

Morphology of bulk SBS block copolymers prepared by wet cryo-ultramicrotomy

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When a polystyrene-polybutadiene-polystyrene (SBS) block copolymer undergoes micro-phase separation, the resulting morphology is dependent on the chemical nature, component ratio, and molecular weights of the constituent molecules. Transmission electron microscopy studies have revealed that the morphology of block copolymers cast in various solvents is determined also by the selectivity of the preparatory solvent. This work compares the morphologies produced by thin-film casting of a toluene-SBS solution on water, with subsequent solvent evaporation, and those produced in bulk, without the use of any solvents. To obtain ultrathin sections of the latter, a new technique using cryo-ultramicrotomy is introduced. The technique utilizes sub-zero temperatures to harden the samples and allow reproducible sectioning; the optimal temperature is accurately predicted as the glass transition temperature for a hypothetical homogeneous blend of the same composition. Difficulties with the trough liquid necessary in wet sectioning are overcome by coating the surface of the glass knives with Teflon. Morphological differences arising from the two preparative methods are identified, and image-enhancing techniques are used to emphasize the interphase region described by various theories.

1. Introduction

When the free energy of a solution tends toward a minimum and the molecules are thermodynamically incompatible, phase separation occurs. If the molecules in such a solution are block copolymers comprised of polystyrene (PS) and polybutadiene (PB), the phase separation results in a microstructure whose morphology is determined by the size of the molecules themselves and by the composition of the PB-PS solution. For example, the morphology of a styrene-butadiene-styrene (SBS) block copolymer varies with increasing PS fraction by first exhibiting spherical PS domains, then PS cylinders, followed by PS and PB planes (lamellae), then PB cylinders, and lastly by PB spheres [1]. An example of the PS cylinders found in a PB matrix is depicted in Fig. 1 (end view). The interphase, which is diffuse, is seen as a regime where both PS and PB segments exist and is an integral part of many thermodynamic models that attempt to describe block copolymer phase separation and morphology [2-8].

These morphologies, which determine the physical properties of the copolymer, have been successfully characterized by transmission electron microscopy (TEM) studies. Diamant [9] found a lamellar structure with vortical patterns superimposed, when an SBS polymer with 48.2 wt% PS was cast from toluene. However, these patterns, which were the result of

solvent casting, were not reported by Hashimoto *et al.* [10]. Similar accounts of morphological variations are common in the literature, and most pertain to the effects of solvent alone on morphologies [11]. Since the free energy of a solution depends on the chemical nature and composition of the components in the solution, the addition of a solvent to the copolymer influences the system energetics and, consequently, the resulting morphology. This influence of solvents, which increases the complexity of molecular interactions, should be avoided in phase-transition studies of block copolymers. Hence bulk polymer samples are desirable; and in order to utilize TEM for such studies, ultrathin sections of the bulk sample must be obtained. The objectives of this work, then, are (i) to introduce a new technique for acquiring such ultrathin sections (70-90 nm) and (ii) to compare the morphologies of SBS block copolymers prepared with and without solvents.

2. Materials and methods

2.1. Materials

Block copolymer samples used in this study were provided by Cosden Oil and Chemical Company (Deer Park, Texas 77536, USA). These samples initially appear as irregularly shaped chunks, each weighing 1 to 5 mg. The sample designations, molecular weights, and PS weight fractions of these copolymers are given

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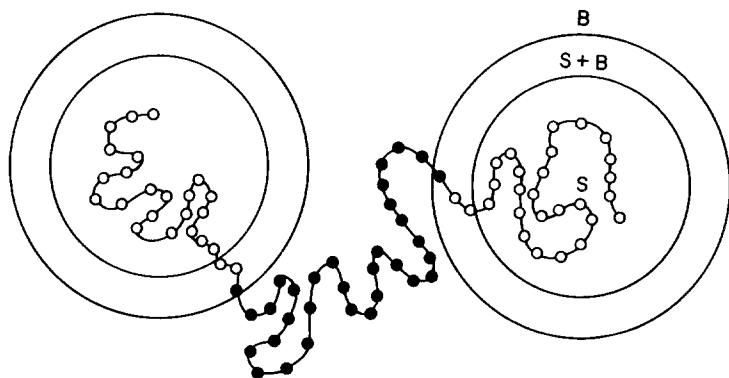


Figure 1 Geometric representation of microphase-separated SBS block copolymers depicting spherical or cylindrical morphology.

in Table I. In order to avoid crosslinking and oxidative degradation, the samples were stored in a darkened desiccator under a vacuum of approximately 750 mbar.

