intensity for the monomers, St/MMA, the coefficient of variance amounts to only 0.45%.

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Separation of Styrene–Methyl Acrylate Copolymer According to Chemical Composition, Using High-Speed Liquid Chromatography

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ABSTRACT: It was shown that copolymer samples can be separated according to their chemical compositions by high-speed liquid chromatography (high-speed LC) and also that high-speed LC is hopeful for the rapid and automatic determination of chemical composition distribution (CCD) of copolymers. The chromatograms of a mixture of styrene–methyl acrylate copolymer samples having sharp CCD and different chemical compositions, respectively, were obtained using columns packed with silica gel particles whose micropore size is smaller than about 50 Å by the gradient-elution method with a mixed solvent (CCl_4/methyl acetate). The chromatograms showed discrete peaks corresponding to the original components. The apparent CCD of a component was determined from the chromatogram using the respective components as inner standards and compared with the theoretical CCD calculated from copolymerization kinetics. The CCD obtained by using a higher efficiency column was in fairly good agreement with the theoretical one. Moreover, it was shown that the molecular sieve effect is negligible in the present columns.

It is no doubt important for the study of copolymers to establish a rapid and automatic method for the determination of chemical composition distribution (CCD) of copolymers, such as gel permeation chromatography in the determination of molecular weight distribution. Several methods have been proposed for the determination of CCD. Among them, cross fractionation[1-4] and thin-layer chromatography (TLC)[5,6] can give quantitative results. However, the former is very laborious, and the latter cannot be operated automatically.

Four mechanisms of separation participate in high-speed liquid chromatography (high-speed LC), which is a powerful, rapid, and automatic method for separation or characterization of chemical compounds, follow: (1) adsorption–desorption, (2) partition, (3) molecular sieve, and (4) ion exchange. Despite the fact that in the characterization of low molecular weight compounds all of these are utilized, in the characterization of high polymers, only mechanism 3 is used in gel-permeation chromatography. In TLC of high polymers, on the other hand, not only mechanism 3 but also mechanism 1 are used.[7] The separation of copolymers according to their chemical compositions[5,8-14] and the determination of CCD[5,6] were successfully carried out in TLC based on mechanism 1. Therefore, if high-speed LC can be operated based on mechanism 1, adsorption–desorption, high-speed LC may be hopeful for the rapid and automatic determination of CCD of copolymers.

It is the purpose of the present work to show that copolymer samples can successfully be separated according to their chemical compositions by high-speed LC and also that the rapid and automatic determination of CCD of copolymers by high-speed LC is promising. Mixtures of copolymer samples with different chemical compositions were eluted out with a mixed solvent whose composition was changed linearly with time (gradient-elution method) and separated into the original components.

Table I
$\overline{M}_n$ and MA Content of Copolymers

sample	$\overline{M}_n \times 10^{-5}$ [a]	MA content, mol % [b]
N-45(w)[c]	2.61	46.6
F-1	4.38	(46.6)
F-4	2.92	(46.6)
F-7	1.40	(46.6)
N-60(w)[c]	2.76	57.3
F-1	6.36	(57.3)
F-4	3.68	(57.3)
F-7	1.62	(57.3)
N-75(w)[c]	3.02	77.9

[a] Osmometry. [b] Elemental analysis (see Experimental Section). [c] Whole copolymer.

Experimental Section

Materials. Whole polymers and their fractions of styrene–methyl acrylate (St–MA) random copolymer were used in the present work. Their preparation, fractionation, and characterization methods were presented elsewhere.[15] These copolymer samples may have narrow CCD because of their low conversions. The MA content of the whole copolymer was determined by elemental analysis. The MA content of the fraction was not measured directly, but its refractive index increment, measured by differential refractometer, was equal to that of the whole

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copolymer, which is an evidence of identical compositions of the fractions and the whole copolymer. A sample of poly(methyl acrylate), whose preparation was carried out by bulk polymerization, was used in TLC experiments. The chemical compositions and molecular weights of the samples are shown in Table I.

Carbon tetrachloride (CCl_4) of the first-grade reagent was refluxed with an aqueous solution of NaOH (10%) for 3 h, washed with water several times, dried with $CaCl_2$, and fractionally distilled. Methyl acetate (MeAc) of the first-grade was purified by distillation after drying with $MgSO_4$.

