Supplementary information

Determining the dispersity in chemical composition and monomer sequence distribution in random copolymers prepared by post-polymerization modification of homopolymers

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1. Determining the chemical composition distribution of random copolymers

We invoke a simple statistical model to make estimates of the expected polydispersity in chemical composition (PCC) in "truly random" copolymers. Consider a collection of N chains of equal length each made of k segments (k = 0, 1, …, K) that can either be "red" or "blue" The populations of the "red" and "blue" segments are P and 1-P, respectively. In reference to our experimental system, if "red" and "blue" represent the 4-BrS and S monomers, respectively, then P corresponds to the molar fraction of 4-BrS (*i.e.,* degree of bromination) within the chain ($x_{4\text{-}BrS}$). Under this set up any given chain of K segments has probabilities of having k = 0, 1, 2, …, K "red" segments. If these segments are selected randomly from the P/1-P population (say, 0.40/0.60 in terms of the fraction of brominated styrene and parent styrene monomers) then the probability of a chain with no "red segments" would be $(1\text{-P})^{10}$ because the first segment has to be "blue" (probability 1-P) as does the second, third, …, K^{th} segment. We then expect that the distribution of the completely "blue" chains within the sample of N chains be given by:

$$N(0) = N \cdot \binom{K}{0} \cdot P^0 \cdot P^K = N \cdot \frac{K!}{0! \cdot K!} \cdot P^0 \cdot (1-P)^K \qquad \text{(S-1)}$$

Extending this to chains comprising both k "red" and K-k "blue" segments, one can write:

$$N(k) = N \cdot \binom{K}{k} \cdot P^k \cdot P^{K-k} = N \cdot \frac{K!}{k! \cdot (K-k)!} \cdot P^k \cdot (1-P)^{K-k} \qquad \text{(S-2)}$$

Equation (S-2) thus represents a binomial distribution with K trials. For instance, consider a collection of 10,000 chains, each having a total of 100 segments that are split on average into 40 "red" and 60 "blue" segments. The number of chains having 30 "red" and 70 "blue" segments within this population will then be equal to:

$$N(30) = 10000 \cdot \frac{100!}{30! \cdot (70)!} \cdot 0.4^{30} \cdot 0.6^{70} = 100.075 \qquad \text{(S-3)}$$

Instead of determining the number of chains from the collection of N chains, one can calculate the probabilities P(k) by simply setting N = 1 in equation (S-2). The resulting normal distribution will have a maximum at k = 40 (or k/K = 40/100 = P = 0.4). We generate such distributions for various values of P and determine the standard deviation (σ) and the full width at half maximum (FWHM) ($= 2\sqrt{2ln2}\sigma$). The data are shown in **Table S-I**.

Table S-I: The standard deviation and the FWHM for "random" copolymers

	Average percent coloring per chain (%)								
	10	20	30	40	50	60	70	80	90
σ[a)]	2.99	4.00	4.59	4.91	5.01	4.91	4.59	4.00	2.99
2σ[b)]	5.99	8.01	9.18	9.82	10.02	9.82	9.18	8.00	5.99
FWHM (%)	7.05	9.43	10.81	11.56	11.80	11.56	10.81	9.43	7.05

[a)] 68% confidence
[b)] 95% confidence

The values of FWHM listed in **Table S-I** can be used as benchmarks to "calibrate" the degree of randomness in the PCC for both r-$PBr_{0.35}S$ and b-$PBr_{0.42}S$ samples, whose experimentally determined values of FWHM are listed in **Table S-II** and **Table S-III**, respectively.

Table S-II: FWHM values and peak in x_{BrS} composition for r-$PBr_{0.35}S$ mother sample and F2-F5 fractions

Sample	**FWHM (%)**	**Peak in x_{BrS}**
Mother	25	0.356
F2	12.0	0.281
F3	11.0	0.329
F4	9.7	0.376
F5	8.9	0.434

Table S-III: FWHM values and peak in x_{BrS} composition for b-$PBr_{0.42}S$ mother sample and F2-F5 fractions

Sample	**FWHM (%)**	**Peak in x_{BrS}**
Mother	8.7	0.448
F2	6.3	0.403
F3	6.9	0.427
F4	6.2	0.440
F5	4.3	0.459