2.2. Casting

Since both PS and PB blocks were to be dissolved in the casting process, toluene, which dissolves both homopolymers very well [11, 12], was selected as the solvent. A solution consisting of 5.0 g copolymer and 100.0 ml toluene was prepared [5] and then cast on clean distilled water.

Since the polymer film deposited on the water surface is in a state of non-equilibrium with respect to the ultimate solvent-free system [13], the most representative morphology is obtained by allowing the solvent to evaporate slowly over a period of 15 h. When this procedure was used here, most of the film agglomerated to a thickness greater than the 100 nm necessary for high-resolution TEM studies [14] and was therefore useless. However, ultrathin films, exhibiting greater transparency than the agglomerated film, were discovered near the edge of the crystallization dish and were lifted onto 100×300 mesh copper grids (Ted Pella Inc., Tustin, California 92680, USA). These mounted samples were then placed in a Mikros-Varian evaporator (Varian Associates, Palo Alto, California 94303, USA) and subjected to carbon vapour deposition from a 2 mm diameter rod with 32 mA for 5 sec. The samples were then stained for 1.5 h in the vapour of a 1% osmium tetroxide aqueous solution. All operations were performed at room temperature.

2.3. Cryo-ultramicrotomy

Since the block copolymers used in this study were quite rubbery due to the PB, microtoming ultrathin sections (< 100 nm thick) was difficult. In order to stiffen the rubber portion, the samples were quenched in liquid nitrogen and then microtomed [15, 16].

Initially, obtaining a polymer thin film that was 0.25 mm thick without using solvents was accomplished by pressing the irregular chunks in a heated press. At

TABLE I Styrene-butadiene-styrene (SBS) polymers used in this study (Fibraprene, characterized by Cosden Oil and Chemical Co.)

Designation	Molecular weight ($\times 10^{-3}$)	Weight fraction PS
F411	230	0.30
F414	150	0.40
F416	140	0.30

150°C , the pressing process was repeated between 10 and 15 times to approach macroscopic homogeneity of the samples. From these films, small blocks measuring $1.5\text{ mm} \times 2.5\text{ mm} \times 0.25\text{ mm}$ were cut by hand. After being quenched in liquid nitrogen [17], the samples were mounted in the sample holder of a Dupont Sorvall MT 6000 ultramicrotome with FS 1000 cryokit (E.I. duPont de Nemours & Co., Claremont, California 91711, USA). The glass knives used in the sectioning process were cut on an LKB knifemaker (LKB Instruments Inc., Los Angeles, California 90025, USA) and were mounted with plastic troughs (Fig. 2) for wet sectioning.

However, the low temperature presented a problem for wet sectioning: water, whose high surface energy and low viscosity make it ideal for floating cut ribbons, cannot be used. The 1-pentanol used in this study was selected for several reasons. Firstly, its normal melting point, -70°C , allowed it to remain a liquid at the sectioning temperature. Secondly, it remained a liquid at room temperature and was thereby easily handled and thirdly, it was not a toxic chemical. Lastly, its solubility parameter ($\delta = 11.6\text{ H}$) was used to predict that it would dissolve neither the polymer ($\delta_{\text{PS}} = 9.1\text{ H}$, $\delta_{\text{PB}} = 8.3\text{ H}$) nor the nail lacquer ($\delta \approx 9.0\text{ H}$) used in sealing the trough to the glass knife. Other liquids such as ethylene glycol, dimethyl sulphoxide, glycerol, freons, and isopentane used in previously cryo-ultramicrotomy work [17], did not satisfy all four of the above criteria.

Since the ultrathin sections will not float on the pentanol ($\rho_{\text{SBS}} \approx 1.01\text{ g cm}^{-3}$, $\rho_{\text{PeOH}} = 0.81\text{ g cm}^{-3}$),

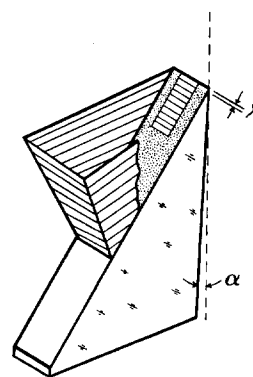


Figure 2 Schematic diagram of the knife-and-trough assembly used in the cryo-ultramicrotomy operation. The clearance length, denoted by X , is the distance from the blade to the Teflon coating, shown as speckles, and is approximately 1 to 2 mm. The clearance angle, α , is the degree of knife tilt and is set at 6° .

