

Carbon-13 Labeling for Quantitative Analysis of Molecular Movement in Heterogeneous Organic Materials Using Secondary Ion Mass Spectrometry

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Secondary ion mass spectrometry (SIMS) is used to probe the movement of macromolecules in heterogeneous organic systems. Using ¹³C tracer labeling and two model systems, polystyrene/poly(2-vinylpyridine) (PS/P2VP) and polystyrene/poly(4-bromostyrene) (PS/P4BrS), the diffusion of ¹³C-labeled PS has been investigated near the respective heterogeneous interfaces using a CAMECA-IMS-6F magnetic sector mass spectrometer. ¹³C labeling has been shown to greatly minimize matrix effects (i.e., changes in secondary ion yields due to changing chemical environment) in heterogeneous systems. P2VP is a nitrogen-rich polymer (C₇H₇N monomer composition), making it an excellent model polymer for exploration of this technique for potential future use in biological applications, and probing the PS/P4BrS interface demonstrates the versatility of this technique for analysis of various heteroatom-containing materials. Results confirm that the ¹³C-labeling method does indeed allow for quantitative analysis of molecular movement in heterogeneous organic systems containing matrix-enhancing heteroatoms such as nitrogen. Therefore, extension of this method to more complicated biological systems involving multiple heteroatoms (oxygen, nitrogen, etc.), layers, and heterogeneous interfaces, as well as two- and three-dimensional profiling and imaging using SIMS, can be envisaged.

For over 50 years it has been known that bombarding a material surface with a charged species of sufficient energy results in emission of positive and negative secondary ions from the surface.^{1,2} Termed secondary ion mass spectrometry (SIMS), this technique has been frequently used to chemically analyze surfaces

or to depth profile organic and inorganic material films.^{3–7} More recently, the use of SIMS for chemical analysis in the field of biotechnology has expanded dramatically.^{7–16} SIMS has been found to be invaluable for investigations such as drug delivery, cancer research, and development of biomedical devices.^{7,8} However, a major drawback of quantitative SIMS analysis is the difficulty in determining absolute concentrations of the probed species due to fluctuations in secondary ion yields as a function of chemical composition (i.e., matrix effects).^{17–20} These matrix effects are particularly prominent when chemical heterogeneities are present in the system.^{19–21} Most bioorganic materials contain heteroatoms, such as nitrogen and oxygen, which have strong carbon matrix-enhancing effects,^{6,22,23} and therefore, techniques such as isotopic labeling have been utilized in an attempt to overcome these drawbacks.^{19,20,24–27}

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Minor-abundance isotopic tracer labels such as ^2H , ^{13}C , and ^{15}N have been used extensively in the biological and soft condensed matter communities.^{19,20,24–27} The ^2H label in particular has been used due to its minimal natural abundance background (0.015%)²⁸ and its ability to provide instrumental contrast with numerous experimental techniques such as infrared spectroscopy, small angle neutron scattering, neutron reflectometry, forward recoil spectrometry, nuclear reaction analysis, and SIMS.^{29–31} However, it has been found that ^2H labeling can cause changes in the thermodynamic behavior of the system being analyzed, particularly near heterogeneous surfaces and interfaces,^{19,32,33} and ^2H is known to have strong mass fractionation effects during SIMS analysis.^{34,35} Mass fractionation, a phenomenon where two isotopes of a particular atomic species have different secondary ion yields, is known to be most influential with light atomic species (e.g., hydrogen and lithium).^{34,36,37} Nitrogen atomic species are not detected in any significant quantities using SIMS,²⁵ but CN^- has a significant secondary ion yield.²⁵ Unfortunately, a mass resolution ($m/\Delta m$) of ~ 7000 is required to completely mass resolve the pertinent species for use of this diatomic fragment³⁸ for quantitative analysis. ^{13}C has been found to provide an excellent tracer for analysis of biological and organic systems using SIMS,^{19,20,24} with $m/\Delta m = 3000$ for complete mass resolution and a reasonable natural abundance background (1.1%).²⁸ Here, we employ ^{13}C labeling to probe movement of macromolecular chains near heterogeneous interfaces. ^{13}C -Labeled polystyrene (^{13}C -PS) is used as the tracer polymer^{19,20} at heterogeneous interfaces formed between PS and poly(2-vinylpyridine) (PS/P2VP)³⁹ and PS and poly(4-bromostyrene) (PS/P4BrS).⁴⁰ P2VP is a nitrogen-rich polymer ($\text{C}_7\text{H}_7\text{N}$ monomer composition) making it an excellent model polymer for probing this technique for use in biological applications, which will invariably contain nitrogen-rich macromolecules. Analysis of the PS/P4BrS interface demonstrates the versatility of this technique for analysis of various heteroatom-containing materials (see Figure 1 for chemical structures). Results confirm that quantitative measurement of molecular movement in such materials using SIMS is indeed