TLC. In order to find suitable experimental conditions in high-speed LC, preliminary experiments by TLC were carried out. The TLC plate used was Replate-50 (Yamato Kagaku Kikai Co., Tokyo); its stationary phase layer was made by sintering a mixture of silica gel and glass powder on a glass plate. Before use, the layer was activated by heating the plate at 110 °C for 1 h and cooling to room temperature in a desiccator. Stock solutions of the samples for TLC were prepared by dessolving 20 mg of each sample in 10 mL of methyl ethyl ketone. A spot of each solution, containing about 20 μg of the sample, was formed on the starting line of the plate with a microsyringe. The spotted plate was dried for about 10 min, and then the development was carried out in a closed chamber at room temperature by the ordinary method.[7] The eluents were mixtures of CCl_4 and MeAc, as reported by Inagaki et al.[5] When the solvent front reached 10 cm from the starting line, the development was stopped by drying the plate with a heated air stream. The positions of the polymer samples were visualized by heating the plate in an oven after it was sprayed with sulfuric acid solution (c = 1.5 mol L^{-1}).

High-Speed LC. High-speed LC measurements were carried out by a high-speed liquid chromatograph HLC-802 of Toyo Soda Manufacturing Co., Ltd. The detector was an ultraviolet spectrophotometer (UV detector), since the differential refractometer cannot be used in the gradient-elution method. The wavelength of UV was 259 nm. However, the UV detector is sensitive only to styrene units. Elution volume (V_e) was measured by a drop counter.

The columns used in the present work were TSK-GEL, LS-310, packed with microporous silica gel particles. Four columns, which were 7.5 mm in inner diameter and 60 cm in length, were used, respectively. In columns 1, 3, and 4, the particle diameter of silica gel was about 15 μm and the theoretical plate number, measured with benzene under the same conditions as those used in the measurements of the copolymer samples, was about 1000 per ft. In column 2, the particle diameter was about 10 μm, and the theoretical plate number was about 2000 per ft. The micropor size of the silica gel was smaller than about 50 Å for all columns.

The measurements were carried out at 30 °C with the same eluent as in the TLC experiments, CCl_4/MeAc, at a constant composition of eluent (constant-composition elution) and by the gradient-elution method. Just before use, the eluent was degassed by ultrasonic wave. The flow rate of eluent was about 1.0 mL min^{-1} in the sample column, and the polymer concentration of the injected solution was 0.2 g dL^{-1} in all measurements. In the gradient-elution method, the gradient was given by a gradient generator, Hitachi, Ltd., type 635.

In constant-composition elution, the sample solution is prepared by dissolving each sample in the eluent, and the solution is injected into the flow of the eluent. In the gradien-elution measurements, an eluent of a certain composition (starting eluent) is flowed through the column and a sample dissolved in the starting eluent is injected into the flow. At the same time as the injection of the sample solution, the composition gradient was given to the eluent. In all measurements, the concentration of the stronger solvent, MeAc, was increased from 7.0 to 35.0 vol % by linear gradient, and the sum of eluent volumes of the sample and the reference columns during the gradient elution was 35.0 mL. The measurements by the gradient-elution method were carried out for mixtures of two whole copolymers (N-45 and N-60) and of three whole copolymers (N-45, N-60, and N-75).

Column 1 was used in the constant-consumption elution. The columns used in the gradient-elution measurements are shown in Table III. In the present experiments, the decomposition of CCl_4 occurred in the columns, and the decomposition products contaminated the columns to decrease the activity of the adsorbent. Therefore, the columns had to be renewed more frequently than in the usual cases.

Table II
The Results of TLC

eluent comp (MeAc), vol %	R_f			
	N-45(w)	N-60(w)	N-75(w)	PMA
7	0		0	0
10	>0		0	0
14	1	>0	0	
16	1	>0	0	
20	1	1	>0	
26.7		1	1	0
33.7		1	1	0
41.0			1	>0
43.3			1	1

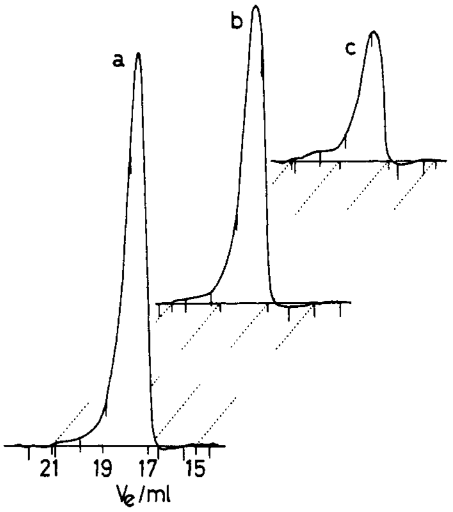

Figure 1. The examples of chromatograms for the whole copolymers. The eluent composition was CCl_4/MeAc = 72/28: (a) N-45(w), (b) N-60(w), (c) N-75(w).

