Surface Composition of Poly(styrene-d_8–styrene) Random Copolymers Studied by Static Secondary Ion Mass Spectroscopy

S. Affrossman,*,† M. Hartshorne,† R. Jerome,‡ H. Munro,§ R. A. Pethrick,† S. Petitjean,‡ and M. Rei Vilar‖

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K., Centre for Education and Research on Macromolecules, Universite de Liege, Sart Tilman B6, B-4000 Liege, Belgium, Courtaulds plc, Lockhurst Lane, Coventry CV6 5RS, U.K., and CNRS, Laboratoire de Spectrochimie Infrarouge et Raman, 4 rue H. Dunant, F-94320 Thiais, France

Received March 2, 1993; Revised Manuscript Received June 29, 1993®

ABSTRACT: The surface compositions of a series of random copolymers of styrene and deuteriostyrene have been determined by SIMS. The mechanism of fragmentation during the SIMS process is examined, and the contribution from naturally occurring isotopes is evaluated. The data are shown to fit a model of a completely random copolymer system if they are corrected for the effects of impurities introduced in the syntheses and for the contribution from ^{13}C.

Introduction

The segment distribution of a homopolymer system in the region of an interface can be nonuniform, even in material with a narrow dispersity, because of variations in chain lengths and/or possible chain end effects. It is important to know the composition near the surface because this region will determine the behavior of the polymer in adhesion. Measurement of the surface segment distributions requires labeling of part of the material. Chemical labeling produces a large perturbation of the system, which may alter the surface composition. Much lesser disturbance to the system is obtained by isotopic labeling. The factors which control the surface composition of polymers are, however, so finely balanced that the slight chemical differences produced by isotopic labeling are sometimes sufficient to product segregation effects; e.g. a blend of hydrogenous and deuterated styrenes behaves like a two component system, as observed by Jones et al.[1] The deuterated component segregates to the surface at a rate controlled by the bulk mutual diffusion constant.[2] Segments in copolymers of hydrogenous and deuterated monomers are more constrained than the components of blends. In block copolymers, the combination of the interfacial energetics and the physical restraint of tying the blocks together may produce very specific effects, as exemplified by the periodicity induced by segregation in poly(styrene-*b*-methyl methacrylate) diblock copolymers.[3] In a random copolymer there is a large number of blocks in a given chain, and the average size of the blocks is correspondingly reduced. Movement of blocks to produce segregation then becomes difficult, and it is generally assumed that random copolymers show no segregation effects.

There are few techniques which can distinguish isotopes. Secondary ion mass spectroscopy, SIMS, is uniquely suited for this purpose. It has been used, in the static mode, SSIMS, to determine the molecular composition of the outermost surface layer of polymers. With the advent of time-of-flight SSIMS, the analysis is even less destructive than with quadrupole SSIMS and can provide high molecular weight and high resolution data.[4] In the dynamic mode, the destructive power of a high flux incident beam is used to advantage to obtain element depth profiles, e.g. for polymer bilayers[5] and microphase separated materials.[3]

In a block copolymer the fragmentation of the polymer within a block during SSIMS will take place in an environment similar to that of the homopolymer. The relative intensities of signals characteristic of each component will be related simply to the surface concentrations. In a random copolymer the environment of a given monomer unit will contain a variable number of neighboring monomer units of the other component. If the fragmentation process involves more than one monomer unit, the chemistry may then differ from that within a block.

The SSIMS process involves the local dissipation of a large amount of energy associated with the incident ion. The relatively nondestructive nature of SSIMS is a consequences of the small number of events. The energy absorbed during the ion–solid interaction can cause mobility of hydrogen or even carbon atoms.[6] Migration of hydrogen during the fragmentation of random copolymers of two chemically distinct hydrogenous components will not be observable from the mass spectrum. The correlation between the SSIMS signal and the concentration will depend, however, on the relative contribution of such processes, as the matrix is changed from poor to rich in one component. Random copolymers of similar components should give linear correlations, e.g. poly(styrene–*p*-methylstyrene).[7] Random copolymers of dissimilar components may or may not give good correlations, depending on the particular fragments chosen for measurement. In the case of random copolymers of hydrogenous and deuterated analogues migration will produce fragments at new masses. Other important factors are (a) the effects of impurities, which will be invariably hydrogenous, (b) the contributions from initiators and end capping agents, for low molecular weight polymers, and (c) the possibility of isotopic kinetic rate effects.