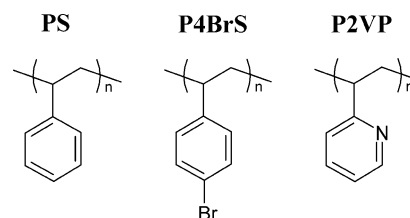


Figure 1. Chemical structures of the polymers used here.

possible using ^{13}C tracer labeling due to the minimization of matrix effects.

EXPERIMENTAL SECTION

Polymer Synthesis. Unlabeled PS (^{12}C -PS) and ^{13}C -PS were synthesized previously²⁰ using atom transfer radical polymerization (ATRP).⁴¹ ^{13}C -PS contains 10.3% ^{13}C relative to total carbon, as determined previously.^{19,20} A portion of the synthesized ^{12}C -PS was converted to P4BrS using established procedures.⁴² To a 100-mL round-bottom flask, 5 g of ^{12}C -PS was dissolved in 50 mL of nitrobenzene (Fluka). After complete dissolution, 3.7 mL of Br_2 (Sigma-Aldrich) was added, and the solution was stirred at room temperature (25 °C) for 18 h. The solution was precipitated into methanol, filtered, and dried. It was then redissolved in tetrahydrofuran (THF), precipitated in methanol, filtered, and dried. The degree of conversion (styrene segments to 4-bromostyrene segments) was determined to be 89% (n/n) using differential scanning calorimetry (DSC).⁴³

P2VP-93 was synthesized using living anionic (LA) techniques.⁴⁴ 2-Vinylpyridine (Sigma-Aldrich) was dried over CaH_2 overnight and distilled under dry nitrogen at reduced pressure just before use. THF (Fisher Scientific) was distilled from Na/K and benzophenone. *sec*-Butyllithium (1.4 M in cyclohexane) was purchased from Sigma-Aldrich and used as received. Into a 200-mL Schlenk flask equipped with a stir bar, THF (150 mL) was transferred via gas phase. After the flask was sealed with a rubber septum, *sec*-butyllithium solution (85 μL , 1.2×10^{-4} mol) was added to THF by a gastight syringe. The flask was immersed in a dry ice/acetone bath to fix the reaction temperature at -78 °C. 2-Vinylpyridine (12.0 mL, 111 mmol) was added by a gastight syringe, and the color of the reaction mixture instantaneously became orange-red. The reaction mixture was stirred at -78 °C for 12 h. The polymerization reaction was quenched by addition of a small amount of degassed methanol to convert the living anion into a dormant chain-end. The solution was poured into cold petroleum ether to precipitate, and the precipitated polymer was filtered and vacuum-dried.

The molecular weight (M_w) and polydispersity (M_w/M_n) of the P2VP-93 product were measured via gel permeation chromatography using a Jasco PU-1580 pump and a Jasco RI-1530 refractive index detector at a flow rate of 1 mL/min at room temperature (25 °C). Tetrabutylammonium bromide (0.1% w/v) in DMF was used as the eluent, and calibration was accomplished using P2VP

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Table 1. Properties of the Polymers Used Here

polymer	source	$^{13}\text{C}/(^{12}\text{C} + ^{13}\text{C})$	M_w	M_w/M_n	T_g (°C)
^{12}C -PS	ATRP	0.011	73 700	1.19	100
^{13}C -PS	ATRP	0.103	79 400	1.20	100
P4BrS	ATRP	0.011	125 000	1.19	137
P2VP-93	LA	0.011	92 700	1.07	100
P2VP-219	SPP	0.011	219 000	1.11	100