the high surface energy of the glass must be decreased so that the cut ribbons can slide freely along the glass surface while immersed in the pentanol and not wrinkle upon successive sectioning. This was achieved by spraying most of the knife surface with the Teflon found in the commercially available Slide-All (Borden Inc., Columbus, Ohio 43215, USA) as depicted in Fig. 2. The clearance length (the distance from the knife blade to the edge of the Teflon coating) denoted by X , was about 1 to 2 mm and was fixed by holding a glass slide cover over the knife blade during the coating process. Once the knife was coated, the pentanol was added and the entire assembly installed into the cryokit.

After much trial and error, the optimum sectioning temperature was found to be between -65 and -60°C . The cutting speed of the knife was set to 5 mm sec^{-1} [15] and the clearance angle of the knife, α , was 6° [18]. With enough ribbons collected in the trough, the entire knife assembly was removed, and the pentanol was allowed to evaporate completely. The trough was then removed, but the ribbons were still adherant to the Teflon coating. The knife was placed directly in the evaporator under the same operating conditions as above; after carbon deposition, which is used to stabilize the section, the knife was submerged in distilled water so that the ultrathin ribbons floated to the surface. They were then collected on grids and stained as before. All operations, except for the pressing and cryo-ultramicrotomy, were conducted at ambient temperature.

2.4. Electron microscopy

Ultramicrotomed sections ranging 70 to 90 nm in thickness and solvent-cast sections approximately 100 nm in thickness were examined in a Jeol JEM 100CX transmission electron microscope (Jeol Ltd., Peabody, Massachusetts 01960, USA) at 100 kV.

3. Results

Microphase-separated morphologies of the SBS block copolymers vary considerably depending on whether solvent casting or cryo-ultramicrotomy is used. For example, sample F414, which is 40 wt % PS, is expected to exhibit a lamellar morphology [19]; this type of morphology is shown in Fig. 3, which depicts a solvent-cast film. The uniaxial direction of the lamellae indicates that the section experienced strain, probably due to the high surface energy of the water, during the casting process; Fig. 4, on the other hand, is also of F414 but shows the effects of ultramicrotomy. The planar morphology is not as clearly visible; in fact the structure does, at various points, resemble PS cylinders viewed in cross-section.

This sample preparation effect is much more pronounced for the F411 sample, which contains 30 wt % PS. At this composition, either cylinders or lamellae or a combination of the two [9] can be expected. Fig. 5, which shows a microtomed section clearly shows that lamellar morphology; however Fig. 6, which depicts a solvent-cast film, reveals a cylindrical PS morphology. Observed as circles [20], the cylinders also possess a diffuse interface, which is characteristic of these

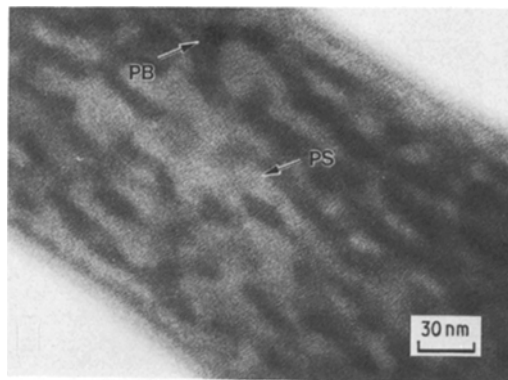


Figure 3 Section of sample F414 which has been cast in a 5% toluene solution. Lamellar morphology, seen along an axis of strain, is present.

polymer systems [19]. (Circles can be interpreted as either spheres or cylinders, but cylinders are expected due to the PS fraction.) Additionally, variations in background light intensity in Fig. 6 prove that the film is not of uniform thickness [21]. The results from the F416 sample duplicate those from the F411 sample very closely and are not reproduced here.