Results

TLC. The results of TLC are summarized in Table II. The table shows that a copolymer sample begins to migrate from the starting line when the content of the stronger solvent, MeAc, reaches a critical value. If the sample is developed with the eluent containing more MeAc than the critical composition, R_f of the sample becomes unity.

High-Speed LC. Examples of chromatograms obtained by the UV detector for the whole copolymer samples are shown in Figure 1. The chromatograms were obtained by the constant-composition elution method at a strong solvent power. The peak areas of the respective samples are proportional to the weight fractions of styrene monomer units in the samples. The shapes, the breadths, and the values of V_e of the peaks are almost independent of polymer concentrations, if the polymer concentration is lower than 0.2 g dL^{-1}. As is clear from these examples, chromatograms obtained with the eluents strong enough to elute out all molecules of the samples show very sharp peaks, in spite of broad molecular weight distributions of the samples ($\bar{M}_w/\bar{M}_n$ = 1.65–2.30[15]). In Figure 2, moreover, molecular weight dependence of V_e is shown, using the fractions of N-45 and N-60 at CCl_4/MeAc = 82/18 of eluent composition. The value of V_e is independent of molecular weights of both series of samples. Both results in Figures 1 and 2 imply that the molecular sieve effect is negligible in high-speed LC with the present silica gel.

In the experiments with fractions of N-45 and N-60, it was found that V_e at the same eluent composition is not equal in the chromatograms for both series. This is clearly

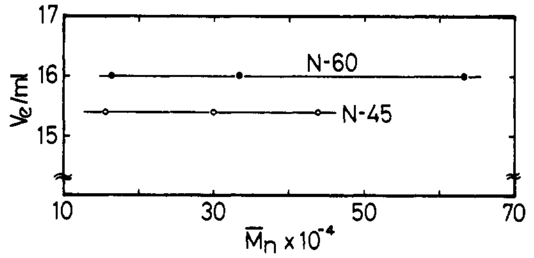

Figure 2. The relationships between V_e and molecular weight of copolymer fractions of N-45 and N-60 with CCl_4/MeAc = 82/18: (○) N-45 series, (●) N-60 series.

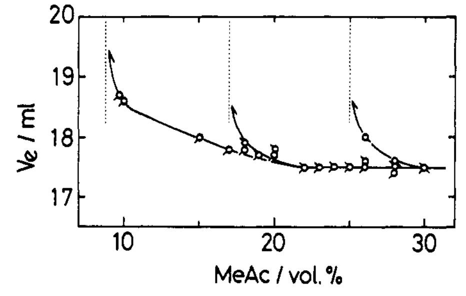

Figure 3. The relationships between V_e and eluent composition for the whole copolymers, obtained by the constant-composition elutions: (ϙ) N-45(w), (ɗ) N-60(w), (Q) N-75(w).

due to the poor reproducibility of the activity of the adsorbent. Several days after the experiments with sample series N-60, the experiments with N-45 were carried out. The activity of the adsorbent was found to be decreased due to contamination by the decomposition products of CCl_4. No good method was found to keep the activity of adsorbent constant in the experiments with CCl_4.

In the constant-composition elution, the relationship between V_e and eluent composition is shown in Figure 3. If the content of MeAc is higher than a critical value, the value of V_e is almost constant and is nearly equal for three samples. If the content of MeAc in the eluent decreases and approaches a critical composition, however, V_e for a sample increases sharply. In the eluents near the critical composition, the chromatogram shows more appreciable tailing than those obtained in the eluent with a higher content of MeAc. Moreover, if the content of MeAc decreases beyond a critical composition, V_e for the sample becomes very large, or the sample is not eluted out. The lower the MA content of the sample is, the lower the MeAc content at the critical composition is. These results are consistent with the results of TLC. The results obtained by the constant-composition elution imply that the copolymer samples can be separated according to their chemical compositions if a gradient in composition is given to the eluent.

Examples of chromatograms obtained by the gradient-elution method for mixed samples are shown in Figures 4 and 5. In these figures, V_e is shown by the sum of eluent volumes of the sample and the reference columns during the gradient elution. The chromatograms have two or three discrete peaks. The areas of the peaks are proportional to the weight fractions of styrene units in the respective components. It is clear from the figures that the mixtures were separated into the original components.