Table 2. Various Samples Prepared for Diffusion Analysis^a

sample	substrate	P_1	h_1 (nm)	P_2	h_2 (nm)	P_3	h_3 (nm)
A	SiH	^{13}C -PS	200	^{12}C -PS	230		
B	$\text{SiO}_x/\text{P4VP}$	P2VP-93	200	^{13}C -PS	37	^{12}C -PS	230
C	$\text{SiO}_x/\text{P4VP}$	P2VP-219	200	^{13}C -PS	37	^{12}C -PS	230
D	SiH	P4BrS	200	^{13}C -PS	37	^{12}C -PS	230

^a P_i is the polymer in layer i and h_i is the thickness of layer i . Layer 1 is the first layer on the substrate.

standards (Polymer Standards Service-USA). P2VP-219 was purchased from Scientific Polymer Products, Inc. (SPP; Ontario, NY). Figure 1 contains the chemical structures of PS, P2VP, and P4BrS. The glass transition temperatures (T_g) of the polymers were determined using DSC, and the properties of all of the polymers are listed in Table 1.

Materials and Sample Preparation. Silicon (100) wafers were cut to 2 cm \times 2 cm squares, soaked in BakerClean JTB-111 (J.T. Baker), and rinsed with deionized (DI) water. They were then soaked in aqueous hydrofluoric acid (10% v/v) and again rinsed with DI water. This provided a hydrogen-passivated substrate (SiH). For some samples, a native oxide layer ($\text{SiO}_x \approx 2$ nm) was created by exposing the samples to UV-ozone for ~ 30 min. All layered assemblies used here are shown in Table 2. A ^{12}C -PS/ ^{13}C -PS bilayer sample (sample A) was prepared to measure the ^{13}C -PS tracer diffusion coefficient (D_0). ^{13}C -PS (~ 200 nm) was spin-cast from toluene (Acros) onto SiH and annealed for 1 h at 130 °C to remove residual solvent. ^{12}C -PS (~ 230 nm) was cast from toluene onto SiO_x , scored with a sharp tip, floated into DI water, and picked up with the ^{13}C -PS layer. The bilayer assemblies were annealed at 80 °C for 24 h to remove residual solvent while preventing ^{13}C -PS/ ^{12}C -PS interdiffusion.⁴⁵

For samples where P2VP was the bottom layer, an amorphous poly(4-vinylpyridine) (P4VP; SPP) passivation layer (~ 5 nm) was grafted to an SiO_x surface. P4VP is completely immiscible with P2VP and strongly binds to SiO_x .⁴⁶ This prevents the P2VP from interacting with the substrate,⁴⁷ which could change the mobility of the polymer chains at the heterogeneous interface.⁴⁸ P2VP-93 (sample B) and P2VP-219 (sample C) were each cast onto the P4VP passivation layer from chlorobenzene (Sigma-Aldrich) to a thickness of 200 nm (approximately) and annealed at 150 °C for

Table 3. Sputter Rates (S_R) of the Individual Polymers and Sputter Rates Relative to (100) Si ($S_R/S_{R,\text{Si}}$) under the Analysis Conditions Implemented Here

material	S_R (nm ³ /ion)	$S_R/S_{R,\text{Si}}$
PS	0.23	1.4
P2VP	0.24	1.5
P4BrS	0.21	1.3
(100) Si	0.16	1.0

1 (P2VP-93) or 4 h (P2VP-219). All anneals were performed in vacuo to prevent polymer degradation. The P4BrS layer (sample D) was cast onto the SiH surfaces from chlorobenzene to a thickness of 200 nm (approximately) and annealed for 24 h at 150 °C. The ^{13}C -PS layer was directly cast onto P2VP from toluene or floated from DI water onto P4BrS²¹ to a thickness of 37 nm. The ^{13}C -PS/P2VP and ^{13}C -PS/P4BrS bilayers were annealed for 4 h at 105 °C followed by 1 h at 140 °C to ensure complete solvent removal and formation of equilibrium interfaces.⁴⁹ Onto the ^{13}C -PS layer, a 230-nm (approximate) ^{12}C -PS was floated from DI water, and the film assemblies were annealed at 80 °C for 24 h. Immediately prior to SIMS analysis, a sacrificial deuterium-labeled PS layer (~ 50 nm) was placed onto all layered assemblies to allow the primary ion beam to equilibrate,⁵⁰ and a thin Au coating (~ 20 nm) was sputtered onto the samples to assist in charge neutralization.²¹