4. Discussion

Transmission electron microscopy has been successfully used to quantify some features of microphase-separated block copolymers (e.g. domain sizes, inter-domain spacing, and block repeat distances). TEM has also been used to qualify the morphologies produced by various sample-preparation methods; the effect of solvent used in the casting process best exemplifies this point. For example, Hirata *et al.* [22] have shown that using ethyl benzene (a selective solvent) and benzene (a non-selective solvent) to cast a block copolymer comprised of ethylene oxide and isoprene resulted in two entirely different morphologies. Furthermore, other studies [19] using a copolymer with blocks of isoprene and *n*-propyl *p*-styrene sulphonate have revealed that adequate microphase separation occurs if the casting solvent is tetrahydrofuran (THF) but that similar separation must be induced by annealing if the solvent is chloroform or dimethylsulphoxide (DMSO). Using Kraton 1101 (Shell Chemical Co., Torrance, California 90509, USA), which contains 24.5 wt % PS, Leary and Williams [5] have reported that the copolymer, when cast from toluene, exhibited PS cylinders in a PB matrix at 100°C but exhibited a different morphology after the sample was heated to 227°C .

Many studies in which ultramicrotomy has been used on bulk samples have induced changes in the original chemistry by subjecting the sample to various stiffening and staining agents [20, 23]. This is done so that (i) the sample can be ultramicrotomed successfully, and (ii) contrast between microphases is enhanced. Stiffening agents, such as osmium tetroxide or osmic acid, react with the unsaturated double bonds in the rubbery polymer block; this oxidation of the rubber results in the local deposition of reduced osmium [23] and consequently hardens the block copolymer. Another method by which this stiffening is accomplished is embedding of the sample. Rusnock

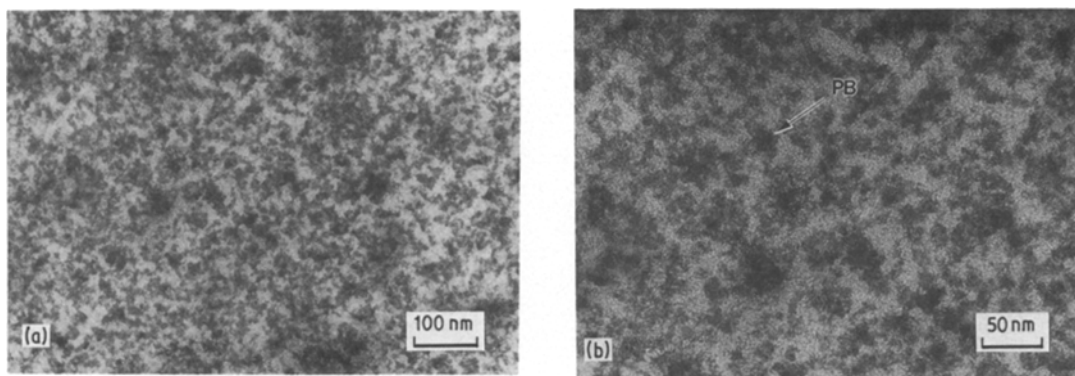


Figure 4 Effects of cryo-ultramicrotomy on sample F414 which is 40 wt % polystyrene. The lamellar morphology is seen in (b), which shows an enlarged section of (a).

and Hansen [24] claim that this is necessary for clean knife contact; but Andrews *et al.* [15], on the other hand, report that the embedding materials swell and distort the polymer.

In order to avoid altering the chemistry of the polymer too drastically, cryo-ultramicrotomy is used. The temperature at which the sectioning is done has conventionally been below the glass-transition temperature (T_g) of the rubbery component so that the entire sample is glassy [17]. Andrews *et al.* [15] agree, stating that the sectioning temperature should be at least -140°C for rubbers. After many trials, however, it was determined here that sectioning temperatures in the range of -65 to -60°C were best suited for producing uniform and reproducible sections for the SBS polymers being examined. For reasons not entirely clear, these optimum temperatures are close to the T_g that would be expected for a single-phase blend of these two components (i.e. either a true solution of two miscible polymers or a random copolymer of the same composition). Among the many formulae available for T_g estimation with such systems, the two relations [25] that usually predict the upper and lower limits of T_g and, consequently, a reasonable range for the optimum ultramicrotomy temperature, are as follows:

$$T_{g,SB} = w_S T_{g,S} + w_B T_{g,B} \quad (1)$$

$$\frac{1}{T_{g,SB}} = \frac{w_S}{T_{g,S}} + \frac{w_B}{T_{g,B}} \quad (2)$$

where $T_{g,SB}$, $T_{g,S}$, and $T_{g,B}$ are the glass transition temperatures of the copolymer, the PS(373 K), and the PB(165 K), respectively, and w_S and w_B are the weight fractions of PS and PB, respectively. Predictions

of $T_{g,SB}$ by Equations 1 and 2 for F411 are -45.8 and -75.0°C , respectively. The average of these two extreme temperatures (-60.4°C) is identical to the experimental ultramicrotomy temperature (-60.0°C). The latter is about 14°C below the prediction of Equation 1, in fair agreement with previous studies [26] showing that microtomy is best done about 10°C below the Equation 1 value of T_g .

