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Surface-Induced Orientation of Symmetric, Diblock Copolymers: A Secondary Ion Mass Spectrometry Study

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Received September 23, 1988; Revised Manuscript Received December 14, 1988

ABSTRACT: Secondary ion mass spectrometry, SIMS, has been used to investigate a surface-induced orientation of symmetric, diblock polystyrene/poly(methyl methacrylate) copolymers, PS/PMMA, where either the PS or PMMA block was perdeuterated. SIMS yields a secondary ion intensity for carbon, hydrogen, and deuterium produced by sputtering of the copolymer film as a function of time (depth) from the surface with a measured depth resolution of 125 Å. Solution cast films of the copolymer from toluene, with thicknesses of 5×10^3 Å or less, were found to exhibit no preferential orientation of the microdomain morphology with respect to the surface. Annealing the copolymer films at 170 °C for 24 h produced dramatic orientation of the microdomains parallel to the surface of the film. This preferential alignment resulted in a periodic variation in the composition of either block that persisted through the entire thickness of the film. The periodicity, determined from model calculations, agreed with small-angle X-ray scattering results on the same but thicker films. PS exhibited an affinity for the free surface, while PMMA was preferentially located at the copolymer/substrate interface. At equilibrium and near-equilibrium conditions, the copolymer microdomains were aligned primarily parallel to the film surface with extensive lateral coherence. The thickness of the PS-rich layer at the air/copolymer surface was found to be one-half that of the microdomain in the bulk. Finally, interference microscopy results show that the thickness of an annealed film is quantized in that it is dictated by the alignment of the microdomains with respect to the surface and the periodicity of the microdomain morphology. Annealed films of the copolymer exhibit steps near the perimeter of the specimen, the height of which corresponds to precisely one period of the copolymer morphology.

Introduction

Most of the investigations involving molten block copolymers have focused on the bulk properties of these materials. Many of these studies have dealt with the microphase separation transition (MST) and the resulting equilibrium morphology. The type of ordered morphology that forms at the MST can be either spherical, cylindrical, or lamellar, depending on the relative molecular weights of the blocks in the copolymer. The size of the ordered domains is governed by the molecular weight of the blocks. Although block copolymers are finding increasing applications as thin-film adhesives and surfactants, only a few studies have focused on the behavior of block copolymers near surfaces.[1-9]

In this article we report on the investigation of the morphology from symmetric diblock copolymers of polystyrene/poly(methyl methacrylate) (PS/PMMA) near the copolymer/air and copolymer/substrate interfaces and in the bulk as measured by secondary ion mass spectrometry (SIMS). Up to now, most experiments on the surface behavior of block copolymers have focused on the use of X-ray photoelectron spectroscopy (XPS).[7-9] While XPS has good surface depth resolution, it is limited in penetration depth to ca. 70 Å. Transmission electron microscopy has also been used to study both the surface morphology and the effects of surface constraints on the block copolymer morphology.[3,4]

SIMS yields the relative secondary ion intensity profile of the atomic species under consideration as a function of time as an ion beam sputters through a specimen. Up to now, SIMS has been used mainly for the characterization of elemental distributions in inorganic materials; however, its application to organic materials is expanding.[10] SIMS

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0024-9297/89/2222-2581$01.50/0

is quite sensitive to the mass difference between the proton and deuteron. Hence, isotopic substitution of components in a multicomponent system or isotopic substitution of one component in a copolymer should make such systems suitable for investigation by SIMS. With a depth resolution of ca. 125 Å, as will be shown, this permits a detailed investigation of the interfacial and bulk behavior of polymeric films.

In the copolymer system of interest here, with selective deuteration of either the PS or PMMA block, a depth profile of relative intensity from each block normal to the surface is obtained. It is shown that annealing treatments of the copolymer above the glass transition produces a dramatic orientation of the domains parallel to the film surface. These results are consistent with interdiffusion studies[11] and are supported by interference microscopic investigations of the copolymer films.

Experimental Section

Two symmetric, diblock copolymers of PS/PMMA, purchased from Polymer Laboratories, were used in this study. The first was a diblock copolymer where the PS block was deuterated, designated as PSD/PMMA. Here the weight average molecular weights of the PSD and PMMA blocks were 52 900 and 48 000, respectively. The ratio of the weight to number average molecular weight, M_w/M_n, for the diblock copolymer was 1.07. In the second case, the PMMA block was deuterated, designated as PS/PMMAD. M_w for the PS and PMMAD blocks were 56 300 and 65 000, respectively, and M_w/M_n for the copolymer was 1.12. The molecular weights were determined by size-exclusion chromatography references to polystyrene standards. Copolymer films ca. 800, 1200, and 5000 Å thick were prepared by spin coating toluene solutions of the copolymers onto a silicon substrate. The substrates were first cleaned in an acid bath, rinsed with deionized water, soaked in deionized water to remove any water soluble contaminants, placed in refluxing ether vapors for 5 min, and dried. The substrates were subsequently handled by using nylon gloves to avoid contamination. The copolymer films on the substrates were further annealed at 170 °C for 24 and 72 h under vacuum and then cooled to room temperature over 8 h under vacuum. For a few cases, the thin specimens were quenched in liquid nitrogen. However, this was not found to alter the ordering observed. Debonding of the films from the substrate was not observed as was found for thicker specimens. Interference microscopy was performed on these specimens without further treatment. For the SIMS experiments, a 20-Å gold layer was first deposited on the air surface of both as cast and annealed samples to serve as a marker for the air/copolymer interface. As it will be pointed out in the following, the etching rate undergoes a transition over the first sputtered 100 Å to establish a constant sputtering rate. This transition occurs as the bombarding ion beam sputters from the unaltered surface to a depth where the ion beam has been implanted. To ensure that this transition is complete before reaching the copolymer, a 200-Å film of PS was placed on the gold-coated copolymer. The film was prepared by spin coating toluene solutions of the homopolymer onto a glass substrate. The thin PS film was then removed from the substrate by floating onto water and picked up on top of the gold-coated copolymer samples. The samples were dried at room temperature under vacuum to remove residual water.