Secondary Ion Mass Spectrometry. SIMS was performed using a CAMECA-IMS-6f magnetic sector mass spectrometer (Courbevoie, France). Analyses were made at 6.0-keV impact energy (1 kV primary, -5 kV sample bias) with 4 nA of Cs^+ primary ion current rastered over a 120 μm \times 120 μm area. Negative secondary ions were detected from a 30- μm -diameter optically gated area positioned in the center of the raster. The angle of incidence for the primary ions was 27°, and a mass resolution $m/\Delta m = 3000$ was used to completely separate $^{13}\text{C}^-$ from $^{12}\text{C}^1\text{H}^-$ secondary ions.^{19,20} Charge neutralization was accomplished using the so-called “electron cloud” method.^{20,51} Electrons at normal incidence to the sample are provided with a potential just below that of the sample and are present just above the surface. In this self-compensating method, any charging due to ion bombardment of the surface of the sample is compensated by electrons that are drawn from the electron cloud. This method avoids high-energy electron impact, which would degrade the sample.

RESULTS AND DISCUSSION

The sputter times of PS, P2VP, and P4BrS single-layer films (~ 200 nm) were measured without sacrificial or Au layers. The linear erosion rates (nm/s), as determined from the measured sputter times and profilometry-determined crater depths, were converted to sputter rates (S_R) using the known crater area (120 μm \times 120 μm) and Cs^+ primary ion current (4 nA).²⁰ These values are shown in Table 3 along with the values relative to (100) Si

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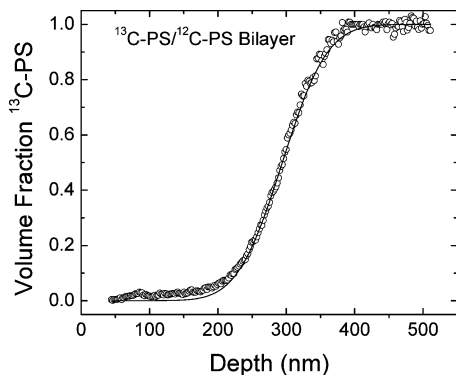


Figure 2. ^{12}C -PS/ ^{13}C -PS bilayer (sample A) used to evaluate D_0 for ^{13}C -PS. After 1 h at 130 °C, D_0 was found to be 0.36 nm²/s from a fit to eq 3 after convolution to eqs 4 and 5.

($S_R/S_{R,SI}$). All polymer S_R 's are within 10% of the nominal value for PS, and as such, the sputter rates were assumed to be constant through the entire layered assemblies (i.e., the sputter rate of PS was used). The relative detected intensities for ^{12}C were interpolated to match the detection times of ^{13}C for all analyses performed.

The ^{13}C -PS tracer diffusivity (D_0) at 130 °C was determined from the ^{12}C -PS/ ^{13}C -PS bilayer after annealing for 1 h under vacuum. By taking into account the small, but finite, mass fractionation effect³⁵ and subtracting the background natural abundance ^{13}C , the detected intensities were converted to ^{13}C -PS concentration without any calibration measurements^{19,20} using the relationship

$$\varphi(\tau) = \frac{f_{13}(\tau) - f_{\text{NA}}}{f_p - f_{\text{NA}}} \quad (1)$$

where $\varphi(\tau)$ is the volume fraction of ^{13}C -PS at sputter time τ , f_{NA} is the fraction of ^{13}C natural abundance background (0.011), f_p is the fraction of ^{13}C in the pure ^{13}C -PS used here (0.103), and $f_{13}(\tau)$ is the fraction of ^{13}C relative to total carbon ($^{12}\text{C} + ^{13}\text{C}$) at sputter time τ according to