With the new trough liquid and the Teflon coating, sectioned ribbons are completely reproducible. Care should be taken, however, not to immerse the knife-and-trough assembly into water while alcohol is still in the trough, for the turbulence that occurs when the alcohol and water come in contact will fold and wrinkle the sections, thus making them useless [14].

When viewed with an electron microscope, the sections do not exhibit much contrast between the PS and PB microphases [21, 27]. Hence staining is used for enhancement, and various methods of staining have been reported in the literature [28, 29]. Nevertheless, staining does alter the chemistry of the copolymer, and this must be considered in *in situ* dynamic studies, such as straining experiments [30].

In static studies, however, where the stain simply increases contrast, no adverse effects should be encountered from the altered chemistry, providing preferential swelling of the stained regions does not occur. After TEM images are obtained, computerized image enhancement (IE) can be used to deduce additional information from electron micrographs. For example in Fig. 7 (a magnification by IE of one of the PS cylindrical domains found in Fig. 6) the diffuse interface is much more clearly visible. Also, this interfacial regime is approximately 3 nm wide, in accord with theory [8].

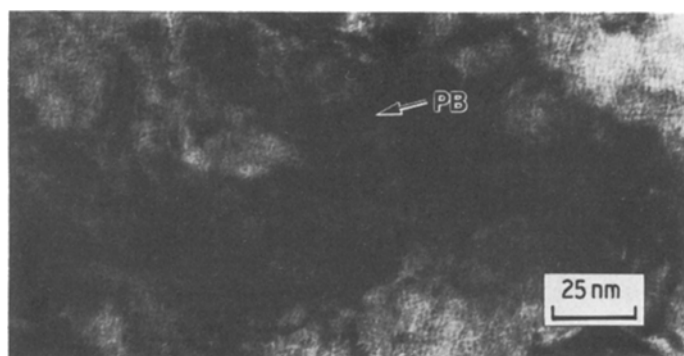


Figure 5 Ultrathin section of microtomed sample F411, which is 30 wt % polystyrene. The lamellar morphology, due to its degree of contrast, was initially thought to be a conglomeration of osmium precipitates but diffraction patterns verified the fact that this was the actual polymer sample.

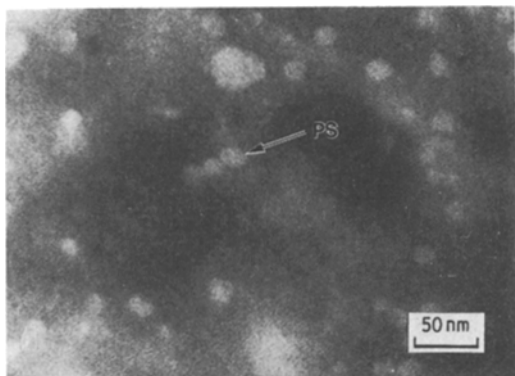


Figure 6 Cylindrical morphology in the solvent-cast F411 sample. The cylinders, seen in cross-section, appear in a random pattern.

Another useful bit of information acquired from IE is the ratio of light to dark areas, which should correspond to the ratio of PS fraction to PB fraction. This is accomplished by assigning intensities to the full light-to-dark spectrum of the electron micrograph; the number of pixels having a particular intensity is referred to as the bin population. Representing the light-dark threshold, the intensity corresponding to the maximum bin population (2820 in Fig. 8, for Figs 4a and b) is used to separate light and dark areas. In this way, the shades of grey in the interphase are assigned to one of the two populations in an objective fashion. The area under the curve to the left on this intensity (2820) represents the dark area (PB) of the electron micrograph, and that to the right the light area (PS). Each electron micrograph in this study exhibited a light-to-dark ratio that agreed within a few percent with the PS and PB volume fractions of the sample to which it referred.