PS (M_w = 170 000) and PMMA (M_w = 107 000) films have been prepared by spin coating toluene solutions of the homopolymers onto a silicon wafer. These films, ca. 2000 Å thick, were used to measure the etching rate in both PS and PMMA homopolymers. A PSD/PS bilayer sample was prepared to determine the depth resolution of the SIMS experiment. The bilayer was prepared by spin coating a PS (M_w = 170 000; M_w/M_n = 1.03) layer onto a silicon wafer. The thickness of this film was ca. 2000 Å. A PSD (M_w = 110 000; M_w/M_n = 1.05) film, ca. 850 Å thick, was spin coated onto a glass substrate, floated off onto water, and retrieved from the water with the PS film on the silicon wafer.

Interference microscopy studies were performed using a Zeiss Axiophot Pol photomicroscope. The microscope was used under reflection conditions to obtain interference colors from the white-light source. The interference colors can be used, by comparison with Newton's scale, to determine the sample thickness. The lamp iris was closed down to ensure a parallel beam of light, and the analyzer was set parallel to the polarizer. To demonstrate the presence of a terraced surface for the annealed copolymers, the optics of the microscope were set to Nomarski conditions. The micrographs shown in this article were obtained with the polarizer and analyzer slightly shifted from their crossed position. This was done to increase the light intensity on the film so as to operate with reasonable exposure times.

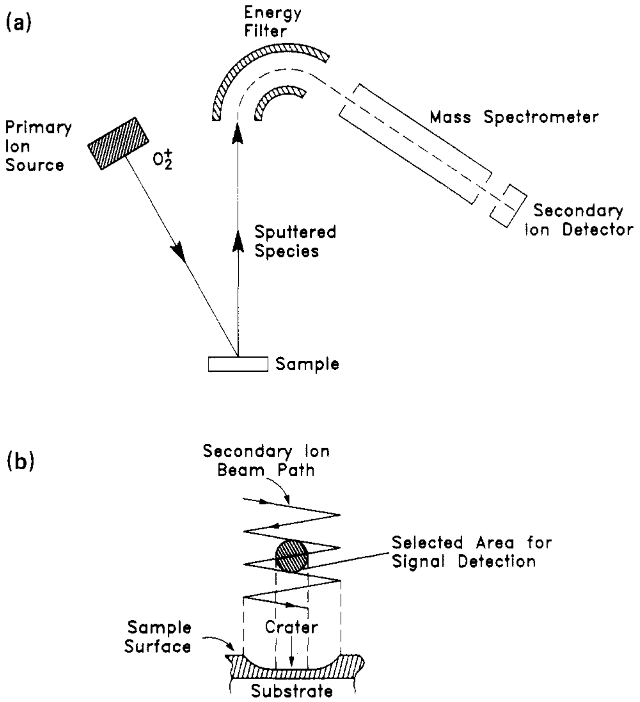

Figure 1. (a) Schematic of SIMS apparatus. (b) The primary IS ion beam is swept across a large area of the sample and the signal detected from the central portion (ϕ = 80 μm) of the sweep.

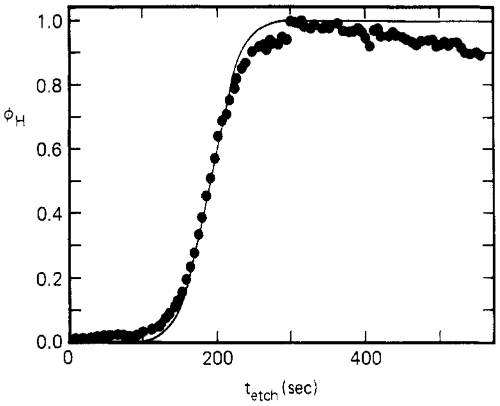

Figure 2. Relative concentration of protons, ϕ_H, as a function of the etching time, t_{etch}, from a PSD/PS bilayered system: (●) SIMS measurements, (—) fitted curve obtained by using an instrumental resolution of 125 Å and an interfacial roughness of 60 Å.

Figure 1 shows a diagram of the essential components of the SIMS instrumentation. A primary ion source produces ions that are accelerated to a few kiloelectronvolts, focused, and rastered to provide a means of sputtering neutral and ionized atomic and polyatomic particles from a surface. The rastering of the primary ion beam ensures that the center of the sputtered crater where the secondary ions are extracted for detection is sputtered with a uniform current density so that the depth profiling proceeds parallel to the surface. The secondary ions sputtered from the selected area at the center of the sputtered crater are extracted, energy analyzed, and mass separated with the use of a mass spectrometer. The mass spectrometer can be either a quadrupole mass filter or a magnetic mass spectrometer.

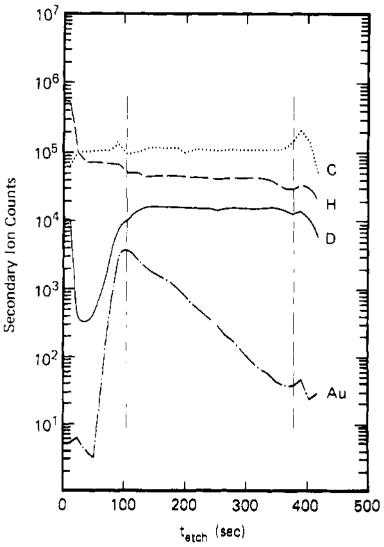

Figure 3. SIMS profile of an as-cast, 1000-Å-thick PS/PMMAD sample shown as secondary ion counts versus etching time. The dashed vertical lines at lower and higher etching or sputtering times mark the position of the air/copolymer and copolymer/silicon substrate interfaces, respectively. The C, H, and D secondary ion events remain constant throughout the entire thickness of the sample.

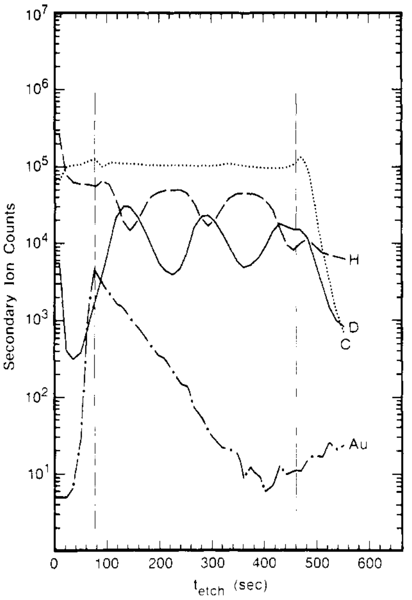

Figure 4. SIMS profile of a 1000-Å-thick PS/PMMAD sample annealed 24 h at 170 °C, shown as secondary ion counts versus etching time. The dashed vertical lines at lower and higher etching or sputtering times mark the position of the air/copolymer and copolymer/silicon substrate interfaces, respectively. The C signal remains constant throughout the whole film while H and D signals exhibit pronounced oscillations.