This paper forms part of a study of polymer surfaces by several European laboratories, initiated by the European Science Foundation, to evaluate analytical techniques for

---

† University of Strathclyde.
‡ Universite de Liege.
§ Courtaulds plc.
‖ CNRS.
® Abstract published in *Advance ACS Abstracts*, September 1, 1993.

quantification of polymer surface composition. A series of random copolymers of hydrogenous and deuterated styrene have been prepared for this work. These are investigated here in detail by SSIMS to provide information on the fragmentation process and to examine the quantification of the data. A parallel study of the quantification of analysis by HREELS of the above polymers is published separately.[8]

Experimental Section

Preparation of Polymers. Polymers were prepared by the living anionic method. Polymerization was initiated by naphthalene–lithium in THF at −78 °C. The polymerization was terminated by methanol, and the polymers were recrystallized several times from chloroform. This procedure gave polymers with identical end groups. Dispersities varied from M_w/M_n = 1.46 to 3.05. Molecular weights varied from M_n = 26 000 to 54 000. One sample, prepared from *s*-butyllithium, had a molecular weight of 8300 and a dispersity of 1.04. This polymer is terminated by a *s*-butyl group at one end and hydrogen at the other. The preparations will be reported fully.[8]

Bulk Analysis. The compositions of the copolymers were determined by elastic recoil detection analysis, ERDA, and by infrared spectroscopy. The infrared intensities of the aromatic C–H and C–D vibrations were measured and corrected for cross-section. A detailed account of the quantification of the bulk will be published.[8] It should be noted that for the correlations between the SSIMS and bulk compositions obtained below, the aromatic infrared signal was chosen as a measure of bulk composition. This selects the styrene monomer and discriminates against a nonaromatic impurity.

Preparation of Samples. Dilute solutions, ca. 1% w:w, of the polymer in chloroform or carbon tetrachloride were dropped onto a section of silicon wafer spinning at 4000 rpm. Alternatively, a drop of solution on the substrate was allowed to evaporate. Film thicknesses varied from ca. 0.5 to several microns. No effect was observed on the SSIMS spectra by variation in film thickness.

Surface Analysis. Samples were analyzed with a Vacuum Generators 12-12 quadrupole mass analyzer fitted with an einzel lens energy filter designed in house. A Vacuum Science Workshop mass filtered ion gun and electron flood gun were used to provide the incident ion beam and charge compensation, respectively. The incident beam of argon ions, at 3 keV and with a current measured at the ion gun of 0.2 nA, was focused onto ca. 5 mm^2 of the sample. The flood gun energy was set to 30 eV.

Results

Surface Analysis. SSIMS Spectrum of Polystyrene. The dominant fragment in SSIMS analysis of polystyrene is the tropylium ion, $C_7H_7^+$, mass 91 Da.[9] In the deuterated polymer this becomes $C_7D_7^+$, mass 98 Da. The SSIMS spectra of hydrogenous (H) styrene and deuterated (D) styrene in the range 90–102 Da are shown in Figure 1. There is little overlap of signals from the two polymers in the region of interest; i.e., the contribution at 98 Da is very low for the (H) polymer, and the contribution at 91 Da is low for the (D) polymer. The tropylium ion signals should therefore provide a good measure of the relative concentrations in a partially deuterated polymer, even near the ends of the composition range.

In order to ensure that the behavior of a partially deuterated polymer is understood, it is necessary to examine the spectra in detail in the region where fragments of mixed isotope composition will be expected. The contribution of 94 Da for the (D) styrene is assigned to C_7D_5 and corresponds to an analogous fragment found in the spectrum of the (H) polymer.