Examining first the data corresponding to r-$PBr_{0.35}S$ it is apparent that the mother sample (*i.e.*, as made copolymer) is not "truly" random because its FHWM exceeds that of the expected normal distribution. This is consistent with our earlier work, which established that the bromination reaction performed in 1-chlorodecane produced PBr_xS copolymers that had a lower degree of randomness than those made in nitrobenzene [1]. However, the chemical heterogeneities of fractions F2-F5 (particularly those of F4 and F5) are close to "truly random". Interestingly, both the mother b-$PBr_{0.42}S$ sample and its fractions (*cf.* **Table S-III**) possess "truly random" PCC. This is because the average compositions of the F2-F5 fractions in b-$PBr_{0.42}S$ are very close to that of the mother b-$PBr_{0.42}S$ sample.

2. Derivation of Fitting Equation for Figure 3

The retention behavior in liquid chromatography is often described by the column retention constant k, defined as:

$$k = \frac{t_r - t_0}{t_0} \tag{S-4}$$

where t_0 and t_r are the solvent and solute retention times, respectively. Ryu and Chang showed that this treatment leads to the following equation [16]:

$$\ln k = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} + \ln \phi \quad , \tag{S-5}$$

where $\phi = V_s/V_m$., the ratio of the volume of the stationary phase (V_s) to the volume of the mobile phase (V_m). ΔH^o represents the difference between the enthalpy of the polymer chain in the stationary phase and the enthalpy of the polymer chain in the mobile phase. Accordingly, ΔS^o is the difference between the entropy of the polymer chain in the stationary phase and the entropy of the polymer chain in the mobile phase.

According to the Martin's rule, $\Delta H^o_{polymer}$ is proportional to the number of adsorbing segments for intermediate molecular weights. When the total number of segments, N, becomes too large, the relationship is no longer linear. The molecular weight used in this investigation (≈30 kDa) is well within the linear range [16]. Because of the LCCC condition for styrene, only

the 4-BrS units are responsible for adsorbing the copolymer to the stationary phase. As a result, the enthalpy of adsorption per chain should be proportional to the number of adsorbing segment, $N_{4\text{-BrS}}$:

$$\Delta H^{o} = N_{4-BrS} \cdot \Delta H^{o}_{4-BrS} = N \cdot x_{4-BrS} \cdot \Delta H^{o}_{4-BrS}, \quad \text{(S-6)}$$

where N is the total number of segments and $x_{4\text{-BrS}}$ is the mole fraction of 4-BrS in the copolymer. Substituting into Eqs (S-4)-(S-6) leads to:

$$x_{4-BrS} = \alpha \ln(t_r - t_0) + \beta. \quad \text{(S-7)}$$

where α and β are fitting parameters.

3. Chemical distributions of the individual fractions F1-F6 in copolymers

Table S-IV lists the average chemical compositions of both the mother sample as well as the individual fractions F1-F6 for both copolymers. Those were employed in determining the conversion of the retention time to chemical composition of the copolymer by using the experimental data and equation (S-7).

Table S-IV: The average chemical composition of all fractions collected from r-$PBr_{0.35}S$ and b-$PBr_{0.42}S$

Sample	r-$PBr_{0.35}S$	b-$PBr_{0.42}S$
mother	0.350	0.421
F1	(0.304)*	(0.382)*
F2	0.278	0.398
F3	0.338	0.432
F4	0.363	0.451
F5	0.439	0.451
F6	(0.453)*	(0.407)*

* These values of the average mole fraction of brominated PS in parenthesis are not considered for the calibration of chemical composition distribution.