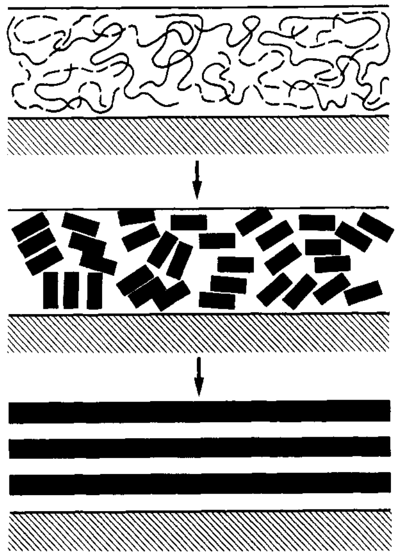

Figure 5. Schematic of the surface-ordering process in a diblock copolymer. The top diagram shows the diblock copolymer in a phase mixed state. This is not accessible for PS/PMMA copolymers via solvent-casting processes. The center diagram corresponds to a microphase-separated morphology where the periodic lamellar microdomains are randomly oriented in the specimen. After annealing for 24 h at 170 °C, the copolymer exhibits a lamellae morphology oriented parallel to the surface as shown in the bottom picture.

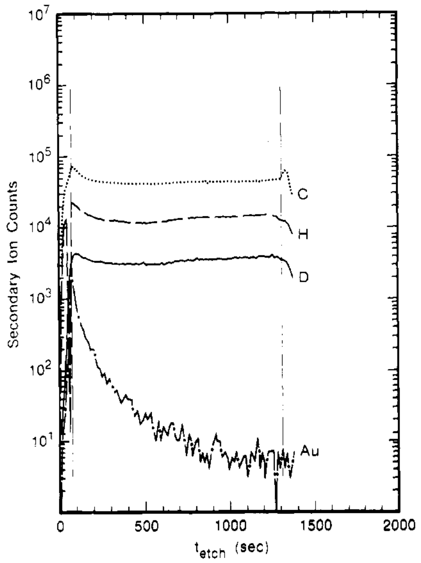

Figure 6. SIMS profile of an as-cast, 5000-Å-thick PSD/PMMA sample, shown as secondary ion counts versus etching time. The dashed vertical lines at lower and higher etching times mark the position of the air/copolymer and copolymer/silicon substrate interfaces, respectively. The C, H, and D signals are constant throughout the entire sample.

A Cameca IMS-4F secondary ion microscope was used to obtain the depth profiles in this experiment. The sputtering was accomplished with the use of a 3-keV O_2^+ primary ion beam, which has been shown to provide enhanced positive secondary ion signals and good depth resolution by the low kinetic energy bombarding O_2^+ ions.[12] The primary ion current for these measurements was approximately 200 nA, and the primary ion beam was rastered over an area of 500 μm × 500 μm. An immersion lens and a transfer lens are used to extract the secondary ions from the sputtered surface and project an ion image plane on a selected area aperture. Secondary ions passing through the selected area aperture originate from an 80-μm-diameter area at the center of the sputtered crater. A double-focusing magnetic sector mass spectrometer is used to provide the energy and mass analysis. The mass-separated secondary ions were measured with an electron multiplier, and the intensity of the measured secondary ions versus sputtering time gave the depth profile.

Depth profiles of $^1H^+$, $^2H^+$, $^{12}C^+$, and $^{197}Au^+$ were obtained from each sample. Either the PS or the PMMA block was perdeuterated to give that polymer a distinguishing $^2H^+$ secondary ion signal, and the nondeuterated block gave a normal $^1H^+$ signal. The $^{12}C^+$ was measured as a reference signal, and the $^{197}Au^+$ signal was measured as an indicator of the interface between the surface homopolymer and the copolymer. The surface homopolymer was placed on the copolymer so that initial sputtering transition and secondary ion sensitivity could be stabilized before sputtering into the copolymer.

Resolution Limits of SIMS

Ideally, the resolution limit of the SIMS experiment can be defined by the breadth of an infinitely sharp interface

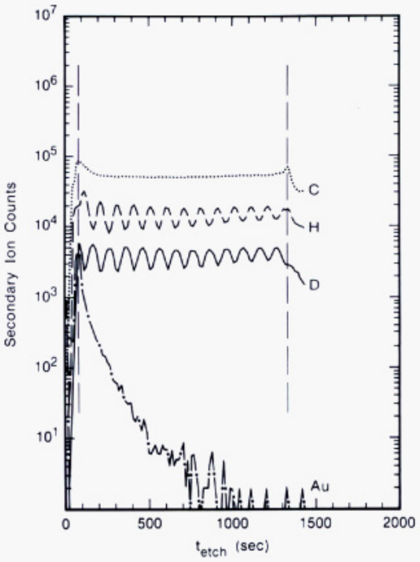

Figure 7. SIMS profile of a 5000-Å-thick PSD/PMMA sample annealed 72 h at 170 °C, shown as secondary ion counts versus etching time. The dashed vertical lines at lower and higher etching times mark the position of the air/copolymer and copolymer/silicon substrate interfaces, respectively. The C signal remains constant throughout the whole sample, while the H and D signals show pronounced oscillations.