$$f_{13}(\tau) = \frac{I_{13}(\tau)}{I_{13}(\tau) + I_{12}(\tau) \left(\frac{M_{12}}{M_{13}} \right)^\alpha} \quad (2)$$

where $I_{13}(\tau)$ is the relative detected intensity of ^{13}C at sputter time τ , $I_{12}(\tau)$ is the relative detected intensity of ^{12}C at sputter time τ , M_{13} is the mass of ^{13}C , M_{12} is the mass of ^{12}C , and α is a parameter based on the mass fractionation mechanism ($\alpha \approx 0.5$ for the conditions used here).³⁵ The profile shown in Figure 2 was fit to an analytical solution to the diffusion equation for semi-infinite systems,⁵²

$$\varphi(x) = \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{x - x_0}{2\sqrt{D_0 t}} \right) \right] \quad (3)$$

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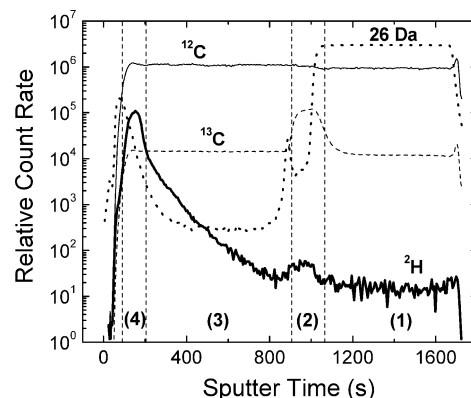


Figure 3. Raw SIMS profiles of sample B (PS/P2VP-93) at $t = 0$. The individual layers are (1) P2VP-93 layer, (2) ^{13}C -PS layer, (3) ^{12}C -PS layer, and (4) ^2H -PS sacrificial layer. Even though the 26-Da signal (dotted line) does provide information about the PS/P2VP interface, the $^{12}\text{C}^{14}\text{N}$ secondary ions from the P2VP are not mass resolved from the $^{13}\text{C}_2$ secondary ions at $m/\Delta m = 3000$.

where $\varphi(x)$ is the volume fraction of the tracer polymer (^{13}C -PS) at depth x (sputter time \times linear erosion rate), t is the annealing time, and x_0 is the distance from the surface to the initial ^{12}C -PS/ ^{13}C -PS interface, after numerical convolution⁵³ to a previously established convolution function and parameters.^{19,20} The semiempirical convolution function combines a Gaussian with a standard deviation $\sigma_{\text{eff}} = 1.7$ nm, which accounts for ion-induced mixing, and an exponential, which has a characteristic decay length $\lambda_d = 9$ nm and accounts for the observed tailing (i.e., implantation of sample species further into the sample). The Gaussian convolution function is

$$G(x) = \frac{1}{\sqrt{2\pi} \sigma_{\text{eff}}} \exp \left[-\frac{1}{2} \left(\frac{x}{\sigma_{\text{eff}}} \right)^2 \right]; \quad x \rightarrow (-\infty, \infty) \quad (4)$$

and the exponential decay is described by

$$F(x) = \frac{1}{\lambda_d} \exp \left(-\frac{x}{\lambda_d} \right); \quad x \rightarrow (0, \infty) \quad (5)$$

Even though ion-induced mixing is a consequence of SIMS analysis, ion-induced diffusion (macroscopic changes) was ruled out previously with measurement of ^{12}C -PS/ ^{13}C -PS bilayers without any thermal treatment, as indicated by the sharp interface.^{19,20} From sample A, D_0 was determined to be 0.36 nm²/s at 130 °C, which is consistent with previously reported values of PS diffusivity.⁵⁴ From analysis of the region in Figure 1 from 430 to 500 nm, the experimental error (standard deviation) associated with each point was determined to be $\sim 2\%$ of the experimental volume fraction.