5. Conclusions

Variations in the morphologies resulting from microphase-separated SBS block copolymers prepared with and without solvents were presented. These differences

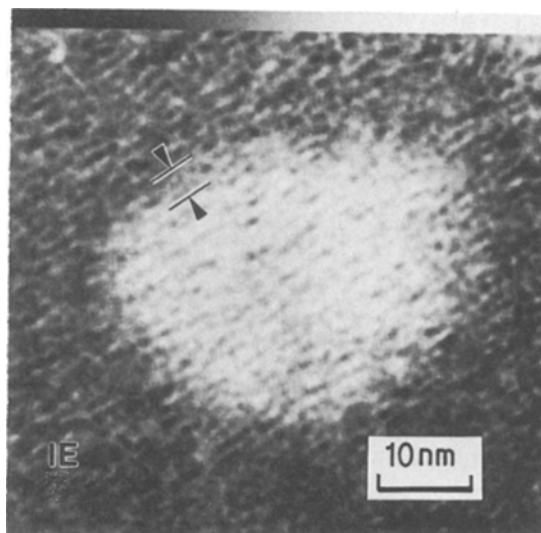


Figure 7 Computerized image enhancement of one of the cylinders shown in Fig. 6. The diffuse intensity is clearly visible and is approximately 3 nm wide.

demonstrated the significance of solvent effects on the polymer system. For *in situ* dynamic TEM studies, these effects are not desirable since the solvent-cast morphologies are not representative of the actual binary block copolymer.

To obtain ultrathin sections of a bulk rubbery polymer, cryo-ultramicrotomy was successfully utilized. The temperature at which the sectioning of the block copolymer was best accomplished is very closely approximated by the glass transition temperature of a hypothetical miscible blend of the same PS/PB composition; an average of the T_g predictions of Equations 1 and 2 worked extremely well in the present case. Since this temperature is too low for water to be employed as a trough liquid when rubbery polymers are involved, 1-pentanol was used. In addition, the glass knife was treated with Teflon to avoid difficulties with the high surface energy of the glass.

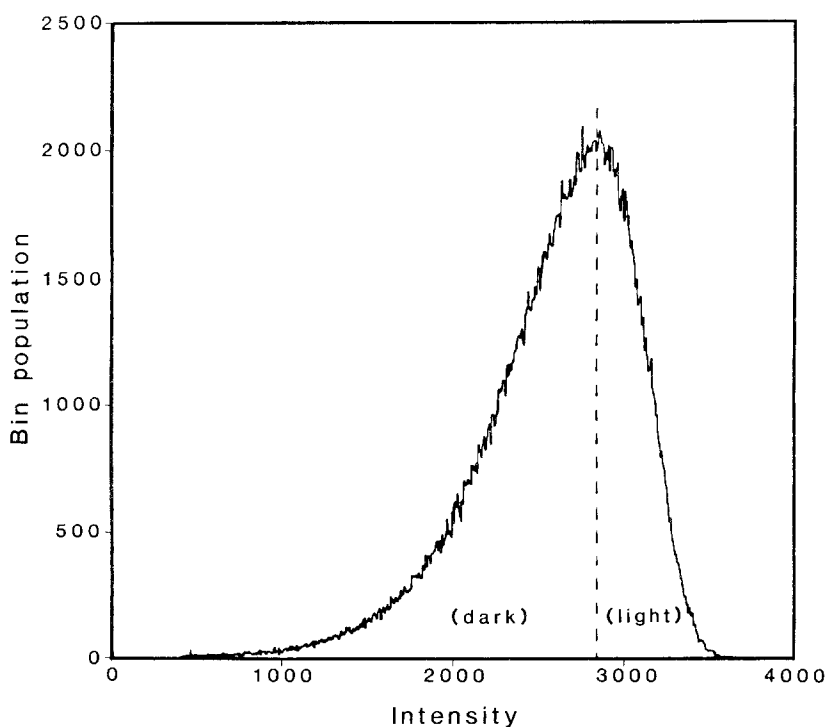


Figure 8 Image-enhanced relationship between the pixel bin population and light intensity for sample F414. The intensity corresponding to the maximum bin population (2820) is used to determine the ratio of light to dark areas, which should correspond to the ratio of polystyrene (PS) fraction to polybutadiene (PB) fraction. The actual sample distribution is 40 wt % (38 vol %) PS and 60 wt % (62 vol %) PB; image enhancing shows here 34.8% light (intensity >2820) and 65.2% dark (<2820) areas, close to the volume percentage.

Electron micrographs of the stained samples prepared with and without solvent were computer-enhanced to reveal a 3 nm wide interfacial regime. The overall light:dark ratio closely corresponded to the composition ratio (PS:PB) of the polymer.

Acknowledgements

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