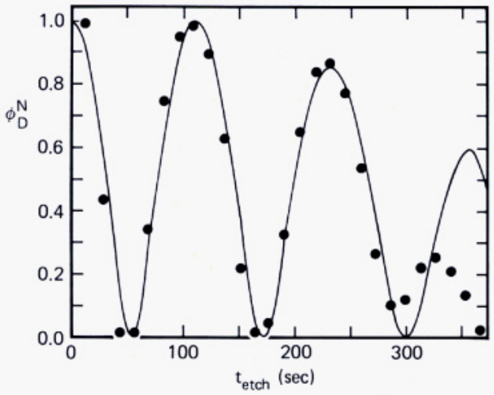

Figure 8. Normalized concentration of deuterium arising from PS, ϕ_D^N as a function of the etching time for PSD/PMMA annealed at 170 °C for 24 h: (●) experimental data, (—) calculated curve obtained by using the parameters in Table I.

separating, for example, a protonated and deuterated layer of two polymers. Experimentally it is impossible to achieve this end, since all interfaces will contain a finite roughness. Independent of this, the resolution will depend upon the conditions under which the experiment is conducted. At best, with use of conditions identical with those used during the copolymers studies, the instrumental resolution was approximated by investigating a bilayered specimen of protonated and deuterated polystyrene. A PSD/PS bilayer specimen, prepared as described previously, was used. Under the preparation conditions stated, neutron reflectivity measurements have shown that the roughness of the interface between the two layers of PS is at most 60 Å.[13]

The SIMS measurements showing the relative concentration of protons as a function of the etching time (which is readily converted to depth since PS sputters at a rate of 2.7 Å/s for the experimental conditions chosen) is shown in Figure 2. Assuming that the ideal profile between the deuterated and protonated layers can be defined by an error function with a characteristic width of 60 Å, a profile of the hydrogen signal can be calculated by convolution of the error function with a step function of width R and height $1/R$. The solid line shown in this figure represents the best fit obtained by using a resolution of $R = 125$ Å. From the calculations, an uncertainty of ±10% was found in this value. This, however, will not affect the overall conclusions of this study.

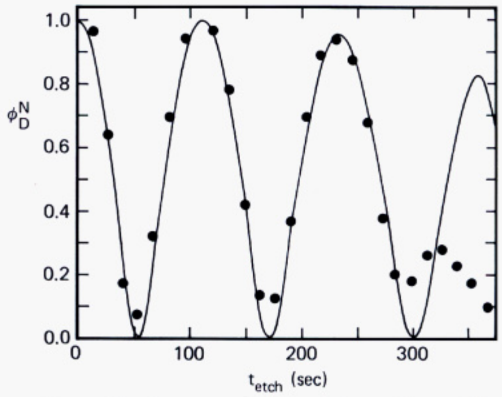

Figure 9. Normalized concentration of deuterium arising from PS, ϕ_D^N, as a function of the etching time for PSD/PMMA annealed at 170 °C for 72 h: (●) experimental data, (—) calculated curve obtained by using the parameters in Table I.

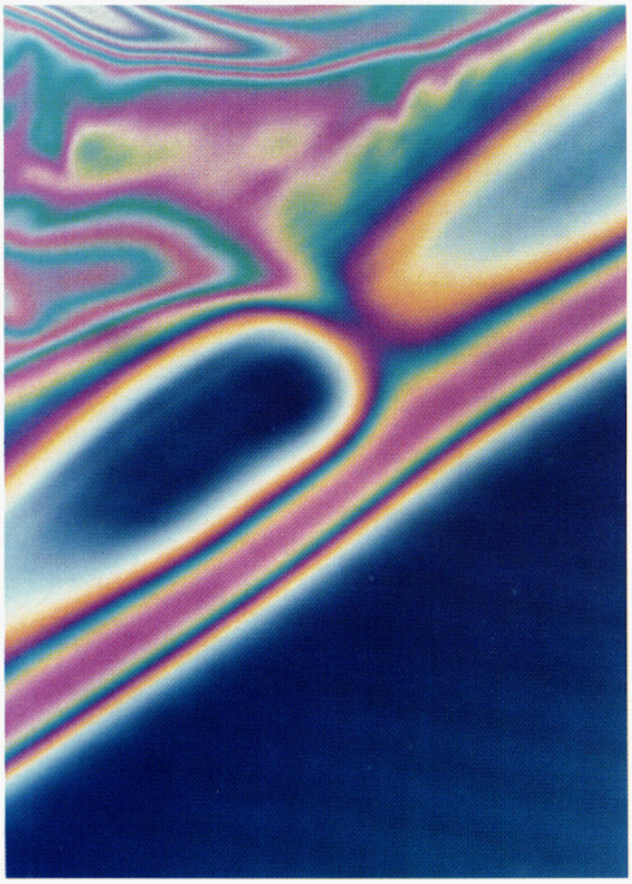

Figure 10. Interference colors observed at the edge of a PSD/PMMA copolymer sample spin coated onto a silicon wafer from a toluene solution. The full, long dimension of the micrograph shown here is 280 μm. The blue color on the lower part of the micrograph is characteristic of the central portion of the specimen.

Treatment of SIMS Data

SIMS measurements yield simply the ionized intensity of a particular atomic species as a function of the etching time. It does not provide an absolute concentration, and therefore the results are relative. The experimental data also contain contributions from instrumental background

Table I
Model Calculation Parameters

	annealing time at 170 °C, h	film[a] thickness, Å	period, Å	C, Å	E, Å
PSD/PMMAH	24	950	370	400	50
	72	950	388	1200	50
	24	1400	388	2500	50
	24	1100	350	1000	50
	72	1100	350	4000	50
PS/PMMAD	24	600	380	2000	50
	72	600	370	3000	50
	24	950	390	1750	50
	72	1000	400	2000	50

[a] As measured with a stylus.

