Surface Concentration of Chain Ends in Polystyrene Determined by Static Secondary Ion Mass Spectroscopy

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ABSTRACT: Diblock and triblock copolymers of hydrogenous and deuterated styrene are synthesized to investigate chain-end segregation by static secondary ion mass spectroscopy. Films of the diblocks on silicon wafers show no significant chain-end segregation. In contrast, the triblocks show marked chain-end segregation on silicon wafers with or without the native oxide. Triblocks of isotopic structure D–H–D and H–D–H both showed end-group segregation, suggesting that the surface free energy differences between C–D and C–H are not the dominant factor.

Introduction

The surface region of a polymer can differ in chemical and/or physical properties from the bulk. In homopolymers, the distribution of molecular weights in even a low-dispersity sample may result in lower molecular weight chains segregating to the surface, producing a local change in the glass transition temperature and associated mechanical properties.

The segregation of low molecular weight chains is driven by the relationship between free energy and chain length. The factors which determine the free energy of the surface are complex and include the relative ease of filling the free volume at the surface by chains of various lengths, i.e., the packing of molecules. Maximum efficiency in filling the volume at the surface may also be related to the ability of chain ends to occupy the interstitial space between molecules. Chain ends will have additional free energy associated with the greater entropic freedom compared to segments within the chain.

The determination of chain-end distributions is difficult experimentally because of the low concentrations of the ends in the usual polymer systems, with molecular weights in the region of 10^5 or more. Low molecular weight materials, with a relatively high proportion of ends, are more amenable for study. Reliance on low molecular weight polymers must be balanced by the argument that excessive reduction of the molecular weight gives a material which is no longer representative of a polymer.

An equally important problem is the chemical nature of the chain end. In the polymer synthesis the initiated end and terminated end generally differ from the other segments. The surface energy associated with these ends may be significant in determining the surface composition. Generally, for quantification of the surface chain-end concentration, it is expedient to label the ends with groups which facilitate detection, e.g., by addition of a group with a strong ESR signal.[1] The high sensitivity of ESR allows materials with a low proportion of ends to be examined. Though the chemical nature of the ends is altered, the small number of ends may not be sufficient to alter the interfacial energetics substantially.

Ideally, the detection of chain ends should depend on the chemical differences between the ends and other segments in the polymer, as normally synthesized. Lub and Benninghoven have shown by static secondary ion mass spectroscopy (SSIMS) that the negative ion spectrum of poly(methyl methacrylate) enables chain ends to be identified because of the slight difference in segment composition produced by termination.[2] Such fortuitous chemistry is rare. A method with wider applicability is to combine the sensitivity of SSIMS with its ability to discriminate between isotopes. Substitution of hydrogen by deuterium produces new fragment masses for analysis. Deuterium substitution is not entirely free of "chemical" effects. There is a free energy difference between hydrogenous and deuterated segments which can be significant in the case of polymer systems, which have a fine balance of energy contributions.[3]

We have analyzed random copolymers of hydrogenous and deuterated styrene to determine surface segment concentrations, and the mechanism of the SSIMS process, and have shown that careful examination of the data is necessary to obtain quantitative results.[4] In this paper we use labeling with deuterium to examine the concentration of end groups in polystyrenes with M_n in the region 1×10^4–3×10^4. Polymers are prepared with one or both ends labeled.

Experimental Section

Polymers were prepared by the living anionic method. For samples 1 and 2, initiation was by *sec*-butyllithium in toluene at 0 °C, followed by propagation at room temperature overnight. The deuterated monomer was then added, and the polymerization was terminated by methanol.

Polymer 3 was synthesized by preparing a hydrogenous styrene until the termination step and then adding perdeuteriobenzyl chloride.

Samples 4 and 5 were prepared from naphthyllithium.

The polymers were reprecipitated from chloroform. The compositions were determined by infrared, except for those terminated by perdeuteriobenzyl chloride, which were assumed to have only one perdeuterio, unit at each chain end.

The factors which cause segregation in polymers are many and complex. As far as possible, the polymers in this study were prepared with low dispersities and treated in similar ways, and the samples were prepared identically, to maximize the probability that observed differences were a true function of the polymer structure.