Next, the diffusivity of ^{13}C -PS at the PS/P2VP-93 interface was probed with sample B at 130 °C. The raw SIMS intensities of ^2H (sacrificial layer), ^{12}C , ^{13}C , and 26 Da negative secondary ions are shown in Figure 3 as a function of sputter time. At $m/\Delta m = 3000$, the intensity at 26 Da is not mass resolved, and as such, it is a

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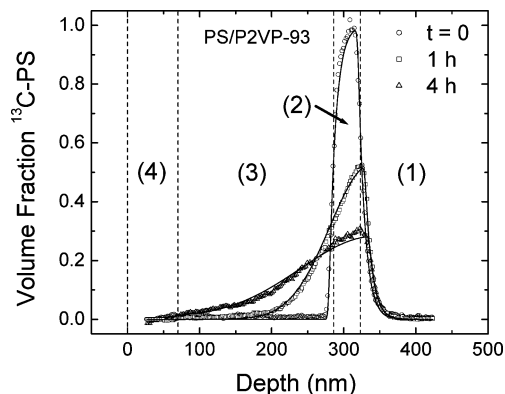


Figure 4. ^{13}C -PS diffusion profiles for sample B (PS/P2VP-93) after (○) $t = 0$, (□) $t = 1$ h, and (Δ) $t = 4$ h at $130\text{ }^{\circ}\text{C}$. The individual layers are (1) P2VP-93 layer, (2) ^{13}C -PS layer, (3) ^{12}C -PS layer, and (4) ^2H -PS sacrificial layer. The model diffusion profiles are also shown (solid lines) using $D_0 = 0.36\text{ nm}^2/\text{s}$.

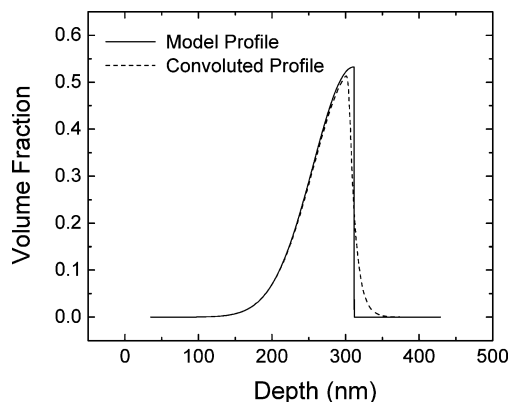


Figure 5. Comparison of the model (Fickian) diffusion profile (solid line), generated using eq 3 superposed over periodic boundaries, with the convoluted (see eqs 4 and 5) model diffusion profile (dashed line) for sample B after 1 h at $130\text{ }^{\circ}\text{C}$ ($D_0 = 0.36\text{ nm}^2/\text{s}$). The model profile approximates the true ^{13}C -PS concentration profile before ion-induced mixing and tailing effects are introduced with the 6.0-keV Cs^+ bombardment.

mixture of species such as $^{13}\text{C}_2$, $^{12}\text{C}_2^2\text{H}$, and $^{12}\text{C}^{14}\text{N}$.³⁸ If future work does require complete resolution of the $^{12}\text{C}^{14}\text{N}$ ($m/\Delta m \approx 7000$),³⁸ the degree of ^{13}C substitution, primary ion impact energy, or both can be increased if needed to maintain high detection sensitivity and signal-to-noise ratio. However, for probing the movement of ^{13}C -PS in this system, $m/\Delta m = 3000$ is sufficient, and by normalizing the ^{13}C detected intensity by the total carbon intensity ($^{12}\text{C} + ^{13}\text{C}$), the matrix effects are greatly reduced. The concentration depth profiles showing the transition from $t = 0$ to 4 h at $130\text{ }^{\circ}\text{C}$ for sample B are shown in Figure 4 with a comparison to a convoluted diffusion equation using $D_0 = 0.36\text{ nm}^2/\text{s}$. In order to obtain an analytical solution to the diffusion equation, eq 3 was superposed over periodic boundaries to account for the zero-flux conditions at the vacuum surface and heterogeneous interface.⁵⁵ Figure 5 shows a comparison of the model (Fickian) diffusion profile with the convoluted model diffusion profile for sample B after 1 h at $130\text{ }^{\circ}\text{C}$. The model profile approximates the true ^{13}C -PS concentration profile before ion-induced mixing and tailing effects are introduced with the 6.0-keV Cs^+ bombardment. Clearly,

(55) Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Oxford University Press: New York, 1975.