The eluent composition at the peak for the respective sample is listed in Table III. It can be concluded that the copolymer samples are separated according to their chemical compositions by the gradient-elution method of high-speed LC. However, it can be pointed out from the table that the reproducibility of the MeAc content of the eluent at the peak of the chromatogram for the same sample is not high, probably because of the effect of decomposition products of CCl_4.

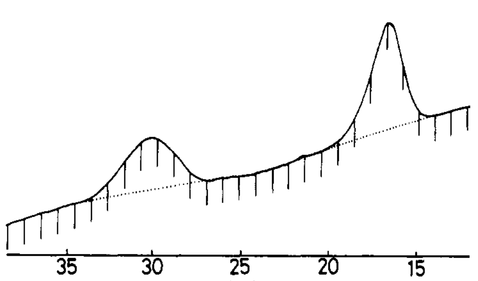

Figure 4. An example of a chromatogram of the mixture of two copolymer samples [N-45(w) and N-60(w)] obtained by the gradient-elution method [Table III, 2b].

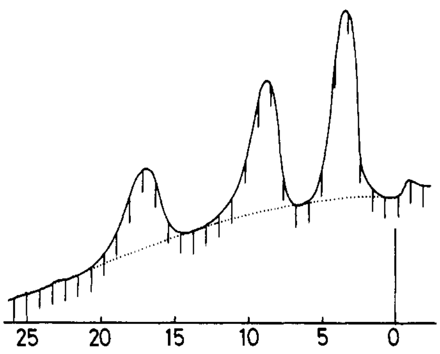

Figure 5. An example of a chromatogram of the mixture of three copolymer samples [N-45(w), N-60(w), and N-75(w)] obtained by the gradient-elution method [Table III, 3b].

Table III
The Eluent Composition [(MeAc) vol %] of the Sample Peak by the Gradient-Elution Method

column no.	^{a}	sample		
		N-45(w)	N-60(w)	N-75(w)
2	a	22.5	33.8	
	b	20.3	31.1	
3	a	11.9	16.0	22.8
	b	10.1	14.2	20.8
4	a	14.6	22.9	29.4
	b	13.4	22.0	30.0
	c	12.4	21.2	28.6

^{a} Experiments a, b, and c were carried out in order.

Discussion

The chromatogram for the respective peak in Figures 4 and 5 is expected to correspond to CCD of the component. Evaluation of CCD of sample N-60 from the figures is possible, if three or two components in the mixed samples are used as inner standards. The relationships between the MA content of those components and the MeAc content of the eluent at peaks in Figures 4 and 5 are plotted in Figure 6. It was assumed that the MA content of the sample at the peak equals the average MA content of the sample, since the CCD of each sample must be nearly symmetrical, for example, as shown by line c in Figure 7. The chromatograms for N-60 in Figures 4 and 5 can be converted to CCD of the sample, if we use the relationship in Figure 6. The height of the chromatogram in Figures 4 and 5 gives the concentration of the component at the position, if the MA content of the component is taken into account. The MA content at V_e can be estimated from Figure 6. The apparent CCD of sample N-60 thus obtained from Figures 4 and 5 are shown by lines a and b in Figure 7, respectively.

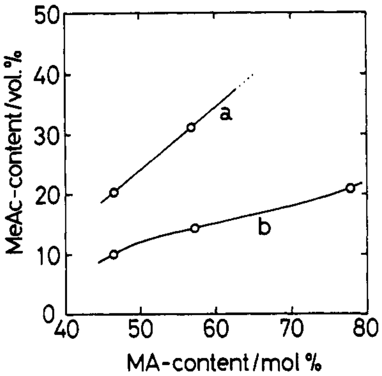

Figure 6. The relationships between the MA content of copolymer samples and the MeAc content of eluent at the peaks: (a) from Figure 4, (b) from Figure 5.

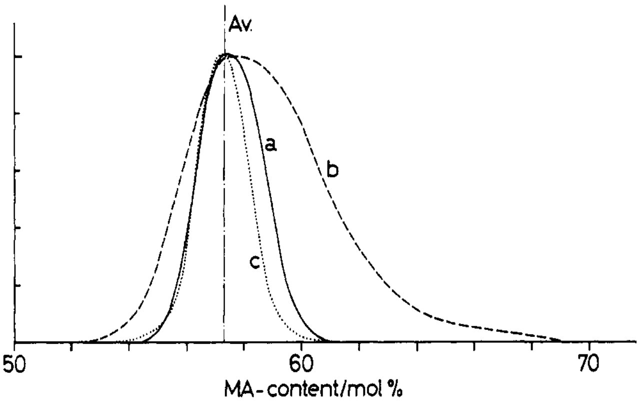

Figure 7. The CCD curves of copolymer sample N-60(w): (a) evaluated from Figure 4, (b) evaluated from Figure 5, (c) calculated from the copolymerization theory.