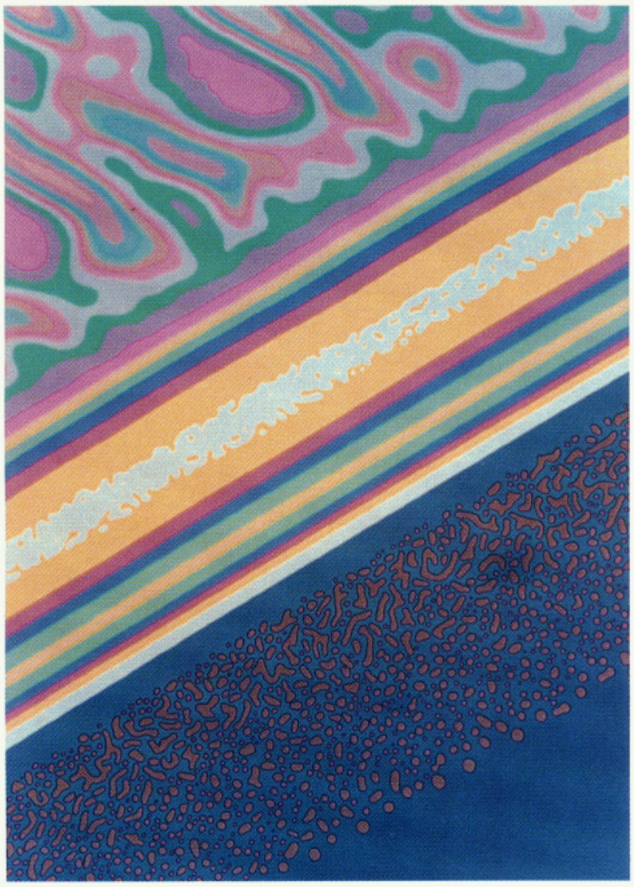

Figure 11. Interference colors observed at the edge of a PSD/PMMA copolymer sample annealed at 170 °C for 24 h. The full, long dimension of the micrograph shown is 280 μm. The orientation of micrograph is the same as that in Figure 10.

that depend strongly on the operating conditions, in particular, the pressure of the experimental chamber. Since these studies are principally concerned with the observation of a periodic structure normal to the surface of the film and less with the absolute concentrations, the following treatment of the data was used. Considering only the signal arising from the PS, the minimum observed proton or deuterium signal for protonated or deuterated PS was assumed to be due to the background. This was subtracted from the total PS signal, and the difference was scaled to yield a maximum value of 1 and a minimum value of 0. This normalized profile designated as ϕ_H^N or ϕ_D^N for protonated or deuterated PS, respectively, was then compared to the calculated profile. The sputtering (etching) time in the copolymer was set to zero at the peak in the Au profile since this corresponds to the air/copolymer interface.

Table II
Periodicity of Diblock Copolymers

copolymer	$M_{w,PS}/M_{w,PMMA}$	measured long period,[a] Å	predicted long period,[b] Å	step ht from interference microscopy, Å
PS/PMMA	(58 600/55 000)	465 ± 10	450	480 ± 10
PS/PMMAD	(56 300/65 000)	528 ± 10	456	520 ± 10
PSD/PMMA	(52 900/48 000)	389 ± 10	416	390 ± 10
PSD/PMMAD	(55 900/59 200)	452 ± 10	436	430 ± 10

[a] Measured by small-angle X-ray scattering. [b] Predicted from $d = 13.5N^{0.5}$. [c] Measured by step height from interference microscopy.

Figure 12. Nomarski micrograph of a PSD/PMMA copolymer sample annealed at 170 °C for 24 h. The color bands at the edge of the sample are clearly demarcated by bright white lines. The full, long dimension of the micrograph is 280 μm.

Calculation of SIMS Profiles

Experimentally the SIMS data are obtained as a function of the sputtering or etching time. For homopolymer films or for homogeneous, multicomponent films conversion of the sputtering time to a distance is done by multiplication of the sputtering time by the sputtering rate. The sputtering rate was determined by dividing the crater depth measured with a stylus by the total sputtering time. For polystyrene and poly(methyl methacrylate) these were found to be 2.7 and 4.4 Å/s for a 200-nA, 3-keV O_2^+ bombarding beam rastered over an area of 500 μm × 500 μm. However, for the microphase-separated PS/PMMA copolymers investigated, which clearly show an orientation of the lamellar microdomains with respect to the surface, the direct conversion of the etching time to distance is not possible. This arises from the large difference in the etching rates between the PS and PMMA microdomains, which makes the conversion nonlinear.

To circumvent this and to relate the SIMS data to the morphology of the block copolymers, models of the concentration of the block components as a function of depth in the specimen were used and compared to the measured profiles. From examination of the experimentally measured SIMS profiles, it is evident that the ordering of the copolymer is such that the PS domains are located preferentially at the air/polymer interface, whereas the PMMA domains are preferentially located at the silicon/polymer interface. If we let z be the coordinate describing the distance from the air/copolymer interface and positive values of z represent penetration into the copolymer film, then $z = 0$ is located at the copolymer/air interface. We construct first a concentration profile of polystyrene segments as a function of z such that from 0 to $L/4$ the concentration of PS, $X_{PS}(z)$, is 1; from $L/4$ to $3L/4$, $X_{PS}(z) = 0$; from $3L/4$ to $5L/4$, $X_{PS}(z) = 1$; etc. Here, L is the periodicity of the copolymer morphology, which is used as a fitting parameter. This is simply a box function with a periodicity of L where the first layer of PS is only one-half that of the PS in the bulk. This function extends through the entire specimen ending with a PMMA layer of thickness $L/4$ on the silicon substrate. This simple box function is then convoluted with a function $S(x)$ that describes the interface between the PS and PMMA microdomains. Both square waves and Gaussian functions have been used in this study to produce linear and sigmoidal concentration gradients between the microdomains, respectively. Due to the resolution of the experiment, ca. 125 Å, as discussed previously, and typical widths of the concentration gradient, ca. 50 Å as determined from small-angle X-ray scattering studies,[14] the SIMS experiments were not sensitive to the actual shape of the gradient. Thus, incorporating the diffuse phase boundary yields

$$X'_{PS}(z) = X_{PS}(z + x) * S(x) \tag{1}$$

where the asterisk denotes a convolution, and for a linear gradient

$$S(x) = 1/E, \quad x \leq |E/2|$$
$$S(x) = 0, \quad \text{otherwise} \tag{2}$$

The amplitude of the oscillations observed in the SIMS experiments on the annealed PS/PMMA copolymers varied as a function of depth in the specimen. The extent to which the amplitude diminished depended upon the sample thickness and the time of annealing. In general, this reduction in the amplitude was taken into account by multiplying $X'_{PS}(z)$ by an exponential function with a characteristic distance, C, at which the amplitude would be reduced by $1/e$. Therefore, $X''_{PS}(z)$ can be defined as

$$X''_{PS}(z) = X'_{PS}(z)e^{-z/C} \tag{3}$$

As is evident, the larger the value of C, the less pronounced is the reduction in the amplitude with depth.

