# Dielectric Spectroscopy of Binary Polystyrene/Poly[styrene-*b*-(ethylene oxide)] Blends and Ternary Composites of Polystyrene/Poly[styrene-*b*-(ethylene oxide)] Swollen with Homopoly(ethylene oxide)

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ABSTRACT: The effect of incorporating poly[styrene-*b*-(ethylene oxide)], PS-*b*-PEO into PS/PEO composites has been examined microscopically and dielectrically. The addition of block copolymer stabilizes the dispersion of PEO in PS and can produce composites of PEO in PS in which the PEO domain size ranges from the size of the micelle core in binary PS/PS-*b*-PEO composites to larger PEO-swollen micelles to micron-sized phases of PEO stabilized by small amounts of PS-*b*-PEO. Dielectric spectra have been obtained as a function of frequency and temperature for binary composites of PS/PS-*b*-PEO and ternary composites of PS/PS-*b*-PEO/PEO, wherein the total content of PEO residues is held constant at 4.7% by weight. The dispersion of PEO in PS enables the observation of the full dielectric spectrum of the PEO phase. The dielectric spectrum of binary composites of PS/PS-*b*-PEO shows a predominant peak for the $\beta'$ relaxation of PEO chain segments covalently tethered to the glassy PS continuum. Ternary PS/PS-*b*-PEO/PEO composites show significant $\beta$ and $\beta'$ relaxations. The $\beta$ peak corresponds to that observed in pure PEO and in PS/PEO composites. The $\beta'$ peak corresponds to the higher temperature WLF type molecular relaxation observed in binary PS/PS-*b*-PEO composites and in PS/PEO composites. In the binary systems containing only PS and PS-*b*-PEO, the crystallinity of PEO is suppressed or disturbed. Accordingly, the $\gamma$ and $\alpha$ peaks which present themselves in pure PEO and in PS/PEO composites are not observed.

## Introduction

Following on a companion study[1] of morphology, phase distribution, and dielectric properties in composites of polystyrene, PS, and poly(ethylene oxide), PEO, the effect of incorporating poly[styrene-*b*-(ethylene oxide)], PS-*b*-PEO, into PS/PEO composites has been examined. The addition of block copolymer stabilizes the dispersion of PEO in PS and can produce composites of PEO in PS in which the PEO domain size ranges from the size of the micelle core in binary PS/PS-*b*-PEO composites to larger PEO-swollen micelles to micron-sized phases of PEO stabilized by small amounts of PS-*b*-PEO. In the present work, dielectric spectra have been obtained as a function of frequency and temperature for binary composites of PS/PS-*b*-PEO and ternary composites of PS/PS-*b*-PEO/PEO, wherein the total content of PEO residues is held constant at 4.7% by weight. As in the prior study on PS/PEO composites, the dispersion of PEO in PS enables the observation of the full dielectric spectrum of the PEO phase.

## Experimental Section

**Materials.** Poly[styrene-*b*-(ethylene oxide)], referred to herein as PS-*b*-PEO, without specification of molecular weight or composition, was prepared by living anionic polymerization in tetrahydrofuran, using a procedure analogous to that employed by O'Malley and Marchessault.[2] Gel permeation chromatographic analysis of the PS-*b*-PEO, used exclusively in this study, gave a number-average molecular weight ($M_n$) for the styrene block of 88 200 Da and a polydispersity of 1.3. The $M_n$ of the ethylene oxide block was calculated to be 27 000 Da on the basis of the ethylene oxide content of the block copolymer. The molar composition of the block copolymer, as determined by $^1$H NMR, is $(60/40)_M$, PS/PEO. The polystyrene employed as the matrix in all composites was a polystyrene standard (Lot No. 61126) obtained from Pressure Chemical (Pittsburgh, PA). The manufacturer reports its $M_n$ to be 105 000 Da and its molecular weight distribution to be 1.04. Poly(ethylene oxide) homopolymer employed in this study and hereafter referred to as PEO, without specification of molecular weight, was poly(ethylene glycol), $M_w = 3400$ Da and obtained from Aldrich Chemical Co.