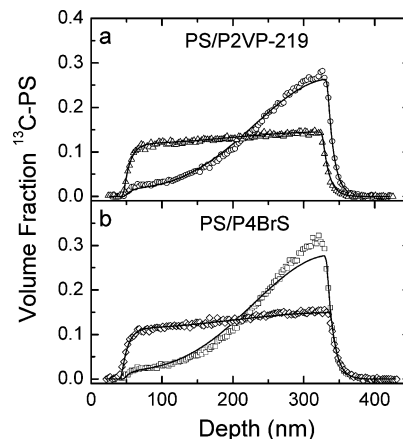


Figure 6. ^{13}C -PS diffusion profiles for (a) sample C (PS/P2VP-219) after (□) $t = 30$ min and (Δ) $t = 2$ h at $140\text{ }^{\circ}\text{C}$, and (b) sample D (PS/P4BrS) after (□) $t = 30$ min and (◇) $t = 2$ h at $140\text{ }^{\circ}\text{C}$. The individual layers are analogous to those identified in Figures 3 and 4. The model diffusion profiles are also shown (solid lines) using $D_0 = 3.3\text{ nm}^2/\text{s}$.

no major artifacts or line-shape changes are introduced into the ^{13}C -PS concentration profile as a result of SIMS analysis, and as such, nearly ideal Fickian diffusion⁵² of ^{13}C -PS is directly observed near the heterogeneous PS/P2VP interface. This demonstrates that the SIMS analysis and data reduction using eqs 1 and 2 provides quantitative results.

Finally, samples C and D were used to compare the diffusion of ^{13}C -PS at PS/P2VP and PS/P4BrS interfaces at $140\text{ }^{\circ}\text{C}$. In order to determine D_0 for ^{13}C -PS at $140\text{ }^{\circ}\text{C}$, the known temperature dependency of PS diffusion,⁵⁶

$$\log \left[\frac{D_0/T}{D_g/T_g} \right] = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \quad (6)$$

was used, where D_g is the tracer diffusivity at $T = T_g$ ($1.8 \times 10^{-6}\text{ nm}^2/\text{s}$ for ^{13}C -PS, as determined from D_0 at $130\text{ }^{\circ}\text{C}$), and C_1 and C_2 are previously reported constants (13.7 and $48\text{ }^{\circ}\text{C}$, respectively⁵⁶). As shown in Figure 6, results are in agreement with ideal Fickian diffusion using $D_0 = 3.3\text{ nm}^2/\text{s}$ calculated from eq 6, as expected. The PS/P4BrS interface seems to have a subtle slowing down of the ^{13}C -PS diffusion, but this is due to the higher T_g of the P4BrS, causing a slight reduction in chain mobility at the PS/P4BrS interface (see Table 1).⁴⁹ However, it is obvious that the ^{13}C -labeling method does indeed promote quantitative analysis of molecular movement in heterogeneous organic systems containing matrix-enhancing heteroatoms. Therefore, extension of this method to more complicated biological systems involving multiple heteroatoms, layers, and heterogeneous interfaces, as well as two- and three-dimensional profiling and imaging using SIMS, can be envisaged.⁷⁻¹⁴

CONCLUSIONS

^{13}C labeling has been shown to greatly minimize matrix effects (i.e., changes in secondary ion yields due to changing chemical environment), thereby allowing detailed chemical analysis and depth profiling of heterogeneous organic systems.^{19,20} Here, the

(56) Allen, V. R.; Fox, T. G. *J. Chem. Phys.* **1964**, *41*, 337.

minimization of these matrix effects permitted quantitative analysis of ^{13}C -PS diffusion near the interfaces formed from PS/P2VP and PS/P4BrS. P2VP is a nitrogen-rich polymer ($\text{C}_7\text{H}_7\text{N}$ monomer composition), making it an excellent model polymer for exploration of this technique for potential future use in biological applications, and analysis of the PS/P4BrS interface demonstrates the versatility of this technique for analysis of various heteroatom-containing materials. In all cases, nearly ideal ^{13}C -PS diffusion was observed near the heterogeneous interfaces, as confirmed with a comparison to Fickian diffusion models. Therefore, we expect the utility of this analysis method to be further extended to systems

of technological relevance, such as drug delivery,^{7,15} along with capabilities extending to quantitative two- and three-dimensional profiling and imaging using SIMS.

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