The model concentration profile $X''_{PS}(z)$ cannot be directly compared to the experimentally observed profile because the SIMS profiles contain finite depth resolution that introduces a broadening. If we define R as the instrumental resolution, which was shown to be ca. 125 Å, then we can define a normalized instrumental resolution function, $R(x)$, as

$$R(x) = \frac{2}{(2\pi)^{1/2}R}e^{-2x^2/R^2} \tag{4}$$

Convoluting $X''_{PS}(z)$ with $R(x)$ yields the calculated, model concentration profile of PS segments $X_{C,PS}(z)$, as a function of depth. Therefore

$$X_{C,PS}(z) = X''_{PS}(x + z) * R(x) \tag{5}$$

As stated previously, if the sputtering rates of PS and PMMA were identical, then the experimental sputtering time could simply be converted to a distance scale. Since this was not the case, the distance scale of the calculated profile was converted to a sputtering time. This is possible provided the composition dependence of the sputtering rate is known. The sputtering rate as a function of composition was determined by investigating a series of mixtures of the PS/PMMA copolymers with PS and PMMA homopolymers where the films were prepared by rapid solvent casting from toluene following by drying the films under vacuum to remove residual solvent. The molecular weight of the homopolymer was ca. one-half the molecular weight of the corresponding block to ensure miscibility. Surprisingly, it was found that the etching rate for pure PS equaled the sputtering rate of the PS/PMMA copolymer or, in other words, the sputtering rate remained virtually constant for PS monomer fractions ranging from 1.0 to 0.5. As stated previously, this sputtering rate was 2.7 Å/s. As the concentration of PS decreased further, the sputtering rate increased and finally reached that of PMMA, 4.4 Å/s. This result shows that the sputtering of PS is rate controlling and, provided PS forms a continuous phase, the sputtering rate of PS is observed. Due to this, the rate at which PMMA is removed from the copolymer is somewhat uncertain and would introduce significant errors and artifacts into the profiles observed for PMMA. Consequently, comparisons between the experimental results and the model calculations will focus only on the profiles for PS segments whether it be the protonated or deuterated species. Thus, with the experimentally determined etching rates, the profiles of $X_{C,PS}(z)$ vs z could be readily converted to profiles of $X_{C,PS}(t)$ vs t_{etch}, where t_{etch} is the experimental etching time.

Results and Discussion

Typical SIMS results for a PS/PMMA diblock copolymer, where either block is perdeuterated, after spin coating onto a silicon wafer from a toluene solution are shown in Figure 3. In particular, the results shown here are for the PS/PMMAD diblock copolymer. The dashed vertical line at lower etching or sputtering times marks the position of the surface of the copolymer specimen. It should be recalled that a homopolymer layer was placed on top of the copolymer film simply to serve as a region where the initial sputtering transition takes place. The transient signal at early etching times where the number of secondary ion counts of carbon (C), hydrogen (H), and deuterium (D) varies markedly is clearly evident in the data. By the time the ion beam has etched through this layer of homopolymer, which in the example shown is a layer of PS, a steady-state sputtering rate has been achieved. The sharp increase in the Au signal marks the surface of the copolymer specimen under investigation. The actual surface of the copolymer was taken to be the point at which the Au signal began to decrease. In figure 3 the gold signal does not fall off as rapidly as would be desired. First, it is well-known that thin films of Au do not form a continuous film but rather cluster into islands of Au that have a range of thicknesses. It was also found that Au sputtered at a rate equal to that of PS under the experimental conditions used. Consequently, the island formation will not effect the results of this study, which are on a relative basis. Second, during the evaporation process it is also possible that some Au atoms have penetrated into the copolymer film. The data in Figure 3 are plotted on a logarithmic scale, and therefore the decay in the Au signal is approximately exponential.

The C, H, and D secondary ion counts obtained as the ion beam penetrates into the copolymer are seen to remain constant as a function of sputtering time or depth from the copolymer surface. This invariance in the number of counts remains throughout the entire thickness of the film down to the silicon substrate indicated by the dashed, vertical line at longer etching times.

Independent small-angle X-ray scattering studies on these copolymers have shown that the copolymers are microphase separated into PS and PMMA domains when cast from toluene solution.[11] These studies also indicated that, in films ca. 10^4 Å thick, the microdomains were not oriented with respect to the film surface. SIMS cannot differentiate between a homogeneously mixed diblock morphology and a microphase-separated morphology if the microdomains assume a random orientation. With the reasonable assumption that the copolymer film under investigation here is microphase separated, the results in Figure 3 demonstrate that the morphology is randomly oriented with respect to the film surface. It should also be mentioned that the total film thickness for this copolymer is on the order of 10^3 Å.

A separate PS/PMMAD film was annealed at 170 °C for 24 h, coated with Au, and covered with a PS homopolymer layer. Results of the SIMS analysis on this copolymer is shown in Figure 4. Up to the surface of the copolymer, indicated by the vertical dashed line at early etching times, the characteristics of the SIMS data are similar to those shown in Figure 3 for the unannealed specimen. However, as the ion beam penetrates into the copolymer, pronounced oscillations in the H and D signals are clearly evident. The carbon signal remains invariant throughout the sputtering of the copolymer film. These results show unambiguously that annealing has produced a strong orientation of the copolymer microdomains parallel to the film surface.

Several features of the data are important to notice. First, it is clear that the PS microdomains are preferentially located at the surface. This result was found previously[9] and reflects the lower surface energy of PS. It should be recalled, however, that the surface energy of PS is only a fraction of a dyne per centimeter less than that of PMMA, yet this is sufficient to cause the PS to reside preferentially at the surface. Second, the PMMA microdomains reside preferentially at the silicon substrate surface. This may not be surprising since the silicon wafer more than likely has an oxide layer on the surface, which would interact more strongly with the PMMA, the more polar of the two species. As will be shown by interference microscopy studies, the preferential location of PS microdomains at the air/copolymer interface and the location of PMMA at the substrate interface coupled with the periodicity in the copolymer microdomain morphology will dictate the thickness of the annealed specimen. Finally, it must be emphasized that the lateral area being probed in the SIMS experiment in ca. 80 μm in diameter. Consequently, these data show that the orientation of the copolymer domains with respect to the surface persists over a very large area. Thus, there is a large, lateral coherence of the microdomains.