**Sample Preparation.** Films, nominally 50 $\mu$m in thickness, were puddle cast onto glass substrates from a mixed solvent (toluene/tetrahydrofuran/methanol, 85/10/5, by volume). The concentrations of the solutions were about 12% solids by weight, and the composition is specified in Table 1. The glass substrates were warmed to 65 °C on an aluminum block during film formation to prevent crystallization of PEO phases prior to solidification of the PS matrix. Dried films were annealed at 120 °C for 16 h prior to transmission electron microscopy or dielectric spectral measurements.

**Microscopy.** Transmission electron micrographs were taken with a Philips CM 12 microscope operated at an accelerating voltage of 60 kV. Specimens examined were microtomed cross sections of the ∼50 $\mu$m films which had been embedded in epoxy (Araldite 620, resin/Ancamide 503, hardener). The sections were cut at a 4° tilt on a Reichert-Jung Ultracut E microtome. The thin sections were floated on distilled water and collected on 3 mm carbon-coated, 200 mesh copper grids. The PEO domains in the sectioned films were selectively stained with phosphotungstic acid.

**Dielectric Measurements and Data Analysis.** Dielectric measurements were carried out in the frequency range between $10^2$ and $10^6$ Hz using a combination of digital RLC

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**Table 1. PEO Micelle/Domain Size Composite Dielectric Properties**

| sample no. and composition | rel PEO vol fraction | | PEO domain diameter (nm) |
|---|---|---|---|
| | $\Phi_b$ | $\Phi_h$ | |
| 1-1<br>PS/PS-*b*-PEO(80/20)$_{\mathrm{w}}$ | 1 | 0 | 20–40 |
| 2-1<br>PS/PS-*b*-PEO/PEO (87.6/10/2.4)$_{\mathrm{w}}$ | 0.462 | 0.507 | 30–60 |
| 3-1<br>PS/PS-*b*-PEO/PEO (91.5/5/3.5)$_{\mathrm{w}}$ | 0.250 | 0.750 | 50–200 |
| 4-1<br>PS/PS-*b*-PEO/PEO (92.8/3.3/3.9)$_{\mathrm{w}}$ | 0.165 | 0.835 | 50–500 |
| 5-1<br>PS/PS-*b*-PEO/PEO (94.1/1.5/4.4)$_{\mathrm{w}}$ | 0.074 | 0.926 | 150–1000 |

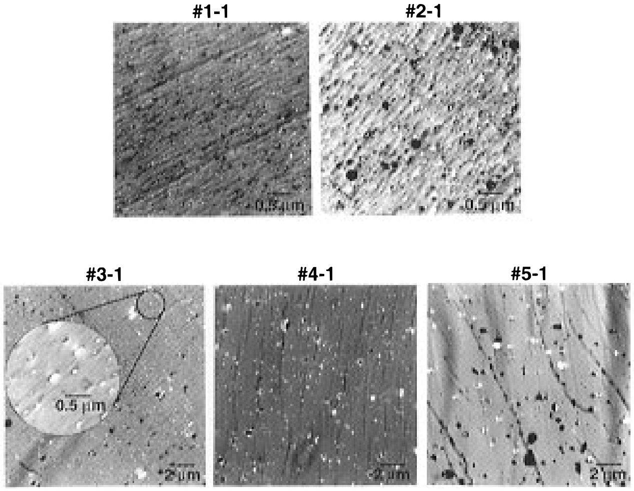

**Figure 1.** Transmission electron micrographs of cross-sectioned $\sim$50 $\mu$m films of binary PS/PS-*b*-PEO and ternary PS/PS-*b*-PEO/PEO composites. The microtomed sections were stained with phosphotungstic acid which is a preferential stain for the PEO domains and phases. Because of the relative softness of the PS/PS-*b*-PEO and PS/PS-*b*-PEO/PEO composite films, the thin sections were very susceptible to damage. Defects which are present in these micrographs include knife marks (striations) in the microtome direction, periodic compression and knife chatter folds which accept stain and produce linear discoloration perpendicular to the microtome direction, and holes where PEO has dissolved out of the sectioned film.

bridges under computer control. The samples in a capacitive geometry were mounted on an isolated Cu plate in contact with thermocouple and Pt resistance thermometers. The specimen holder was contained in a temperature chamber where the temperature (under computer control) could be maintained to a precision of 0.5 K over the temperature range of the measurements. Dielectric spectra were deconvoluted into the minimum number of component peaks using commercially available software (Peak Fit, Jandel Scientific, Corte Madera, CA). In the deconvoluted spectra, the $\beta'$ peak was fitted to a Gaussian and the $\beta$ peak was fitted to Lorentzian. The goodness of all of the fits (correlation coefficient, $R$) was $R >$ 0.9995.