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polymer	$10^{-3}M_n$	Δ	structure	av monomer ratio	x_D
1	27.5	1.09	H–D	255.6/7.4	0.028
2	14.6	1.06	H–D	130.9/8.1	0.058
3	7.6	2.26	H–D	71.4/1.0	0.013
4	10.4	1.10	D–H–D	2.3/95.4/2.3	0.047
5	10.4	1.10	H–D–H	3.1/86.0/3.1	0.933

Sample preparation and analysis by SSIMS are described in ref 4. Briefly, films were cast from solution onto glass or silicon wafers, cleaned with a sulfuric/peroxide mixture, and analyzed by SSIMS using a quadrupole mass filter. In one case the silicon wafer was treated with HF to remove the native oxide.

Results

The fragmentation pattern of block copolymers with large blocks is simply the addition of those of the pure homopolymers. In random copolymers the individual block sizes will vary with composition, and a proportion will be small. Fragmentation will be more complicated because of rearrangements involving adjacent monomers. Examination of the fragmentation of random copolymers of hydrogenous and deuterated styrene has shown that the data can be predicted by a simple statistical model involving H/D abstraction.[4] The samples studied in this work consist of small blocks of deuterated material attached to a hydrogenous chain, or vice versa. The blocks in the samples are small enough to require that the effect of the neighbor monomer, or termination group, should be considered in the analysis of the data. At the low deuterium contents of the polymers studied, the effects of impurities are emphasized. It is important therefore to analyze the fragment intensities critically.

Polymer 1. Figure 1a shows the SSIMS data for polymer 1, in the region 90–102 Da. The large intensity at mass 91 Da is the tropylium ion, $^{12}C_7H_7^+$, characteristic of a hydrogenous polystyrene spectrum. The signal at 92 Da, 8% of the 91 Da intensity, is the contribution from $^{12}C_6{}^{13}CH_7^+$.[4] The contribution from the deuterated tropylium ion, $^{12}C_7D_7^+$, appears at 98 Da and is seen to be small, consistent with the bulk analysis.

From the molecular weight, M_n, the monomer weights, and the fraction deuteration given by IR, the average ratio of H/D monomers in the polymer can be calculated. The value for polymer 1 is 255.6/7.4.

Formation of a tropylium ion *within* the chain requires cleavage of two C–C chain bonds and abstraction of a hydrogen or deuterium atom, $-CH_2CH(C_6H_5)CH_2- \rightarrow [H-CH(C_6H_5)]^+ \rightarrow C_7H_7^+$ or $-CD_2CD(C_6D_5)CD_2- \rightarrow [D-CD(C_6D_5)]^+ \rightarrow C_7D_7^+$ On the other hand, breaking the *terminal* C–C chain bond gives a tropylium ion without further H or D abstraction. Termination is effected by CH_3OH after growth of the deuterated end group, which results in a terminal $-CDH(C_6D_5)$ group. The corresponding tropylium ion is therefore given by $-CDH(C_6D_5) \rightarrow [CDH(C_6D_5)]^+ \rightarrow C_7D_6H^+$; i.e., the terminal monomer group gives a 97 Da ion, whereas the other deuterated monomer groups give 98 Da, $C_7D_7^+$ signals. The deuterium content can be determined, therefore, from the ratio of the 98/91 SSIMS signals, corrected for the end monomer group. Taking polymer 1 as an example, the corrected 98 Da signal is given by $I_{98}(7.4/6.4)$.

It was shown previously that a hydrogenous impurity can reduce the 98 Da signal intensity and produce a 97 Da signal.[4] Because of the low deuterium content of the samples, such effects would be negligible here. The question then arises of the origin of the 97 Da signal observed in Figure 1. Taking the above scheme for ion formation, the contribution to the 97 Da signal from the terminal D monomer is estimated from the number of D monomers to be only ca. 0.3 of the observed value. To have confidence in the relationship between the observed low signal intensities and the concentrations, we must explore the sources of the "excess" intensity. The spectrum also shows small signals at 93 and 95 Da. It was observed that before reprecipitation the intensities of the 93, 95, and 97 Da signals were relatively high and that they decreased on purification. The "residual" 97 Da intensity can therefore be assigned to five possible sources: (1) an impurity contribution with an intrinsic fragment at 97 Da at the lowest level attainable; (2) intrinsic hydrogenous styrene fragments; (3) an additional terminal group contribution; (4) mixing of D monomer with H from further along the chain during fragmentation; (5) "backward" addition of D monomer during synthesis to produce $-CH_2-CH(C_6H_5)[CD(C_6D_5)CD_2]_nCD(C_6D_5)CD_2H$.