Correction for ^{13}C Contributions. In the spectrum for (H) styrene, a signal, approximately 8% of the intensity of the 91-Da peak, is observed at 92 Da. If this corresponded to a C_7H_8 fragment, then there should be an analogous C_7D_8 contribution at 100 Da, in the (D) styrene spectrum. In fact there is no evidence of a signal of such intensity in the (D) spectrum (Figure 1). There is, however, a contribution at 99 Da of approximately 8% of the 98-Da peak.

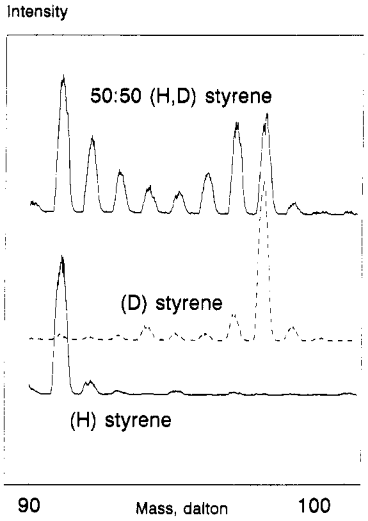

Figure 1. SSIMS spectra of poly(styrene), poly(styrene-d_8), and poly(styrene-d_8–styrene).

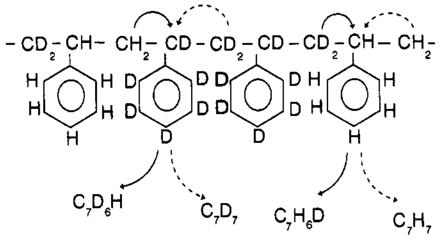

Figure 2. Fragmentation of styrene.

It is well-known in mass spectroscopy that fragments containing several carbon atoms are accompanied by satellites which result from the natural ^{13}C abundance. Little use has been made of this phenomenum in the SIMS literature. The intensity of the satellite at M + 1 can be calculated from the probability of the fragment containing one ^{13}C atom. For the C_7 fragments this is 7 × ^{13}C abundance), i.e. 7.77%, which agrees with the observed values for the 92:91 Da relative intensities for (H) and 99:98 Da relative intensities for (D) styrene; i.e. the 92- and 99-Da signals are postulated to be $^{12}C_6{}^{13}CH_7$ and $^{12}C_6{}^{13}CD_7$, respectively. A similar argument does not apply, in practice, to naturally occurring deuterium in hydrogen, because of its very low abundance.

Mechanism of Fragment Formation. For a tropylium ion to be formed from polystyrene, hydrogen/deuterium has to be abstracted from the backbone (Figure 2). The SSIMS spectrum of a typical random copolymer for the range 90–102 Da is shown in Figure 1. The increased intensities of signals from fragments in the range 92–97 Da are evidence of the proximity of (H) and (D) monomer units, resulting in tropylium fragments with mixed isotopes. An (H) monomer adjoining a (D) monomer would give either a C_7H_7 or C_7H_6D fragment, and similarly, a (D) monomer adjoining an (H) monomer would give either a C_7D_7 or C_7D_6H fragment. The relative intensities, 91:92 and 98:97, will depend on the kinetics of abstraction of the H or D atoms, and so may show an isotope effect.

In a partially deuterated polymer, the 92-Da signal contains contributions from $^{12}C_6{}^{13}CH_7$ and $^{12}C_7H_6D$. The former contribution can be estimated from the intensity of the C_7H_7 peak, as above.

Impurities and Intramolecular Transfer. The 97-Da signal should consist only of C_7D_6H, and as such should not appear in the spectrum of pure (D) styrene. All samples of pure (D) styrene examined gave signals at 97 Da in appreciable amounts. Pure (D) styrene has intrinsic hydrogen because the initiator is (H) *n*-butyllithium, and generally the chain is terminated with (H) methanol to leave a–$C(C_6D_5)DH$ end group. However, the relative signals, 97:98 Da, were obviously too large in several samples to be associated with end groups. A more likely source of hydrogen is the (D) monomer used for synthesis, which is only ca. 98% pure.

