bromostyrene units (4-BrS), prepared by electrophilic substitution of bromine in the para-position of the phenyl ring of the parent polystyrene. Upon fixing the total number of repeating units, we tune the distribution of styrene and 4-BrS segments in PBr_xS by carrying out the bromination reaction on polystyrene homopolymers in different solvents. While PBr_xS with relatively random comonomer distribution is prepared in 1-chlorodecane, random-blocky sequences of 4-BrS in PBr_xS are achieved by carrying out the bromination reaction in 1-chlorododecane. The PCC in both copolymers is established by fractionating both polymers using interaction chromatography (IC) and determining the chemical composition of the individual fractions by neutron activation analysis (NAA). The NAA data along with IC experiments reveal that the random-blocky sample possesses a narrowed PCC relative to a specimen with a more random comonomer sequence distribution. The full width at half-maximum (fwhm) in the chemical composition profile from IC is used to quantify PCC; the random mother sample possessed a 25% fwhm, while the random blocky mother sample has a fwhm equal to 8.7%. The change in the adsorption enthalpy per brominated segment due to adsorption is determined to be ≈1.5 times greater for the random-blocky than the relatively random sample, proving that more pronounced cooperative adsorption occurs in the case of the random-blocky sample relative to the random copolymer sample. Computer simulation employing the discontinuous molecular dynamic scheme further reveals that the distribution of comonomer sequences, that is, PMSD, in the random-blocky copolymer is narrower than that in the copolymer with a random distribution of both monomers.

Random copolymers (RCPs) are long chain macromolecules composed of two or more chemically distinct units. Unlike copolymers with ordered sequence distributions, that is, alternating or block, the arrangement of the different monomers units inside RCPs does not possess a long-range order. In addition, due the stochastic nature of processes during the synthesis of RCP (vide infra), the RCPs are not chemically homogeneous and do not possess a unique comonomer sequence distribution. To make the matter even more complicated, just like in any synthetic polymeric systems, there may be a distribution of the lengths (i.e., molecular weights) for all polymers. The existence of the three types of heterogeneities, that is, (1) polydispersity in chemical composition (PCC), (2) polydispersity in monomer sequence distribution (PMSD), and (3) polydispersity in molecular weight (PMW), makes the complete characterization of RCPs very challenging because the mutual contributions of all polydispersities mentioned above are interconnected. In this Communication, we attempt to deconvolute, for the first time, the contribution of the PCC and PMSD in RCPs using a combination of analytical and computational methods.

High performance liquid chromatography (HPLC) was utilized in the past to analyze poly[(methyl methacrylate)-graft-polystyrene] copolymers by Teramachi,1 Kawai et al.2 and Teramachi et al.3 attempted to measure the PCC in poly[styrene-co-(methyl methacrylate)] copolymers via HPLC. Several other groups have also used various HPLC variants, including size exclusion chromatography (SEC), and temperature rising elution fractionation,5 to determine the PCC of RCPs.6−14 However, none of these techniques has been able to quantify the PCC in random copolymers. Several factors may have likely contributed to this difficulty, including a broad PMW, which contributes significantly to the broadness in the
HPLC curves and makes determination of PCC very challenging, if not impossible.

This work employs RCPs that have been prepared by postpolymerization modification of parent polystyrenes (with relatively low PMW) by means of bromination reaction in selective solvents. We have shown in the past that this protocol leads to poly(styrene-co-4-bromostyrene) (PBrS, where \( x \) denotes the mole fraction of the 4-bromostyrene units) with tunable sequence distribution of styrene and 4-bromostyrene comonomers.\(^{15}\) This methodology assures that PMWs in PBrS specimens under investigation are identical to that of the parent polystyrene, which possesses relatively low PMW and can be determined independently via SEC. HPLC can also be used to determine the change in enthalpy due to adsorption (\( \Delta H \)) via van’t Hoff plots.\(^{16}\) In this work, the effects of styrene adsorption can be neglected because the conditions employed correspond to the liquid chromatography at critical condition (LCCC) for styrene. We further employ interaction chromatography (IC) in conjunction with computer simulation utilizing the discontinuous molecular dynamics scheme to gain information about the breadth of the polydispersities in chemical composition and comonomer sequence distribution, respectively.