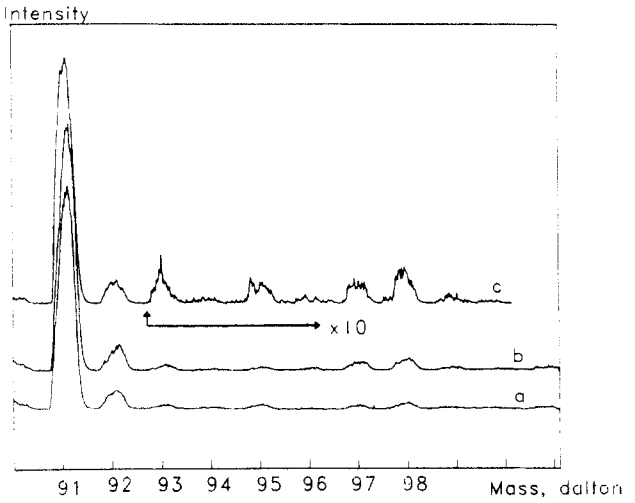

Figure 1. SSIMS spectra of diblock copolymers: (a) polymer 1, 2.8% D; (b) polymer 2, 5.8% D; (c) polymer 3, 1.4% D.

Table I. Surface Deuterium Content

		x_D		
polymer	structure	bulk	from $I_{98}/(I_{91}+I_{98})$[a]	from $(I_{97}+I_{98})/(I_{91}+I_{97}+I_{98})$
1	H–D	0.028	0.022	0.027
2	H–D	0.058	0.042	0.059
3	H–D	0.013	0.013	0.021
4a	D–H–D	0.047	0.18	0.23
4b	D–H–D[b]	0.047	0.19	0.23
		x_H		
polymer	structure	bulk	from $I_{91}/(I_{91}+I_{98})$	from $(I_{91}+I_{92})/(I_{91}+I_{92}+I_{97}+I_{98})$
5	H–D–H	0.067	0.21	0.20

[a] Corrected for the terminal group. [b] On HF-cleaned silicon.

Consider first sources 1 and 2 for the 97 Da signal. These are hydrogenous sources, in which case the residual 97 Da signal cannot arise from $C_7D_6H^+$. The deuterium content is given by the intensity of the 98 Da signal, corrected for the terminal group, and divided by the sum of the intensities of the 91 and 98 Da signals, $I_{98}/(I_{91}+I_{98})$. A minimum value for x_D is then obtained. The deuterium content of polymer 1, corrected as above for the terminal group, is given in Table I. The accuracy of the SSIMS value depends on the relative signal intensities and the impurity levels. In the low deuterium samples studied here the relevant signals are weak. The SSIMS deuterium mole fraction is only accurate to ca. 10% at high deuterium contents. At low deuterium levels an accuracy of ca. 20% is more realistic. The experimental value of 0.022 is then in reasonable agreement with the bulk value of 0.028 and suggests that the concentration of deuterated ends at the

surface is equal to, or slightly less than, the statistically expected value.

If we consider that the residual 97 Da intensity is indeed the result of an additional terminal group contribution, i.e., the residual 97 Da signal is from $C_7D_6H^+$, source 3, this can arise in two ways. There may be a higher exposure of terminal groups at the surface, or cleavage of the single terminal chain C–C bond to produce a tropylium ion may be easier than fragmentation within the chain. The former requires that the 97 Da intensity is included in the calculation of the deuterium content, which is now obtained from $(I_{97} + I_{98})/(I_{91} + I_{97} + I_{98})$, giving a value of $x_D = 0.027$ for polymer 1. This is an upper value for the surface deuterium content and is apparently in better agreement with the bulk value. However, keeping in mind the errors, the conclusion that the end-group concentration is approximately equal to, or slightly less than, the bulk value is not changed.

On the question of differences in relative rates of cleavage of terminal and chain C–C bonds, such an effect would not alter the calculation based on $I_{98}/(I_{91} + I_{98})$ as no $C_7D_6H^+$ is involved. The calculation based on $(I_{97} + I_{98})/(I_{91} + I_{97} + I_{98})$ would overestimate x_D. If there is a difference in the cleavage rates, then the values of x_D calculated from both formulas show that the effect appears to be small (Table I).

The possibility of the mixing of hydrogen from the H monomer adjacent to the D end cap, source 4, cannot be ruled out,[5] but any such effects must again be small for the same reasons as above.

In the synthetic scheme given above, the styrene monomer adds in the expected "forward" direction. Backward addition of monomer, source 5, would give $C_7D_6H^+$ from the joint of the H and D segments. Both calculations would give acceptable measures of the D content.