Another possibility is the transfer of hydrogen to another molecule during fragmentation in the SIMS process. Hydrogen containing solvents, or trapped water, may then be responsible for the observed 97-Da signals. It is difficult to control the amount of entrapped water or solvent in the surface region. Intramolecular transfer was investigated therefore by comparing the spectrum from (D) styrene in carbon tetrachloride with that from a blend of (D) and (H) styrene in the same solvent. The latter solution thus contains a large known source of hydrogen, though it is not necessarily as labile as hydrogen in water impurity. The 97:98 Da relative intensities were not changed significantly by addition of (H) styrene to the system. The 97-Da signal observed from pure styrene was therefore assumed to arise from (H) material incorporated into the (D) polymer chain at some stage in the synthesis. The impurity is not (H) styrene because no corresponding C_7H_7 signal was produced. It is unlikely that the main feature in the spectrum from an impurity would consist of a 97-Da signal, i.e. that the 97-Da signal corresponded to an intrinsic impurity fragment. More probably the 97-Da signal corresponds to C_7D_6H, which is formed from (D) monomer adjacent to the (H) impurity.

End Effects. Chain end segregation, would leave the surface rich in terminal $-C_7H_7$ or $-C_7D_6H$ groups because of termination by CH_3OH at both ends of the polymer. The latter group would readily fragment by breaking only one bond to give a 97-Da fragment. The broad distribution of molecular weights of most of the polymers means that low molecular weight material is present. If this segregated preferentially, then it would also lead to a disproportionately large number of end groups at the surface. The signal for the C_7D_6H fragment will contain contributions from chain ends and hydrogenous impurities. The problem does not arise with the C_7H_6D, 92-Da, signal, as the termination of an (H) monomer end gives $-C_7H_7$.

H/D Migration. The spectrum of the random copolymer (Figure 1) shows that the contributions at 93–96 Da have increased compared to the homopolymers. The increase in intensities in this region are postulated to arise from hydrogen/deuterium transport during molecular rearrangements involving more than one monomer unit. Migration of hydrogen during SIMS fragmentation has been reported.[6] The extent of this process may vary with the fragment examined and will be complicated to interpret. In this system, the signal intensities produced by isotope mixing in the tropylium ion region are small compared to those from the primary H/D abstraction and will be neglected in the following discussion.

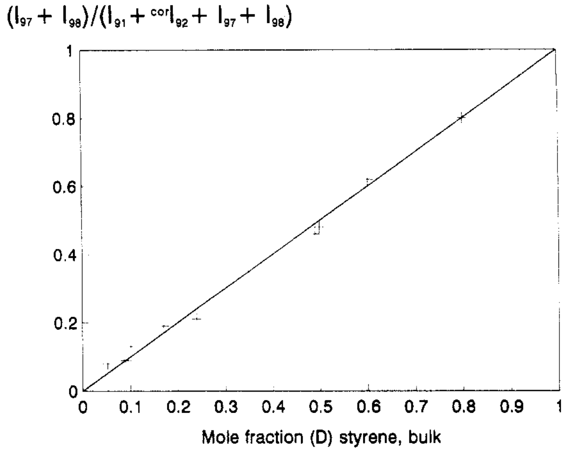

Figure 3. Mole fraction of (D) styrene from SSIMS intensities of "total heavy" fragments, $(C_7D_7 + C_7D_6H)/(C_7H_7 + C_7H_6D + C_7D_6H + C_7D_7) = (I_{98} + I_{97})/(I_{91} + {}^{cor}I_{92} + I_{97} + I_{98})$, versus bulk x_D values.