The difference between the profiles in Figures 3 and 4 can be described schematically. The top diagram in Figure 5 shows a diblock copolymer in a phase-mixed state. Via solvent casting processes it is not possible to achieve this state for PS/PMMA diblock copolymers. By freeze drying a solution of the diblock copolymer from benzene followed by cold pressing the powder at temperatures well below the glass transition temperature, it was possible to attain a phase-mixed morphology in these diblock copolymers. At 170 °C the phase-mixed morphology was found to transform into a randomly oriented, microphase-separated morphology as schematized by the center illustration in Figure 5. Time-resolved small-angle X-ray scattering studies showed that the transition from a phase-mixed to microphase-separated morphology occurred within minutes at 170 °C.[14] SIMS cannot differentiate between either of these morphologies, as stated previously. Upon annealing of the copolymer for 24 h at 170 °C, the random morphology was found to strongly orient with respect to the surface, with a large, lateral coherence of the individual microdomains as shown in the bottom diagram of Figure 5. The kinetics of this orientation process is currently under investigation. It has been shown in a study of the diffusion of PS or PMMA into the PS/PMMA diblocks that the diffusion coefficient of the homopolymer into the copolymer dropped precipitously after the copolymer was annealed for 24 h.[11] This observation is consistent with a strong domain orientation.

The rapid orientation of the microdomains where a strong oscillation persisted throughout the entire specimen thickness was found to occur for samples ranging in thickness from 600 to 1400 Å. In all cases, 24 h was more than sufficient to establish this periodic structure. A specimen was then investigated where the total thickness of the film was ca. 5000 Å. The SIMS result for the film prior to annealing is shown in Figure 6. As with the thinner specimens, the C, H, and D signals are constant throughout the entire specimen. After annealing at 170 °C for 72 h, the dramatic results shown in Figure 7 were obtained. Surprisingly, even for this thick specimen, after 72 h the orientation of the microdomains was evident and the oscillations in the concentration persisted through the entire specimen. This essentially translates into 12 copolymer microdomains being oriented parallel to the film surface. This result reflects the speed at which this orientation occurs and how far reaching are the influences of the surfaces on the copolymer morphology. As in the results on the thinner specimens, the PS microdomains are seen at the air/copolymer interface whereas the PMMA microdomains are located at the copolymer/substrate interface.

Since the orientation process occurred so rapidly it was impossible, from the data, to conclude which interface more strongly effected the copolymer morphology. Experiments are currently in progress to address this issue where the silicon substrate has been coated with Au, which does not form an oxide layer on the surface. Annealing of the copolymer film in the absence of a solid substrate was not possible since, above the T_g, the polymer film flows.

Idealized models of the composition profiles for the PS segment concentration as a function of depth were constructed and used to stimulate the experimentally observed SIMS profiles. The parameters used in the calculations are basically the period or center-to-center distance of the PS domains, the phase boundary, E, between the PS and PMMA domains, and a dampening factor C as described previously. Shown in Figures 8 and 9 are the comparisons between the experimental results and model calculations of a PSD/PMMA diblock copolymer film with a thickness of ca. 950 Å that was annealed at 170 °C for 24 and 72 h, respectively. The data shown in Figures 8 and 9 are normalized concentrations of the deuterium arising from the PS, ϕ_D^N, as a function of the etching time in seconds. The parameters used in these calculations are shown in the first two rows of Table I. The agreement between the experimental profiles and the calculated profiles is seen to be quite good considering the simplicity of the model. The deviations at etching times greater than 300 s are due to presence of the silicon substrate. These calculations show that the initial PS layer at the surface is approximately one-half the thickness of the domain size within the specimen. An identical result was found by Hasegawa and Hashimoto for polystyrene/polyisoprene diblock copolymers using electron microscopy.[4] It is also clear that the period remains constant as a function of depth within the specimen. Finally, the agreement between the parameters used in the calculations for the two specimens is quite good. The major difference between the two data sets is the value of the dampening factor C, which increases with annealing. This suggests that with time the phases are becoming better aligned with the surfaces and/or the purity of the phases is increasing with annealing. Either possibility is quite reasonable and cannot be distinguished unequivocally by SIMS.

Parameters used in the calculations of the SIMS profiles are shown in Table I for all the specimens investigated in this study. Results from both PSD/PMMA and PS/PMMAD diblock copolymers are shown. The results in this table can be summarized as follows. For the PSD/PMMA diblock copolymers an average periodicity of 370 ± 15 Å was found, whereas for the PS/PMMAD diblock copolymers a slightly larger average value of 385 ± 15 Å was observed. This difference, while small, may indeed be quite real as will be discussed shortly. In all cases, the orientation of the microdomains and/or the purity of the microdomains increased with extended annealing at 170 °C. In general, the data show the internal consistency of the measurements and clearly demonstrate the extent of orientation of the microdomains.

It is interesting to compare the results obtained by SIMS for the periodicity with that measured by small-angle X-ray scattering. Desmeared, Lorentz-corrected X-ray scattering profiles obtained from 0.5-mm-thick specimens of the copolymers were used to determine the long period or center-to-center distance of the PS domains. This was done by using Bragg's law ($d = \lambda/2 \sin \theta$) on the position of the peak maximum (2θ maximum). The results for the series of copolymers are shown in the first column of Table II. For the PS/PMMA the periodicity, d, in the diblock copolymer morphology was found to be 465 Å, which compares quite well with the value predicted from the equation reported previously[11] of

$$d = 13.5N^{1/2} \tag{6}$$

where N is the total number of monomer segments in the copolymer. It should be noted that the power of N indicates that these diblock copolymers are in the weak phase-segregation limit as described by Leibler.[14] This is also supported by the large value of the phase boundary, ca. 50 Å, between the PS and PMMA microdomains.[16] Comparison of the measured value of d for the PS/PMMAD copolymer to the predicted value shows a marked discrepancy. The measured d is over 70 Å greater than that predicted. This is far outside the error limits of the experiments and may be indicating that deuteration of the PMMA block has markedly altered the microphase separation characteristics of the copolymer. The effect of deuteration has been described by several authors for homopolymer mixtures.[17,18] The effects of deuteration are most pronounced near a critical point in that the temperature at which the critical point occurs can be altered substantially. This basically reflects the fact that small perturbations to a system where the chemical potential of the components are balanced can produce significant changes in the phase diagram. The marked deviation of the long period for the PS/PMMAD copolymer could, provided the copolymers are in the weak segregation limit, be attributed to a similar effect. For the PSD/PMMA copolymer the measured long period is less than the predicted value by ca. 27 Å. This represents a deviation of ca. 7%, which is only slightly outside the error limits of the measurement. However, if anything, deuteration of the PS block has caused a reduction in the long period. Finally, the long period of the perdeuterated copolymer was found to be 452 Å, which agrees to within 3.7% of the predicted value of the long period. This may result from a balancing of the effects observed in the PSD/PMMA and PS/PMMAD copolymers.