Polymer 2. The spectrum of polymer 2 is shown in Figure 1b. The values of x_D calculated by both methods are given in Table I. The calculation based on $I_{98}/(I_{91} + I_{98})$ gives a lower value than the calculation which assumes that I_{97} is significant, but the values are within the error. The deuterium content of the surface is again less or equal to the bulk value.

Polymer 3. This sample was terminated by perdeuteriobenzyl chloride. Cleavage of the terminal group gives $C_7D_7^+$ directly. The only mechanism for formation of $C_7D_6H^+$, 97 Da, is by mixing with the adjacent H monomer. This effect was noted to be small in the above polymers but may be more significant in this case as the end cap consists of only one D "monomer". The observed 93, 95, and 97 Da signals (Figure 1c) are small and comparable in size; i.e., the 97 Da intensity is comparable with the "impurity/intrinsic" intensities, which decreases the probability that the observed 97 Da intensity is from $C_7D_6H^+$. Making the assumption that the only "heavy" fragment is $C_7D_7^+$, the value of x_D given by $I_{98}/(I_{91} + I_{98})$ is in good agreement with the bulk value (Table I). Making the less probable assumption that the 97 Da intensity is significant increases the value of x_D, but it is still within the error.

Differences in C–C bond cleavage rates would have a maximum effect with this sample because the end cap consists of only one monomer unit. There is no evidence of a significant enhancement of the fragmentation sensitivity from the splitting of the terminal C–C bond.

The polydispersity of this sample was greater than those of the other materials. However, the possible effect of a wide range of chain lengths would be to allow migration of the shorter chains to the surface, producing an artificially high deuterium content. The results show that in this case the increased dispersity did not increase the segregation of low molecular weight material to the surface.

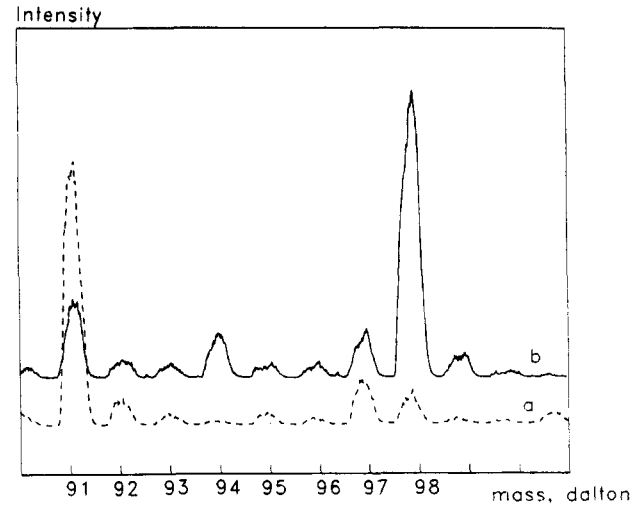

Figure 2. SSIMS spectra of triblock copolymers: (a) polymer 4, D–H–D, 4.7% D; (b) polymer 5, H–D–H, 6.7% H.

Polymer 4. The spectrum of this double-end-capped polymer is shown in Figure 2a. The 98 and 97 Da signals are much more pronounced than in the previous samples, though the bulk deuterium content is comparable. The average number of D monomers at each end is 2.3, which means that the contribution from the terminal D monomer, i.e., $C_7D_6H^+$, will form a high proportion of the heavy fragments. The 93 and 95 Da signals are relatively weak, indicating that the impurity level is low. The values for x_D are given in Table I. Both methods give surface deuterium contents well in excess of the bulk values.

This copolymer was also spun onto a silicon wafer which had been treated with HF to remove the native oxide. The results, in Table I, are similar to those from the oxide-covered substrate.

Polymer 5. The H monomer double-end-capped polymer is the converse of polymer 4, which gives the possibility of separating genuine chain end effects from segregation resulting from D substitution. One difference is that the terminal groups contain only one isotope, H. The spectrum (Figure 2b) shows that the impurity level, as judged from the 93 and 95 Da signals, is low. The 94 Da signal is the expected $C_7D_5^+$ fragment. The marked 97 Da signal probably contains a contribution from the aliphatic H impurity adjacent to the D monomer (see ref 4), as the deuterium content of this material is high.

The $C_7H_7^+$ signal at 91 Da shows that there is a significant exposure of the H monomer at the surface. Correction of the 92 Da signal for $^{12}C_6{}^{13}CH_7^+$ leaves a residual intensity, $^{corr}I_{92}$, of 15% of the $C_7H_7^+$ intensity. If monomer units are added in the forward direction, there should be no contribution to the 92 Da signal intensity from $C_7H_6D^+$. This fragment can only be produced if a proportion of monomer units is reversed or if D migration is used.