Correlation of Surface and Bulk Analyses. The abstraction of hydrogen, or deuterium, from the backbone required for formation of the tropylium ion leads to the deuterated monomers appearing in the SSIMS spectrum as C_7D_7 or C_7D_6H, i.e. 98- or 97-Da fragments. Similarly, the hydrogenous monomers appear as C_7H_7 or C_7H_6D, i.e. 91- or 92-Da fragments. The total deuterium content of the polymer may then be written as

$$^{ssims}x_D = (I_{98} + I_{97})/(I_{91} + {}^{cor}I_{92} + I_{97} + I_{98})$$

where ${}^{cor}I_{92}$ has been corrected for the contribution from $^{12}C_6{}^{13}CH_7$, i.e. 8% of I_{91}. In Figure 3 the mole fraction of deuterium obtained from the SSIMS data for the random copolymers are plotted against the bulk mole fraction of deuterium obtained by infrared analysis. There is good agreement between surface and bulk values. The surface compositions of the random copolymers are expected to be the same as those of the bulk, and the data confirm the correlation between the SSIMS signals and the surface composition.

The above expression for the total deuterium content does not depend on any mechanism for abstraction of hydrogen/deuterium during formation of the C_7 fragment. The hydrogen/deuterium may come from the neighboring aromatic ring,[6] rather than from the backbone, as shown in Figure 2. If we consider the formation of a given deuterated fragment, as opposed to the total deuterium content, then the precise mechanism of fragmentation will be important. The data may then reveal kinetic isotope effects. Also, by comparison of the data with the predictions from a statistical model, information may be obtained on the true composition, i.e. degree of randomness, of the polymer.

The simple mechanism shown in Figure 2 can be used to calculate the probability of formation of a fully deuterated fragment compared to that for a fully hydrogenated one. Assuming that the polymer is truly random, the probability of a given monomer having a right had, or left hand, neighbor of given isotopic composition can be obtained from consideration of all possible structues of three adjacent monomers (see Appendix). The calculated relative intensities of the C_7D_7 and C_7H_7 fragments, expressed as $I_{98}/(I_{98} + I_{91})$, versus the bulk deuterium content, are shown in Figure 4. The experimental points are also given. The theoretical line is a shallow curve convex to the bulk composition axis at low x_D, because the probability of an (H) monomer being adjacent to a (D) monomer is high at small x_D, and therefore there is more chance of C_7D_6H fragment being formed. Similarly, the curve is convex to the bulk x_D axis at high x_D.

The experimental points for the ratio of intensities for the C_7D_7 and C_7H_7 fragments agree generally with the theoretical predictions, except for samples in the region 0.2–0.5 x_D which showed low values. In contrast, the surface composition of samples, as calculated from the

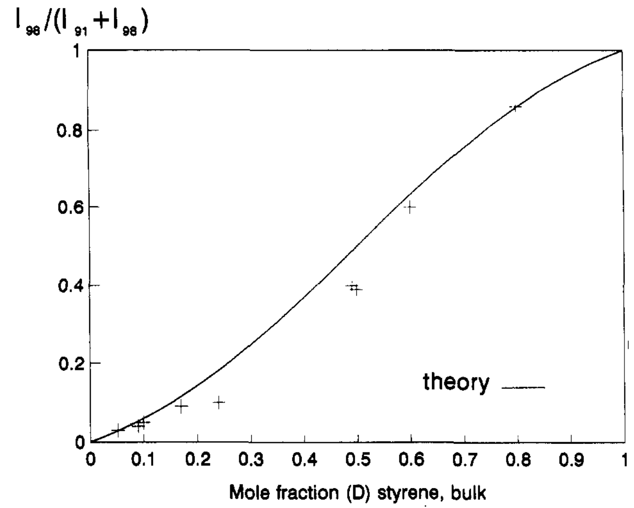

Figure 4. SSIMS intensity ratio, $(C_7D_7)/(C_7H_7 + C_7D_7) = I_{98}/(I_{91} + I_{98})$, versus bulk x_D.