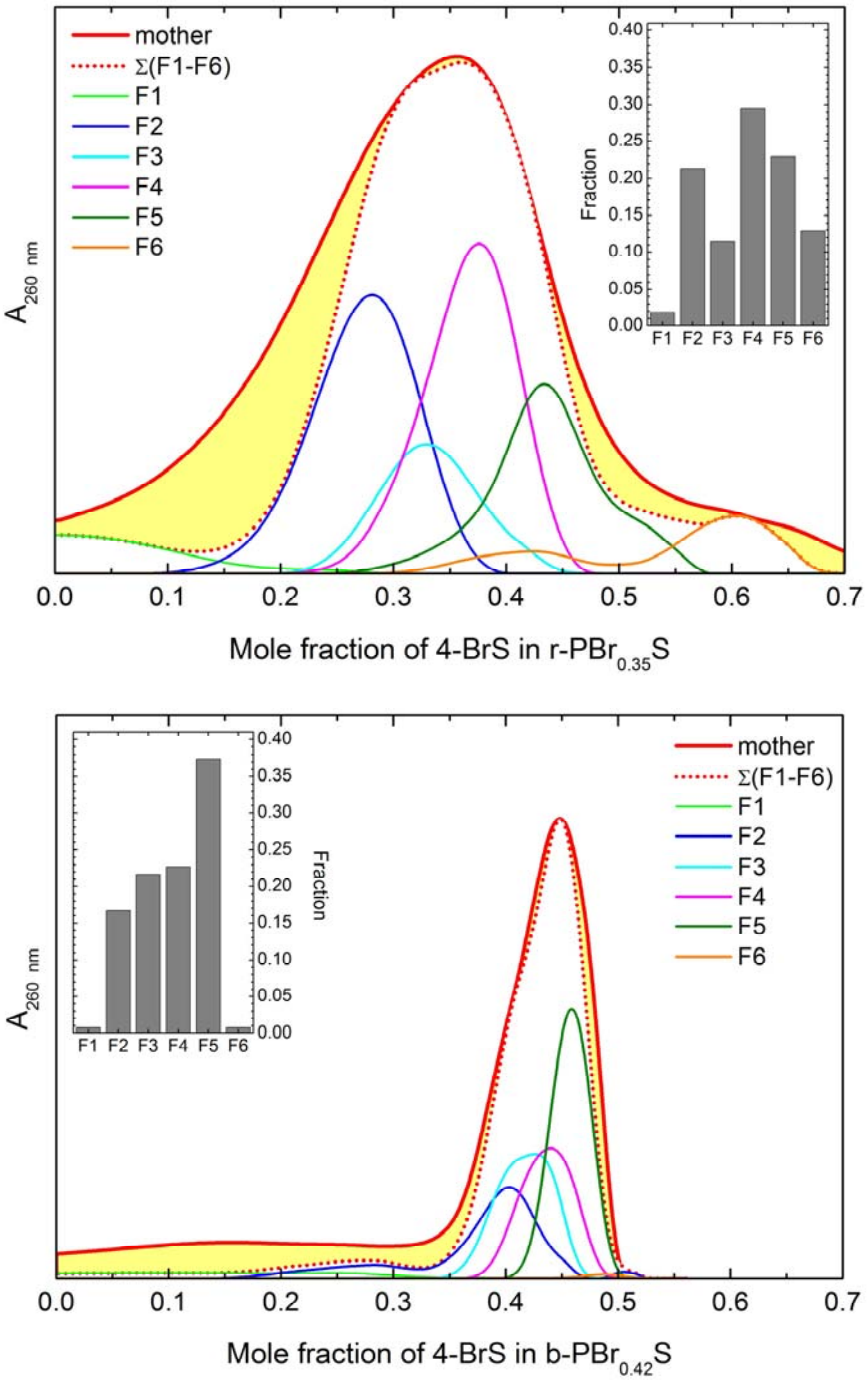

Figure S-1 Chemical distribution of the mother sample and fractions F1-F6 for r-$PBr_{0.35}S$ (top) and r-$PBr_{0.42}S$ (bottom). The white area represents the sum of the contributions of the individual fractions.

In **Figure S-1** we plot the IC eluograms as a function of the composition of the copolymer for both the mother samples as well as the fractions F1-F6 for both r-$PBr_{0.35}S$ (top) and b-$PBr_{0.42}S$

(bottom). In both plots the yellow area represents the mother sample and the white area denotes the overall contribution of the individual fractions. The insets in both parts of **Figure S-1** display the contributions of the individual fractions to the overall composition of each copolymer. The fractions of the white area (*i.e.*, contributions from fractions F1 through F6) relative to the yellow area are 0.80 and 9.86 for r-$PBr_{0.35}S$ and b-$PBr_{0.42}S$, respectively.

References

1. Han, J.; Jeon, B.H.; Ryu, C.Y.; Semler, J.J.; Jhon, Y.K.; Genzer, J., "Discriminating Among Co-monomer Sequence Distributions in Random Copolymers Using Interaction Chromatography". *Macromolecular Rapid Communications* **2009**, *30*, 1543-1548.