In Figure 7, the CCD obtained from Figure 5 is appreciably broader than that obtained from Figure 4. The broadening of the apparent CCD curve is caused by the band-broadening effect of the column used in the measurement in relation to the relative separation of the peaks. Since the band-broadening effect of columns cannot be zero, the measurement carried out under the condition giving a larger difference of V_e between the respective component peaks should generally give narrower CCD. The difference of V_e between the peaks of N-45 and N-60 is only 6 counts (corresponding to the difference of 4.1% MeAc) in Figure 5, whereas in Figure 4 the difference is about 14 counts (10.8% MeAc). Moreover, the theoretical plate number of column 2 used for Figure 4 is twice that of column 3 used for Figure 5. It is reasonable to predict that the apparent CCD obtained from Figure 4 is closer to the true CCD of sample N-60.

Theoretical CCD of random copolymers can now be calculated from the kinetic theory of copolymerization with fairly high reliability. When y is defined by the deviation of chemical composition of the individual copolymer chain from the average composition of the instantaneous copolymer expressed in mole fraction of a monomeric unit, according to the theory of Stockmayer[16] the weight fraction of copolymer radicals with composition deviations between y and $y + \mathrm{d}y$ is given by

$$W(y)\,\mathrm{d}y = \frac{3}{4(1 + z^2)^{5/2}}\,\mathrm{d}z \qquad (1)$$

where $z^2 = \lambda y^2/2F_1(1 - F_1)\kappa$, $\kappa = [1 - 4F_1(1 - F_1)(1 - r_1r_2)]^{1/2}$, F_1 is the average chemical composition of the instantaneous copolymer expressed in mole fraction of monomeric unit 1, λ is the number average degree of polymerization of the overall copolymer radicals, and r_1 and r_2 are the reactivity ratios. The CCD of an instantaneous copolymer can be calculated from the above equation, using $\lambda = \bar{P}_n$ in the case of disproportionation termination and $\lambda = \bar{P}_n/2$ in the case of coupling termination, where $\bar{P}_n$ is the number average degree of polymerization of the stable copolymer. It was previously reported that the theory of Stockmayer gives very good agreement with experimental results.[3] Moreover, the monomer compositions f_1 and f_2 in the reaction mixture can be given as a function of the degree of conversion by

$$M/M^0 = (f_1/f_1{}^0)^\alpha(f_2/f_2{}^0)^\beta(f_1{}^0 - \delta)^\gamma/(f_1 - \delta)^\gamma \qquad (2)$$

where $(1 - M/M^0)$ is the degree of mole conversion, superscript zero shows the initial values, and α, β, γ, and δ are the functions of r_1 and r_2, respectively.[17] The CCD of a finite-conversion copolymer based on the drift of monomer composition, neglecting the CCD of instantaneous copolymers, can be calculated by eq 2, since F_1 and f_1 are correlated to one another by the well-known equation of Lewis and Mayo.[18] This calculation is also in good agreement with experimental results.[5,6]

The CCD of sample N-60 was calculated from these equations by assuming that the copolymer consists of n instantaneous copolymers which have CCD according to eq 1. That is, the CCD caused by the drift of monomer composition was calculated from eq 2 from the data of copolymerization, and the entire range of the CCD was divided into n parts having an equal interval of chemical composition. The CCD of each part was calculated from eq 1. The total CCD of the copolymer was obtained by summing up the CCD of each instantaneous copolymer. In the calculation of the theoretical CCD of sample N-60, indicating MA by 1 and St by 2, respectively, we used $r_1 = 0.18$, $r_2 = 0.75$, $f_1{}^0 = 0.40$, 0.098 for the degree of conversion, and $n = 4$. Moreover, the value of λ, which was assumed to be constant (1473), was calculated from the molecular weight obtained by osmometry, assuming the coupling termination. The theoretical CCD thus calculated is shown by a dotted line (line c) in Figure 7. The theoretical curve was shifted to lower MA content by 2.8 mol % to fit the average composition obtained by elemental analysis with the calculated value. It was already reported that a small difference was found in both average compositions.[15]

Figure 7 shows that the CCD curve evaluated from Figure 4 (line a) is close to the theoretical one. Considering the fact that some assumptions were employed in the calibration of experimental CCD and the theoretical calculation, the agreement between lines a and c is beyond our expectation. That is, it may be concluded that the CCD of copolymers can be determined by the present method, if the columns have high theoretical plate number and high activity. Moreover, it is stressed that the pore size of the silica gel must be small enough so that the molecular sieve effect of the gel is negligible.