## Results

The morphology and dielectric properties of a series of binary mixtures of PS and PS-*b*-PEO and ternary mixtures of PS, PS-*b*-PEO, and PEO were examined. Table 1 shows the compositions examined and the size of PEO domains in each composition as observed in transmission electron micrographs (TEM). Across the series, the weight fraction of PEO (that emanating from PEO and that emanating from PS-*b*-PEO) is held constant at 0.047.

Figure 1 shows a set of transmission electron micrographs of cross-sectioned films of these compositions. The magnification of the micrographs shown for samples 1-1 and 2-1 is 4 times that for samples 3-1–5-1. In order to facilitate comparison, a circular insert equal in magnification to micrographs 1-1 and 2-1 is included in the micrograph for sample 3-1.

The base-line composition in our study is sample 1-1 and is comprised of 20% by weight of PS-*b*-PEO dispersed in PS. TEM cross sections from a $\sim$50 $\mu$m film of this composite reveal homogeneously dispersed domains of PEO (micelle cores) ranging in diameter from 20 to 40 nm. Sample 2-1 is comprised of 10% by weight of PS-*b*-PEO and 2.4% by weight of homopoly(oxyethylene) in PS. TEM cross sections from a $\sim$50 $\mu$m film of this composite reveal homogeneously dispersed PEO domains (micelle cores swollen with PEO) ranging in size from 20 to 60 nm. Sample 3-1 is comprised of 5% by weight of PS-*b*-PEO and 3.5% by weight of PEO in PS. The relative volume fraction of PEO in 3-1 is 3 times the volume fraction of the *b*-PEO segment and significantly exceeds the theoretically predicted micelle swelling limit of about 0.8 times the volume fraction of PEO.[3] TEM cross sections from an ca. 50 $\mu$m film show homogeneously distributed, polydisperse domains of PEO ranging in size from 40 to 200 nm. The polydispersity of the observed domain diameters becomes even more pronounced in samples 4-1 and 5-1 which contain PEO domain structures as large as 1 $\mu$m in diameter.

In our dielectric analyses we have obtained extensive data on the frequency dependence of the dielectric spectra and the temperature dependence of the dielectric spectra at selected frequencies. The dielectric dispersion width in each case has a temperature dependence which is negligible in comparison to the temperature dependence of the central relaxation frequency. In other words, time–temperature superposition applies. We have chosen to plot the data in terms of tan $\delta$ versus temperature because it was crucial to map our data onto previously reported log $\nu$ versus 1/$T$ data.[4]

Figure 2 shows dielectric spectra [($\tan\delta = \epsilon''/\epsilon'$) versus absolute temperature] at $10^3$ Hz obtained from samples 1-1–5-1. In the region of the glass transition of PEO, the spectra exhibit two peaks whose ratio changes with changes in the ratio of PS-*b*-PEO to PEO in the PS host. In the binary composite of PS/PS-*b*-PEO, sample 1-1, the lower temperature peak is very small and is in fact only clearly elucidated by deconvolution of the spectrum. In sample 2-1, the lower temperature peak presents itself as a definite shoulder. Deconvolution is again required to determine the position of the maximum of the lower temperature peak. In samples 3-1–5-1, both peaks are clearly discernible without deconvolution. Figure 3 displays a stack plot in which the frequency dependence of the position of the peaks is illustrated for sample 5-1.