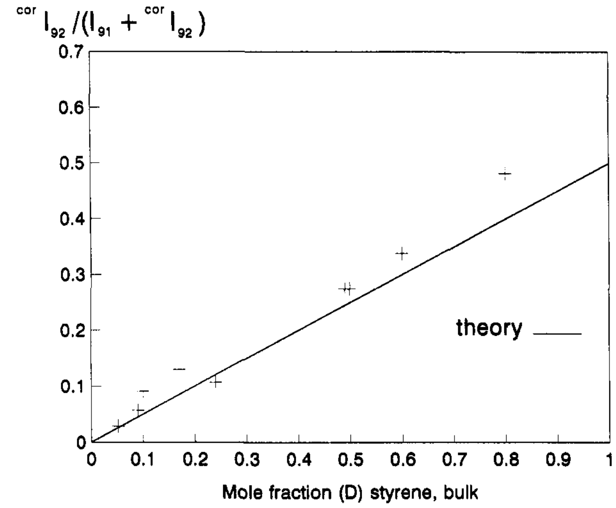

Figure 5. SSIMS intensity ratio, $(C_7H_6D)/(C_7H_7 + C_7H_6D) = I_{92}/(I_{91} + {}^{corr}I_{92})$, versus bulk x_D.

total deuterium content, showed no deviations in this region (Figure 3). Noting that the disagreement between theoretical and experimental data in Figure 4 is apparent in one region only, it is probable that the source is hydrogenous impurities which have entered the polymer chain during some of the syntheses. The impurities would increase the probability of a (D) monomer having a hydrogenous neighbor and would therefore decrease the signal from C_7D_7.

The fragmentation mechanism can be checked further by considering the relative change in the C_7H_6D and C_7H_7 intensities with deuterium content. Experimental and theoretical plots of $I_{92}/(I_{92} + I_{91})$ versus x_D are shown in Figure 5. The theoretical plot is, perhaps surprisingly, linear. The experimental data also give a linear plot, with a slightly higher gradient. A major experimental error will be the accurate determination of ratios of intensities for minor peaks. The experimental data have been derived by correcting the intensity for the 92-Da fragment for the ^{13}C contribution, but assuming no intensity at this mass from (D) polystyrene, i.e. C_7D_4, or from (H) polystyrene, i.e. C_7H_8. Examination of the contributions at mass 92 Da from (H) polystyrene and from (D) polystyrene suggests that the contributions do not exceed 2% of the 98- and 91-Da fragment intensities, though at this level it is difficult to be certain of impurity contributions. We note only that small corrections for the above contributions would improve the agreement.

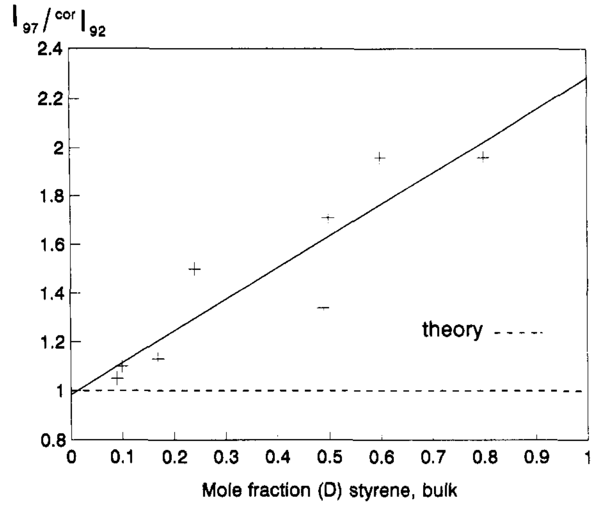

Figure 6. SSIMS intensity ratio, $C_7D_6H/C_7H_6D = I_{97}/{}^{corr}I_{92}$, versus bulk x_D.

Estimation of Blockiness. If we have sufficient understanding of the mechanism of fragmentation, we can calculate the variation in the number of blocks with composition in the random copolymer. From Figure 2 it is seen that each block will contribute one C_7D_6H and one C_7H_6D fragment. The number of blocks expressed as a fraction of the number of monomer units corresponds to the number of block ends, measured by the C_7D_6H, I_{97}, or C_7H_6D, ${}^{corr}I_{92}$, signals, divided by the total (H) + (D) monomer content; i.e. a completely alternating copolymer would give a value of 1.