The molecular sieve effect was observed in a previous work on the separation of copolymer samples by preparative column adsorption chromatography.[14] This was because the adsorbent used in the previous work had the pores comparable to the molecular dimensions of copolymer samples, as mentioned in the paper.[14]

In the present work, the copolymer samples with narrow CCD were employed and, hence, it was possible to use the inner standards in order to convert V_e into the MA content of the copolymer. For copolymer samples with broad CCD, however, inner standards cannot be used, since the chromatogram of the sample may cover the peak of standards. It is, therefore, desired that another method of detection, which can be used in the gradient-elution method, will be found in addition to UV detection. Then, the chemical composition of copolymers could be determined, directly, by dual detections. If the activity of adsorbent can be kept constant, moreover, the calibration curve of Figure 6 may be determined by independent experiments and, hence, the CCD of copolymers with broad distribution may be determined by the present method.

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Surface Studies on Multicomponent Polymer Systems by X-ray Photoelectron Spectroscopy. Polystyrene/Poly(ethylene oxide) Triblock Copolymers

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ABSTRACT: Angular-dependent X-ray photoelectron spectroscopy, XPS(θ), was used to determine the surface compositions and topographies of a series of PEO/PS/PEO triblock copolymer films cast from chloroform. The results indicate that the PS concentration at the air–polymer interface is substantially higher than the known bulk concentration of PS and that the copolymer surfaces are laterally inhomogeneous, i.e., there are isolated domains of PS and PEO residing at the surface. Furthermore, the molar composition of the surface corresponds to the surface area occupied by each component. A comparison of these results on triblock copolymers with those found earlier on the PS/PEO diblock copolymers indicates these two systems have remarkably similar surface compositions and topographies. This study has, for the first time, shown that data from XPS(θ) measurements can provide information bearing on the question of phase-separation behavior in multicomponent polymer systems. Our results on the triblock copolymers suggest that the components in the copolymers are partially miscible in the surface region and that this miscibility is a result of electronic interactions between the PEO and PS blocks in the copolymers.

In the first paper in this series,[2] we reported on our studies of the surface properties of polystyrene (PS)/poly(ethylene oxide) (PEO) diblock copolymers. Our results indicated that solvent-cast films had surface excesses of PS; i.e., the concentration of PS in the surface region at the air–polymer interface was higher than the concentration of PS in the bulk. Furthermore, the surfaces of the block copolymer films were shown to be laterally inhomogeneous in PS and PEO, and isolated domains of each of these components were present at the surface. These domains were found to extend more than 50 Å into the bulk. Models for the surface topography of the copolymers suggested that the surfaces were nonplanar and that the PS domains were elevated above the PEO domains.

The above experimental results, as well as those described in this paper, were obtained, using X-ray photoelectron spectroscopy (XPS) techniques. In the XPS experiment, one measures the binding energies of electrons ejected by the interaction of a molecule with a monoenergetic beam of soft X-rays.[3] Information about the surfaces of solids is derived from measurements of the absolute binding energies, relative kinetic energies, and peak intensities corresponding to the direct photoionization of the core levels (e.g., C_{1s} and O_{1s}). XPS is inherently sensitive to the surfaces (top few monolayers)[3] of solids because of the very short (<100 Å) mean free paths for electrons and their strong dependence on kinetic energy.[4–7] By coupling our knowledge of electron mean free paths in polymers with measurements of the angular dependence of the photoelectron spectra [XPS(Θ)], it is possible to depth profile surface compositional variations and to model the morphology and topography of polymer surfaces.[2]

We now wish to report the results of further work on PS and PEO copolymers. In this paper, we have utilized XPS(θ) techniques to investigate the influence of chemical composition on the surface properties of solvent-cast PEO/PS/PEO triblock copolymer thin films. We will compare the current results on the triblock copolymers with those previously reported on the PS/PEO diblock copolymers of comparable composition in order to assess the influence of copolymer structure on the surface

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