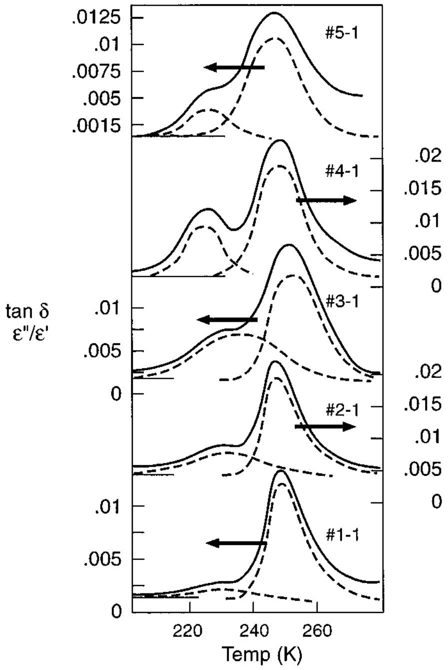

**Figure 2.** Temperature dependence of the dielectric spectra [tan $\delta$ ($\epsilon''/\epsilon'$) versus temperature, K, at $10^3$ Hz] in the glass transition region for binary PS/PS-*b*-PEO and ternary PS/PS-*b*-PEO/PEO composites: sample 1-1 (bottom) and sample 5-1 (top). Dashed lines show deconvoluted peaks.

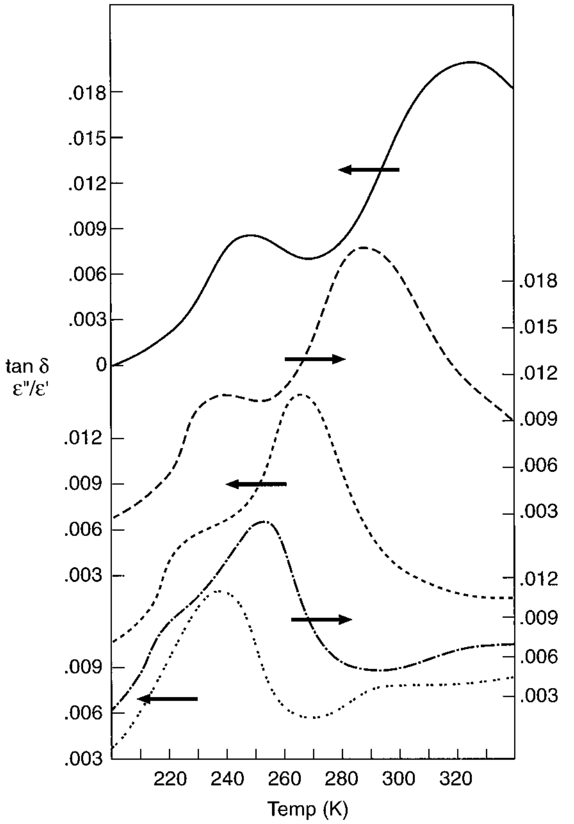

**Figure 3.** Temperature dependence of the dielectric spectra, tan $\delta$ ($\epsilon''/\epsilon'$) versus temperature, K, at $10^2$ (•• •• ••), $10^3$ (—•—), $10^4$ (- - -), $10^5$ (— — —), and $10^6$ (—) Hz for the ternary PS/PS-*b*-PEO/PEO composite, sample 5-1.