Considering firstly the C_7D_6H to C_7H_6D ratio, which should equal 1, a plot of $I_{97}/{}^{corr}I_{92}$ against the deuterium content (Figure 6) shows that the intensities of these fragments are equal at $x_D = 0$, but the ratio of intensities increases with the deuterium content. The discussion above has suggested that a hydrogenous impurity is present in the copolymers, which would lead to a selective increase in the C_7D_6H, I_{97}, signal. The 97-Da signal also contains contributions from chain ends, but we have no evidence that such effects are significant in these samples.

An alternative hypothesis is that there is an isotope effect in the abstraction of H or D. The ratio of the C_7D_6H and C_7H_6D intensities would be the best experimental parameter to show any such phenomenum. An isotope effect, i.e. a difference in the kinetic rates of abstraction, would make the ratio $I_{97}/{}^{corr}I_{92} \neq 1$, but it should remain constant with composition, contrary to the observed behavior.

It is concluded that the most probable explanation for the increase in $I_{97}/{}^{corr}I_{92}$ with deuterium content is hydrogenous impurity, though not (H) styrene. Hydrogenous impurity would not alter the intensity, ${}^{corr}I_{92}$, of the C_7H_6D fragment. Therefore, for these samples, the number of blocks in the copolymer is best derived from the 92-Da intensity. Figure 7 shows the agreement between the calculated curve for the fraction of block ends and the experimental data, calculated from the C_7H_6D signal. The theoretical curve lies slightly below the experimental values. Keeping in mind the errors introduced in correcting the 92-Da signal for the ^{13}C contribution and the fact that there may be further small uncorrected contributions, as discussed with respect to Figure 5, the agreement is satisfactory.

Conclusion

SSIMS data for copolymers of isotopically substituted monomers give information on the mechanism of the

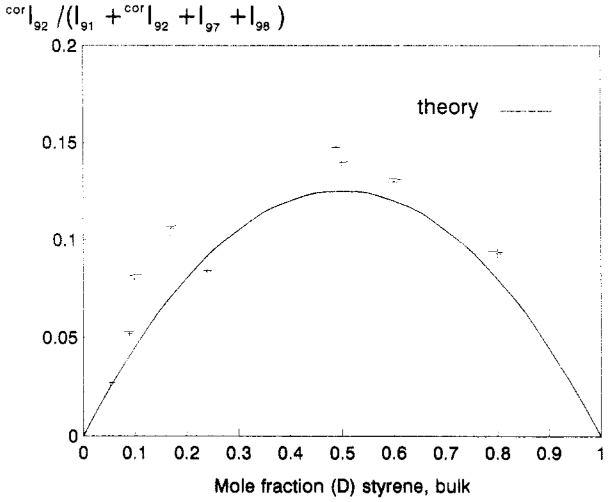

Figure 7. Fraction of blocks, $(C_7H_6D)/(C_7H_7 + C_7H_6D + C_7D_6H + C_7D_7) = {}^{cor}I_{92}/(I_{91} + {}^{cor}I_{92} + I_{97} + I_{98})$, versus bulk x_D.

SSIMS process for polymeric material. The difficulties of purifying the copolymer are emphasized in these systems. The simple mechanism proposed for the fragmentation of polystyrene during SSIMS analysis gives a satisfactory agreement between the calculated and experimental data.

Contributions from ^{13}C should be considered in evaluating SSIMS data.

No account was taken of mixing of isotopes during the derivation. Even a substantial amount of mixing would not necessarily alter the conclusions, if it was symmetric with respect to H and D migration. In the present system the extent of mixing associated with the tropylium ion formation is significant but simple abstraction of H/D is dominant.