The RCPs used in this work were synthesized by brominating polystyrene with low PMW (see Experimental and Computational Methods for details) in 1-chlorododecane (CD) and 1-chlorododecane (CDD) in the dark.\(^{15}\) Under these conditions, the electrophilic substitution of bromine in the \( \text{para} \)-position of the phenyl ring of PS resulted in poly(styrene-co-4-bromostyrene) random copolymers (PBrS, where \( x \) is the mole fraction of the 4-bromostyrene, 4-BrS, units). The bromination time was adjusted to achieve approximately equal degrees of bromination in both solvents. Although PS attained roughly a Gaussian coil conformation in both CD and CDD, as reported earlier,\(^{17-19}\) there were small differences in the \( \theta \) temperatures (\( T_\theta \)) of PS in CD (\( T_\theta = 6.6 \) °C) and CDD (\( T_\theta = 58.6 \) °C). Hence, by brominating PS in CD and CDD at \( \approx 25 \) °C, the parent PS coil would expand and shrink, respectively, and this conformational change would influence the comonomer sequences in PBrS. An additional factor influencing the comonomer distribution in PBrS stems from different solubility of 4-BrS in the two solvents. Specifically, the lower solubility of 4-BrS relative to that in CDD provides additional driving force for collapsing the chain because the 4-BrS segments tend to minimize their exposure of the solvent by moving inside the coil.\(^{20}\) It is, thus, the synergetic effect of these two phenomena that results in different comonomer distributions in PBrS synthesized in CD and CDD. In our previous work, we have utilized the electro-optical Kerr effect measurements to confirm that for the same \( x \) the degree of blockiness of PBrS was higher in the sample prepared in CDD relative to that made in CD.\(^{15}\) Using elemental analysis, we established that the mole fractions of 4-BrS were 0.35 and 0.42 for PBrS prepared in CD and CDD, respectively. Henceforth, we refer to the two samples as r-PBr0.35S and b-PBr0.42S.

Based on SEC experiments, no detectable chain scission took place during bromination of the parent monodisperse polystyrene (\( M_n \approx 30 \) kDa and PMW = \( M_n/M_n = 1.06 \)). The corresponding SEC elugrams collected from r-PBr0.35S and b-PBr0.42S are plotted in Figure 1a. The data confirm that the elution profiles are comparable to that of the parent PS (not shown). Because SEC separates the analytes based on entropic constraints, it is not sensitive enough to distinguish between chemical composition and comonomer sequence in the two polymers. In contrast, IC offers the necessary sensitivity and ability to detect differences in chemical composition and comonomer sequence distribution, as we have demonstrated in our earlier work.\(^{21}\) To maximize the sensitivity of IC, we operated the IC close to the LCCC for styrene by tailoring the chemical composition of the stationary phase, solvent type, and temperature, as detailed in Experimental and Computational Methods. Under these conditions, the styrene segments are nearly “invisible” and the copolymer adsorption inside the column is dictated primarily by the 4-BrS segments. Six fractions were collected from each sample during the IC experiments and their chemical compositions were analyzed with neutron activation analysis (NAA). In Figure 1b,c, we plot the chromatograms of r-PBr0.35S and b-PBr0.42S, respectively, for both the mother sample (thick solid lines) as well as all collected fractions (thin lines). Because of large uncertainty in chemical composition in fractions collected at the shortest (F1) and longest (F6) retention times (thin dashed lines), we have not included those values in the overall analysis and worked with intermediate fractions only (thin solid lines).

The IC data enable us to extract critical information regarding the PCC in both samples. In Figure 2 we plot the IC signal versus mole fraction of 4-BrS for both the mother sample and fractions F2–F5 for random (Figure 2a, left panel) and random-blocky (Figure 2b, right panel) copolymers. The full width half-maximum (fwhm) in IC (see Tables S-II and S-III in the Supporting Information) enables us to quantify the
PCC in each specimen. For instance, the fwhm of the mother sample of r-PBr$_{0.35}$S ($\Delta x_{\text{fwhm}} \approx 0.25$) is nearly 3.5 times larger than that of b-PBr$_{0.42}$S ($\Delta x_{\text{fwhm}} \approx 0.087$). In addition, the fwhm of the F3 fraction collected from r-PBr$_{0.35}$S ($\Delta x_{\text{fwhm}} \approx 0.11$) decreases by a larger amount than that of the F3 in b-PBr$_{0.42}$S ($\Delta x_{\text{fwhm}} \approx 0.069$), indicating that the b-PBr$_{0.42}$S mother sample possesses a narrower PCC compared to the r-PBr$_{0.35}$S specimen. We note that, although we refer to r-PBr$_{0.35}$S as "random" copolymer, the distribution of the 4-BrS segments may not be "truly random". For further discussion, see the Supporting Information and data in Tables S-I-III.