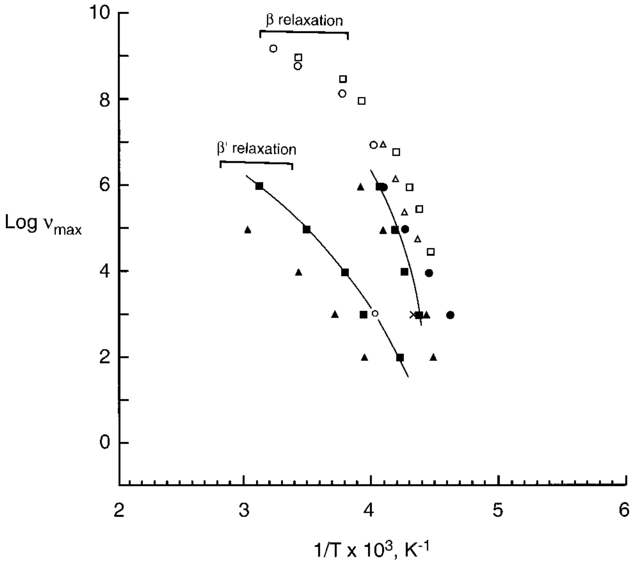

**Figure 4.** log $\nu_{max}$ versus reciprocal of the absolute temperature for the $\beta$ and $\beta'$ (—■—) peaks of sample 5-1. Data for sample 1-1 at $10^3$ Hz are also included ($\beta$, ×; $\beta'$, ○), along with data from the preceding study for PS/PEO (▲) and PEO control (●) and the data of Connor et al. for PEO samples of varying molecular weight ($2.8 \times 10^5$ = ○, $2.8 \times 10^6$ = □, and $8.4 \times 10^5$ = Δ).

Figure 4 shows plots of log $\nu_{max}$ versus the reciprocal of the absolute temperature for the $\beta$ and $\beta'$ (— ■— ) peaks of sample 5-1. Data for sample 1-1 at $10^3$ Hz is also included ($\beta$ = ×, $\beta'$ = ○). This shows that the $\beta$ and $\beta'$ peaks in the binary composite of PS/PS-*b*-PEO derive from relaxation processes which are analogous to those assigned for the ternary PS/PS-*b*-PEO/PEO composites and the binary PS/PEO composites. As in the preceding paper,[1] these plots enable the analysis of the character of the relaxations and correlation with prior studies of the dielectric properties of PEO. In order to facilitate this correlation, data reported by Connor et al.[3] for PEO samples of varying molecular weight ($2.8 \times 10^5$ = ○, $2.8 \times 10$ = □, and $8.4 \times 10^5$ = Δ) are incorporated in Figure 4 along with data from the preceding paper for the PEO control sample (●) and simple PS/PEO composites (Δ). In Figure 4, it should be noted that while the temperature dependence of the frequency of the $\beta$ peak for the binary (PS/PS-*b*-PEO) and ternary (PS/PS-*b*-PEO/PEO) block copolymer composites is virtually identical with that in pure PEO(1,4) and in PS/PEO composites,[1] the temperature dependence of the frequency of the $\beta'$ peak in the block copolymer composites is shifted by nearly 1 decade.

## Discussion

One might expect that the dielectric properties of compositionally identical composites of PS and PEO would be nearly identical. Indeed, the ambient temperature dielectric constants for these compositions fall within a narrow range (3.0-3.6) and are essentially independent of frequency between 100 and 1000 Hz. However, the dielectric loss spectra of this series of composites differ significantly.

In Figure 2, it can be seen that the binary PS/PS-*b*-PEO sample, 1-1, exhibits a predominant process with peak at 248 K. Given the results of the work on the PS/PEO system,[1] we know that both peaks are associated with the relaxation of the *b*-PEO segment. By inspection of Figure 4, it can be seen that the 231 K peak maps well against the $\beta$ relaxation (the dielectrically observed glass transition in samples of pure PEO).[4,5] The 248 K peak corresponds with the $\beta'$ relaxation which we ascribed to glass transition of PEO chains tethered in PEO crystals.[1] The fact that the

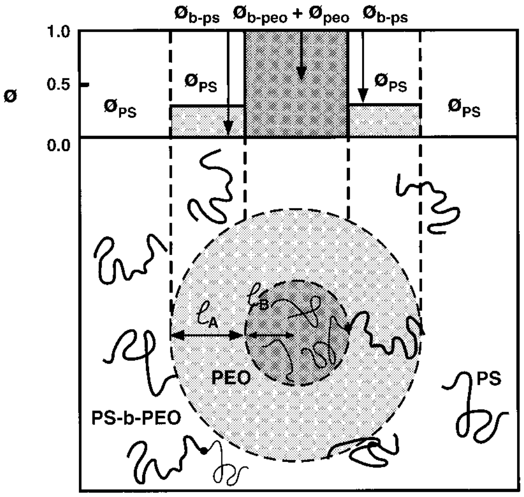

**Figure 5.** Cross section of a spherical, PEO-swollen micelle for PS-*b*-PEO.

magnitude of the 248 K peak relative to the 231 K peak is so great is understandable if one realizes that in PS/PS-*b*-PEO composites, the block copolymer is uniformly dispersed in the host as micelles having a core of PEO and a PS corona. As illustrated in Figure 5, each micelle can be viewed as a spherical core of radius $\ell_\beta$ surrounded by a corona of thickness $\ell_\alpha$ of a homogeneous continuum of PS. The composite is thus comprised of three distinct regions with a specific volume fraction, $\phi$, of PS, *b*-PS, *b*-PEO, and PEO contained in each region. Virtually all of the PEO segments in the block copolymer are in the micelle and tethered to the glassy PS corona.