The composition of the surface can be obtained in a way analogous to the end deuterated materials, by measurement of $I_{91}/(I_{91} + I_{98})$ or, ignoring possible contributions to the 92 and 97 Da intensities from impurities, $(I_{91} + {}^{corr}I_{92})/(I_{91} + {}^{corr}I_{92} + I_{97} + I_{98})$. The values, given in Table I, are in good agreement with each other and are well in excess of the bulk value.

Discussion

Blends of hydrogenous and deuterated polystyrenes show segregation effects. Even at low volume fractions,

segregation of the D fraction is observed in 1-μm films of high molecular weight blends on silicon substrates after annealing.[6] Thinner films of medium molecular weight blends on gold substrates show spontaneous segregation effects at ambient temperature.[7]

Recently, Zhao et al.[8] have shown that segregation in a D–H–D triblock styrene copolymer, M_w = 63 000 containing ca. 4% D monomer by weight, did not exceed a factor of 2, on HF-stripped silicon wafers. On the other hand, they noted that silicon wafers retaining the native oxide did produce segregation effects with this triblock polymer (see ref 8 and references therein).

These reports suggest which factors determine segregation in deuterium-labeled polymer systems. In summary, the free energy difference between C–D and C–H in blends causes segregation of the D component, subject to the limitations of diffusion control, the latter being a function of the molecular weight and the temperature. The behavior of block copolymers is similar, with the additional constraint imposed by the physical attachment of the H and D blocks. In concert with the segment–segment energetics are the polymer substrate interactions, which can tilt the balance of energies toward segregation in very thin films.

The substrates in our study had a native oxide overlayer, except for polymer 4b in Table I. Diblock copolymers 1 and 2, synthesized with a butyllithium initiator, are respectively slightly above and below the entanglement weight. The SSIMS analysis did not show any segregation of the deuterated end groups to the air–polymer interface.

Diblock copolymer 3 is well below the entanglement weight, so diffusion should be facile. The very low deuterium content decreased the accuracy of the SSIMS measurements, but the surface concentration of the ends averaged only ca. 30% more than the bulk value. The low deuterium contents of these samples are evidently insufficient to cause marked segregation led by surface energy differences between the H and D monomers or between polymer and substrate.

The behavior of triblock copolymer 4 is very different from that of the diblocks. A large segregation of the deuterated end groups was observed. The high surface concentration of end groups was observed on silicon with and without the native oxide.

An excess concentration of ends at the surface in the "normal" polymer, i.e., not terminated with chemical or isotopic labeling, may be considered as a specific end effect. The problem, experimentally, is to distinguish between such specific end effects and those caused by isotope free energy differences. Triblock polymer 5 provides a means of separating these effects. The surface concentration of ends for the H–D–H polymer is ca. 300% of the bulk value, well outside the error. There appears to be a marked end effect, which overrides the tendency for the deuterated segments to segregate to the surface.

The value for the D–H–D polymer, ca. 400%, is greater than that for the H–D–H polymer, which would be expected if both segregation effects work in the same direction for the D–H–D triblock.

The behavior of the triblocks suggests that specific end effects are important. We may expect, therefore, to see similar effects with the diblock copolymers. However, the data for the diblocks do not show the marked enhancement of the end-group concentration at the surface. It may be significant that the triblock and diblock copolymers are not exactly analogous in structure. The triblock was synthesized from naphthyllithium, which produces a polymer with identical styrene end groups. The diblock was initiated by *sec*-butyllithium, which gives an hydrogenous alkane end as well as the deuterated styrene terminal end group. The effect of this initiator group on the surface energetics is unknown.

The triblock copolymer of ref 8 showed segregation effects when deposited onto unstripped silicon but not on oxide-stripped silicon. That triblock differs from copolymers 4 and 5 in having a hydrogenous *sec*-butyl group joined to D styrene units at the initiation end. Also its molecular weight is above the entanglement value, whereas the molecular weights of polymers 4 and 5 are below. The behavior of such a material may be more complex than for our triblock polymers, but we note the similarity with our data on unstripped silicon.

Conclusion

Marked end-group segregation has been observed for unannealed films of low molecular weight triblock copolymers of deuterated and hydrogenous styrene, synthesized from naphthyllithium. The origin of the effect is postulated to be the tendency of chain ends to segregate to the surface, because of the similar behavior of D–H–D and H–D–H triblocks. In contrast, diblock materials, initiated with *sec*-butyllithium, with similar low deuterium contents show little or no segregation of deuterated terminal groups.

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