From Table I the average values of the long period determined from the model calculations are 370 ± 15 and 385 ± 15 Å for the PSD/PMMA and PS/PMMAD copolymers, respectively. These should be compared to the values of 389 and 528 Å obtained from the SAXS measurements. The agreement for the PSD/PMMA case is quite good and is well within experimental errors. The nearly 50% deviation of the PS/PMMAD results is much too large to be associated with experimental errors. The exact origin of this discrepancy is unknown at this time.

The copolymers on silicon wafers were examined before and after annealing by using a polarizing microscope. The microscope was used under reflection conditions so as to obtain interference colors with use of white light. The colors are produced by interference between reflections from the upper and lower surfaces of the sample; each color corresponds to a specific thickness. The thickness of the copolymer is constant over the entire surface except at the edges where large increases (1000–6000 Å) in the film thickness were found due to the spinning procedure. Figure 10 shows an optical micrograph of an as-cast PSD/PMMA sample. Interference colors are very diffuse, showing clearly that the thickness varies continuously. In contrast, shown in Figure 11 is a micrograph of the same sample, annealed 24 h at 170 °C. Interference colors with well-defined contours are clearly seen, showing that the thickness increases discontinuously, i.e., in a stepwise manner. Observations near the sample perimeter under optical conditions close to Nomarski conditions where the polarizer and analyzer are slightly shifted from their crossed position confirm unequivocally the existence of steps. Two successive color bands are demarcated by white contours as shown in Figure 12. This behavior has been observed for all the specimens studied. Prior to annealing, there is a continuous variation of the thickness, i.e., the copolymer is either homogeneous or microphase separated with a random orientation of the microdomains. Optical microscopy cannot distinguish between these two different morphologies.

After annealing, the existence of steps on the surface indicates the presence of lamellae parallel to the surface. After identification of all the observed interference colors, the height of the steps can be easily deduced from Newton's scale. By using a mean refractive index $n = 1.55$ ($n_{\mathrm{PS}} = 1.6$ and $n_{\mathrm{PMMA}} = 1.5$) and by assuming, as shown in the SIMS results, that PS resides at the air/copolymer surface and PMMA at the copolymer/Si interface, it was found that for each sample the height of all the steps between consecutive colors is constant and characteristic of the sample. The values, given in Table II, show that the steps observed on the sample surface correspond to the long period of the lamellar morphology as measured by small-angle X-ray scattering. The accuracy of the step height values was ±10 Å for each sample. The accuracy is improved when high-order colors are considered. In this study case, colors up to the 15th order were used. This analysis will be developed in detail in a forthcoming paper.[19]

It should be noted that the agreement between the microscopic results and the SAXS measurements is very good. Even for PS/PMMAD, the large anomalous long-period value measured by SAXS (528 Å) is confirmed.

Conclusion

SIMS has been used to investigate the surface-induced orientation of symmetric, diblock PS/PMMA copolymers. It has been shown that films cast from toluene solutions, while microphase separated, are randomly oriented with respect to the surface of the film. Annealing the copolymers at 170 °C for 24 h produces films with a strong orientation of the copolymer microdomains parallel to the surface. The effect of surface ordering is found to persist through the entire thickness of the film. It was found that PS and PMMA domains of ca. one-half the width of the domains in the film interior were located at the air/copolymer and copolymer/Si wafer interfaces, respectively. This ordering was found in films as thick as 5×10^3 Å. The period of the ordered morphology was found to be in good agreement with results from small-angle X-ray scattering and interference microscopy. Due to the large area of the specimen probed by the ion beam (80-μm diameter) these results suggest that there is extensive lateral coherence of the copolymer microdomains. Finally, interference microscopy studies have shown the formation of steps on the surface of the annealed copolymer films. The heights of these steps correspond to precisely one period characteristic of the microdomain morphology.

Acknowledgment. We thank D. Miller for XPS results that were enlightening though not used in this article explicitly. We also are grateful to H. Werlich for use of his microscope and D. Ausserré of the College de France for several illuminating discussions. We are appreciative of the support of IBM France and to the Ministère de l'Education Nationale for making the visit of G.C. possible.

Registry No. (S)(MMA) (block copolymer), 106911-77-7.

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Polythioamide and Poly(1,3,4-thiadiazole) Synthesis from Dimethyl Tetrathioterephthalate

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Received September 7, 1988;
Revised Manuscript Received December 19, 1988

ABSTRACT: Dimethyl tetrathioterephthalate (DMTT) was synthesized in a one-pot procedure from 1,4-bis(chloromethyl)benzene and sulfur. Condensation of DMTT with various aromatic and aliphatic diamines was explored mainly in order to get high molecular weight polythioamides (A). Best results were obtained in heterogeneous conditions; it must be noted that fairly polar solvents such as chloroform sometimes gave better results than did amide solvents. Hydrazine and DMTT reacted in propylene carbonate to yield poly(*p*-phenylene-1,3,4-thiadiazole) (D).

Introduction

Developing mild and efficient methods for the synthesis of condensation polymers remains a significant aspect of synthetic polymer chemistry. Some polythioamides were obtained by Ogata et al. from bis(thionester)s and diamines at room temperature but in low yields and either were insoluble or presented very low molecular weights.[1]

Levesque and Gressier have prepared many aliphatic polythioamides from bis(dithioester)s and diamines[2] and some aromatic and semiaromatic polythioamides from tetrathioterephthalates and phenylene bis(dithioacetate)s;[3] most of these condensations occurred rapidly between 0 and 30 °C in dimethylformamide–toluene solutions. They have also investigated the relations between polyamides and polythioamides from the point of view of their thermal behavior.[2] Generally, polythioamides afford lower melting and glass transition temperatures than do homologous polyamides.[2,3]

Semiaromatic and fully-aromatic polythioamides were obtained mainly as low molecular weight samples and from

0024-9297/89/2222-2589$01.50/0