In the early 1970s, Pochan et al.[6] examined the dielectric spectra of films of PS-*b*-PEO block copolymers, and they concluded that the dielectric properties of the PS-*b*-PEO system were strongly influenced by the phase separation morphology. They explained all of their data in terms of an Arrhenius-activated process associated with the PEO melting which they termed $\alpha_c$. They did not resolve any lower temperature, WLF type[7] $\beta$-relaxation processes. In working with binary and ternary composites of PS-*b*-PEO in PS, problems of high sample conductivity which these earlier workers faced were eliminated. It is our speculation that their Arrhenius $\alpha_c$ process is a mixed transition caused by lack of resolution of the crystalline melt of PEO segments and the WLF type, $\beta'$ relaxation of covalently tethered PEO chain segments.

In all compositions swollen with PEO (samples 2-1–5-1), the magnitude of the peak near 230 K is greatly enhanced relative to its magnitude in sample 1-1. In Figure 2, it can be seen that the relative ratio of the maximum peak heights for the 230 and 250 K loss processes increases monotonically in going from the binary PS/PS-*b*-PEO composite, 1-1, to the ternary PS/PS-*b*-PEO/PEO composites, 2-1–4-1 ($1\text{-}1 = 0.08 \ll 2\text{-}1 = 0.22 < 3\text{-}1 = 0.43 \cong 4\text{-}1 = 0.44$). That for sample 5-1 $= 0.19$ is diminished relative to that in the other ternary composites but is still significantly greater than the ratio of the 230 and 250 K peaks in the binary composite containing only PS and PS-*b*-PEO. Indeed, the character of the dielectric spectrum of sample 5-1 is reminiscent of that of homopoly(ethylene oxide) in PS. This is not surprising in light of the fact that sample 5-1 contains a relative volume fraction of homopoly(oxyethylene) equal to 0.926. The fact that the relative ratio of the maximum heights of the $\beta$ and $\beta'$ peaks diminishes for sample 5-1 can be attributed to increased crystallinity of the larger PEO domains and increased tethering of homopoly(ethylene oxide) chains in PEO crystals.

The low-temperature $\gamma$ relaxation associated with local motions in PEO crystals and the $\alpha$ relaxation associated with the melt of PEO crystals are not observed in samples 1-1–5-1, ostensibly because of the amorphous or poorly crystalline state of PEO in submicron micellar domains. The $\alpha$ transition is also not observed perhaps due to melting point depression in the tiny PEO domains stabilized by adsorbed block copolymer.

## Summary and Conclusion

Studies of binary composites of PS/PS-*b*-PEO and ternary composites of PS/PS-*b*-PEO/PEO have thus resulted in the observation of two WLF type molecular relaxations, $\beta$ and $\beta'$, which we assign respectively to the onset of segmental motion and free-volume expansion of unrestricted amorphous PEO chains and PEO chain segments physically tethered in crystallites or covalently tethered to rigid PS chain segments. The dielectric spectrum of binary composites of PS/PS-*b*-PEO shows a predominant peak for the $\beta'$ relaxation of PEO chain segments covalently tethered to the glassy PS continuum. Ternary PS/PS-*b*-PEO/PEO composites show significant $\beta$ and $\beta'$ relaxations. The $\beta$ peak corresponds to that observed in pure PEO and in PS/PEO composites. The $\beta'$ peak corresponds to the higher temperature WLF type molecular relaxation observed in binary PS/PS-*b*-PEO composites and in PS/PEO composites. In the systems containing block copolymer, crystallization of PEO is suppressed or disturbed. Accordingly, the $\gamma$ and $\alpha$ peaks which present themselves in pure PEO and in PS/PEO composites are not observed.

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