Further insight into the CPP can be obtained by comparing the IC characteristics of all fractions collected from both samples. In Figure 3 we plot the mole fraction of 4-BrS in the copolymer as a function of the retention time for fractions F2–F5 and the mother samples in both RCPs. The data exhibit two important trends. First, the range of the chemical composition of F2–F5 is much narrower in b-PBr$_{0.42}$S than in r-PBr$_{0.35}$S. This observation is in accord with our earlier assessment (vide supra). Second, the slope of the chemical composition versus retention time ($dx/dt$) is larger for r-PBr$_{0.35}$S than for b-PBr$_{0.42}$S. Hence, for a given breath of the composition drift, the b-PBr$_{0.42}$S samples have a larger width of the corresponding elution times. This is expected for samples that possess more blocky character in the 4-BrS sequences because the 4-BrS units adsorb more effectively when they have long consecutive runs (i.e., trains). The trends in data presented in Figure 3 can be quantified by invoking a simple analysis that is provided below. Equation 1 is used to fit the data in Figure 3:

$$x_{4-\text{BrS}} = \alpha \ln(t_f - t_i) + \beta$$

(1)

where $\alpha$ and $\beta$ are fitting parameters. The full derivation of the equation can be found in the Supporting Information.

The lines in Figure 3 represent the best fits to eq 1. Those lines were obtained using the discrete data points shown in Figure 3 and $t_i = 33$ min. The results of the fitting parameters are listed in Table 1. Realizing that $\alpha$ in eq 1 represents $(RT)/$
contribution of the individual fractions to the overall composition.

While insight into the PCC can be obtained from IC, determining the breath of the copolymer distribution, that is, PMSD, from the IC data is not straightforward. Here we implement a computer simulation to provide insight into the PMSD in RCPs. We recently employed discontinuous molecular dynamics (DMD) to follow the formation of random copolymers by the “chemical coloring” of A homopolymers (240 repeat units, same as in the experiment) by chemical species B. We studied the effect of the interaction strengths between units $j$ and $k$, $\varepsilon_{j,k}$, on the conformation of the A-B copolymers in the surrounding implicit solvent by setting $\varepsilon_{AA} = 0$ and varying $\varepsilon_{AB}$ and $\varepsilon_{BB}$. The initial conformation of the A homopolymer was adjusted by varying $kT/\varepsilon_{AA}$. The A homopolymers adopted a tight globule conformation at low $kT/\varepsilon_{AA}$, while at high $kT/\varepsilon_{AA}$, the macromolecules expanded. The unperturbed Gaussian coil conformation was found at $kT/\varepsilon_{AA} \approx 3$. The effect of the solubility of B in the solvent on the distribution of A and B units in the A-B copolymer was studied by varying the $\varepsilon_{BB}/\varepsilon_{AA}$ ratio ($R_{BA}$) from 1 to 10. For $R_{BA} = 1$, there was no change in the conformation of the A-B copolymer with the addition of B. In contrast, for $R_{BA} > 1$, the coil size changed and for high $R_{BA}$ values displayed a conformational inversion with increasing degree of chemical modification (i.e., concentration of the B units in the copolymer).

We use experimental data and observations to guide the choice of the input parameters in the computer simulation model. First, we note that in spite of the differences in the theta temperatures noted above, PS coils retain approximately a Gaussian shape because, as discussed by others, they are at nearly theta condition. We will thus focus primarily on $kT/\varepsilon_{AA} \approx 3$, which corresponds to the theta condition (vide supra).

Second, in our previous work we have established that the solubility of PBr$_0.35$S in CD is higher than that in CDD due to the differences in the solubility of 4-BrS in those two solvents. Small angle neutron scattering experiments have recently been performed that aimed at monitoring the effect of the bromination reaction in CD and CDD on the dimension of PBr$_0.35$S. While the details of those experiments will be presented in a separate publication, it suffices to say that the original coil size of PS measured in CD (5.62 nm) and CDD (4.95 nm) increased by $\approx 7$–10% and decreased by $\approx 10$–12%, respectively, in the course of bromination. The actual coil size depends on the bromination time and the model employed to model and form structure factors. While we have currently no experimental data available on 4-BrS/CD and 4-BrS/CDD interaction parameters, we know that $R_{BA}$ must be larger for CDD than for CD. We thus choose arbitrarily $R_{BA} = 1$ and $R_{BA} = 10$ to model the coloring reaction of A homopolymer in the two solvents. To provide quantitative insight into the experimental findings, we perform at least five simulation runs and then determine the deviations from the average degree of coloring and the blockiness, which has been defined in our previous work.

In Figure 4 we plot the variation of the degree of coloring (left panel) and the variation in blockiness (right panel) as a function of percent of coloring for $R_{BA} = 1$ (top panels) and $R_{BA} = 10$ (bottom panels). The vertical solid lines denote the range of variation of chemical composition measured experimentally for r-PBr$_{0.35}$S (top panels) and b-PBr$_{0.42}$S (bottom panels). From the data in Figures 3 and 4, it is apparent that the variation of the chemical composition for sample with $R_{BA} = 1$ is larger than that for $R_{BA} = 10$. Importantly, this trend is in agreement with the experimental observations. The computer simulation data thus provide key insight into the blockiness in A-B copolymers. As expected, the A-B copolymer with $R_{BA} = 1$ possesses a random (henceforth referred to as “random”) distribution of A and B comonomers (blockiness < 0.5). In contrast, a random-blocky character (blockiness > 0.5) is higher for A-B copolymers with $R_{BA} = 10$. Importantly, the data suggest that the variation in the comonomer distribution is higher in the “random” sample than in the random-blocky A-B copolymer. The latter information is particularly important as it provides insight into a property that is difficult to interpret based solely on experimental data.