There was no evidence of kinetic isotope effects in the abstraction of H or D. The energy involved in breaking the backbone C–C bonds and rearrangement of the ring fragment ion will be large, reducing the significance of the isotopic variation.

The SSIMS data suggest a completely random copolymer structure, i.e. no evidence of blockiness. This is expected from the synthetic conditions and verifies the assumption that the reactivity ratio of the monomers is 1.

(D) styrene segregates to the surface region in an isotopic blend of high molecular weight polymers at elevated temperatures.[1] HREELS has shown that in a low molecular weight isotopic blend, the (D) styrene segregates to the surface at ambient temperature.[10] SSIMS probes only ca. 0.5 nm normal to the surface, so very local reorientation would be observable. Chains may have more freedom at a surface than in the bulk, but there is no evidence of chain reorientation at the surface of the random copolymers to expose (D) monomer preferentially.

Appendix: Calculation of the Probabilities of Fragmentation of Random Copolymers with $x_D = d$

Consider fragmentation of the central monomer in groups of three. All possible configurations are as follows:

	probability	fragments from central monomer, Da
H-H-H	$(1-d)(1-d)(1-d)$	91 or 91
H-D-H	$(1-d)d(1-d)$	98 or 97
D-H-D	$d(1-d)d$	91 or 92
H-H-D	$(1-d)(1-d)d$	91 or 92
H-D-D	$(1-d)dd$	98 or 98
D-D-D	ddd	98 or 98
D-H-H	$d(1-d)(1-d)$	91 or 91
D-D-H	$dd(1-d)$	98 or 97
	total probability = 1	

Example: ratio of I_{92}/I_{91} for copolymer with $x_D = 0.8$

$$\{0.5[d(1-d)d] + 0.5[(1-d)(1-d)d]\}/ \{[(1-d)^3] + 0.5[d(1-d)d] + 0.5[(1-d)(1-d)d] + [d(1-d)(1-d)]\} = 0.67$$

Acknowledgment. We are grateful to the European Science Foundation for funds for collaboration. M.H. is grateful for funding from SERC and Courtaulds. S.P. is an Aspirant of the National Fund for Scientific Research and expresses his thanks to the NFSR.

References and Notes

(1) Jones, R. A. L.; Kramer, E. J.; Rafailovich, M. H.; Sokolov, J.; Schwarz, S. A. *Phys. Rev. Lett.* **1989**, *62*, 280.
(2) Zhao, X.; Zhao, W.; Sokolov, J.; Rafailovich, M. H.; Schwarz, S. A.; Wilkens, B. J.; Jones, R. A. L.; Kramer, E. J. *Macromolecules* **1991**, *24*, 5991.
(3) Coulon, G.; Russell, T. P.; Deline, V. R.; Green, P. F. *Macromolecules* **1989**, *22*, 2581.
(4) Niehuis, E.; Jurgens, U.; Benninghoven, A. *J. Vac. Sci. Technol.* **1989**, *A7*, 1823.
(5) Whitlow, S. J.; Wool, R. P. *Macromolecules* **1989**, *22*, 2648.
(6) Chilkoti, A.; Castner, D. G.; Ratner, B. D. *Appl. Spectrosc.* **1991**, *45*, 209.
(7) Affrossman, S.; Hindryckx, F.; Pethrick, R. A.; Stamm, M. In *Polymer-Solid Interfaces*; Pireaux, J. J., Bertrand, P., Bredas, J. L., Eds.; IOP Publishing: Great Yarmouth, U.K., 1992; p 337.
(8) Botelho do Rego, A. M.; Lopes da Silva, J. D.; Rei Vilar, M.; Schott, M.; Petitjean, S.; Jerome, R. To be published.
(9) Briggs, D. *Surf. Interface Anal.* **1982**, *4*, 151.
(10) Rei Vilar, M.; Schott, M.; Pireaux, J. J.; Gregoire, C.; Caudano, R.; Lapp, A.; Lopes Da Silva, J.; Botelho Do Rego, A. M. *Surf. Sci.* **1989**, *211/212*, 782.