A few comments are in order. First, we used a Gaussian coil of the A homopolymer in our simulations (i.e., $kT/\varepsilon_{AA} \approx 3$), while in reality there may be a small collapse of PS in CDD and a small expansion of PS in CD that would be reflected in deviation $\delta$ of $kT/\varepsilon_{AA} \approx 3 \pm \delta$. However, from simulations
we have performed with $kT/\varepsilon_{AA} \approx 3$ and $kT/\varepsilon_{BA} \approx 4$ that are well outside the limits describing the experimental conditions (see ref 22 for sizes of the parent A homopolymer as a function of $kT/\varepsilon_{AA}$), the trends pertaining to the variation in chemical composition described above still hold. That is, the random-blocky copolymer possesses a narrower chemical heterogeneity than the “random” copolymer. The same conclusions can be reached for the heterogeneity in comonomer blockiness although the A-B copolymers with $R_{BA} = 10$ at $kT/\varepsilon_{AA} \approx 2$ exhibit an increased degree of randomness. Nevertheless, the computer simulations presented here provide ample evidence that chemical heterogeneity and the width of the comonomer distribution of the random-blocky samples are narrower than those corresponding to the “random” copolymers.

In conclusion, we have shown that the comonomer distribution in random copolymers can be adjusted by varying the solution conditions during postpolymerization brominated reactions performed on parent polystyrene chains. To this end, “random” samples were made in CD, where the expanded polymer chain allowed for the reaction to occur at any point along the chain. Random-blocky samples were synthesized in CDD, where the partially collapsed polymer chain allowed for reaction only on the exterior of the chain. This difference in chain conformation during reaction accounts for the difference in blockiness, or PMSD. This difference in blockiness of the synthesized copolymers accounts for the observed quantitative difference in PCC from the chemical composition profiles and PMSD from the enthalpy of adsorption of the 4-BrS segment. HPLC has been used as a tool in order to quantify these differences. The computer simulations support these experimental findings.

**EXPERIMENTAL AND COMPUTATIONAL METHODS**

The random copolymers used in this study were prepared by the coloring method developed earlier and described elsewhere. Specifically, we dissolved polystyrene (PS, $M_n \approx 30$ kDa, $M_w/M_n = 1.06$, supplied by Pressure Chemical) in 1-chlorododecane (CD) and 1-chlorododecane (CDD) and performed bromination reaction with Br$_2$ in the dark. Under these conditions the electrophilic substitution of chlorine in the $\beta$-position of the phenyl ring of PS resulted in the fractionated samples were reinjected into the HPLC system to determine the $f_0$ of each fraction. Each fraction was analyzed by neutron activation analysis (NAA), by Elemental Analysis, Inc., to establish the overall chemical composition. Small amounts of sample in fractions 1 and 6 precluded accurate determination of the chemical composition. Those data were thus not included in the overall analysis.

Details of the discontinuous molecular dynamic (DDM) model and method used to simulate the formation of random-blocky copolymers have been described elsewhere. Briefly, a system of polymer molecules modeled as chains containing 300 square-well monomers of A-type (corresponding to styrene) is allowed to equilibrate at a selected reduced temperature. After equilibration, athermal reactant particles are placed in the simulation box. When the reactant particles come in contact with A-type monomers, the monomers are “colored” to become B-type monomers (corresponding to 4-BrS). This “coloring” reaction is carried out until a desired number of the parent monomers are colored. Because the solvent in our simulations is implicit, the solubility of A- and B-type monomers is adjusted by varying the $A-A$ and $B-B$ interaction strengths. The ratio of $B-B$ interaction strength to $A-A$ interaction strength ($R_{BA} = \varepsilon_{BA}/(\varepsilon_{AA})$) is varied from 0.5 to 10.0. In this manner, the newly created B unit can be modeled as either more or less soluble than A. Interactions between nonbonded A- and B-units along the chain are modeled as athermal, that is, $\varepsilon_{AB} = 0$. The distribution of A and B units along the polymer chain is determined by evaluating the dispersion as a function of the sampling window size, as detailed in our previous publication.

**REFERENCES**


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**ADDITIONAL RESOURCES**

ACSMacroLetters. Supporting Information Additional experimental details and results. This material is available free of charge via the Internet at http://pubs.acs.org.

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**NOTES**

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