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Effect of Block Copolymer on the Electric Field Induced Morphology of Polymer Blends

Introduction. Moriya et al.[1] were the first to demonstrate that anisotropic structures in blends could be generated by applying ac electric fields to solvent-free blends of poly(ethylene oxide) (PEO) and polystyrene (PS), suggesting a new approach for the modulation of polymer blend morphology. More recently, some of us reported the effect of a dc electric field on blends of PEO and PS (10/90 by weight) during film casting from cyclohexanone[2] or toluene[3] as a function of molecular weight and field strength. Elongated PEO domains were observed using PEO of M_w of about 100 000. Only pearl chains of PEO spheres were observed when a relatively low molecular weight ($M_w = 8000$; M_w = weight-average molecular weight) PEO was employed, even at applied fields of 10 kV/cm. In this paper, we discuss the effect of added diblock copolymer (PS-*b*-PEO) on the morphologies of PEO (M_w ca. 10 000)/PS (M_w ca. 210 000) blends cast from cyclohexanone in an electric field. We show that elongated PEO phases can form in this system at low applied fields (3 kV/cm) with added diblock copolymer and suggest that these are stabilized as a result of a lowering of the interfacial tension between PEO and PS.

Experimental Section. Polystyrene, $M_w = 210\,000$ (Aldrich), was purified by dissolution in chloroform and precipitation in methanol. Poly(ethylene oxide), $M_w = 10\,000$ (Aldrich), was dissolved in chloroform and precipitated from hexane. Poly(styrene-*b*-ethylene oxide), 80/20 wt %, was prepared by living anionic polymerization in THF using a procedure analogous to that employed by O'Malley and Marchessault.[4]

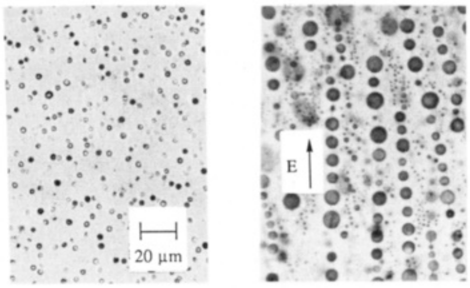
Cyclohexanone (99.8%, Aldrich) was dried over magnesium sulfate and distilled under reduced pressure. All other solvents used were reagent grade and were used as received. All polymers were dried under vacuum and subsequently stored in a desiccator. Polymer solutions contained 4% w/v of a 10/90 wt % blend of PEO/PS in cyclohexanone. Block copolymer was added to produce compositions listed in Table I. The total weight percent of PEO in all samples is comparable. Aluminum interdigitated array electrodes were fabricated photolithographically on glass substrates using standard procedures.[6] The eight fingers (ca. 5 cm in length and 5 mm wide) had a spacing of 2 mm.

A few drops of solution were placed on two fingers of the array at a time, and then the entire array was covered with a Petri dish. The solvent was allowed to slowly evaporate while an electric field of 3 kV/cm was applied.[7] Films were examined using a Leitz Laborlux 12 pol optical microscope equipped with a Wild Leitz MPS Photoautomat camera. Film thicknesses were found to be approximately 25 μm by means of micrometry.

Results and Discussion. Figures 1–4 are optical micrographs of the final film morphology of samples having the compositions listed in Table I which were cast in the absence of an electric field (a) and in a 3 kV/cm applied field (b). In Figures 1a–4a, it is observed that increasing the block copolymer content reduces the phase size. This is the well-known emulsifying effect which is due to a reduction in interfacial tension.[8,9]

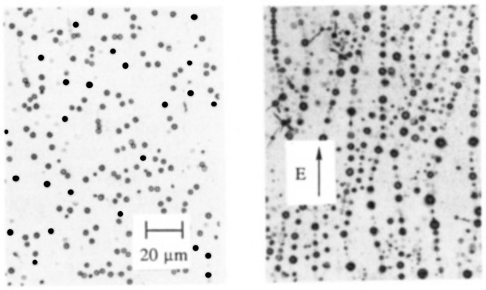
Table I
Compositions of Blends

sample	PS-*b*-PEO, wt %	PEO, wt %	PS, wt %	total PEO, wt %
1		10.3	89.7	10.30
2	0.6	10.0	89.4	10.12
3	1.9	10.2	87.9	10.58
4	4.6	9.5	85.9	10.42



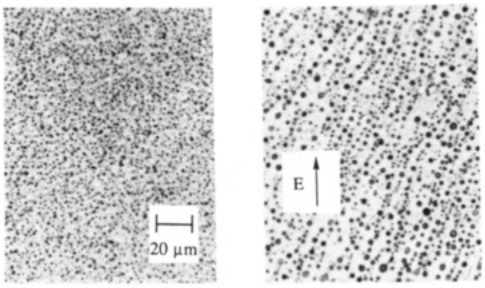
a) b)

Figure 1. Optical micrographs of sample 1 cast in the absence of an electric field (a) and in a 3 kV/cm field (b). The arrow indicates the applied field direction and points toward the negative electrode.



a) b)

Figure 2. Optical micrographs of sample 2 cast in the absence of an electric field (a) and in a 3 kV/cm field (b).



a) b)

Figure 3. Optical micrographs of sample 3 cast in the absence of an electric field (a) and in a 3 kV/cm field (b). The slanting of the pearl chains is probably due to nonuniform fields generated by the solvent on the electrode array.

It is evident that the domain size is larger when films are cast in the field.[10] This was consistently observed by us with PEO/PS blends that did not contain block copolymer[2,3] and may be due to partial coalescence of the domains. However, we note that phase-separation dynamics may be different in an electric field, and this issue is presently under investigation. Of particular interest is the observation that, at sufficiently high block copolymer concentration (sample 4, Figure 4b), elongated phases are observed in the film. We have not seen these in PEO (M_w ca. 8000)/PS blends in the absence of block copolymer, even at applied fields of 10 kV/cm.

The theory of Garton and Krasucki[11] predicts the field strength, E_{DF}, that causes a sphere to deform to a prolate ellipsoid with a specific aspect ratio, γ, will decrease with decreasing interfacial tension between the phases, for a

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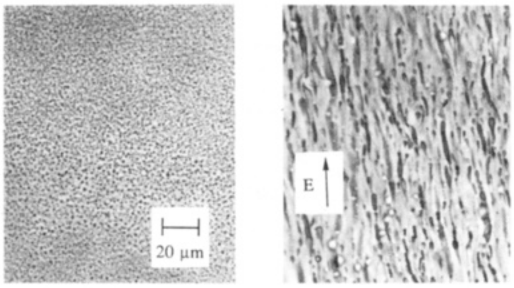
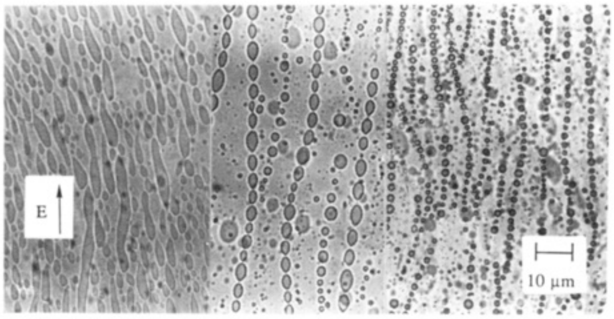


a) b)

Figure 4. Optical micrographs of sample 4 cast in the absence of an electric field (a) and in a 3 kV/cm field (b).



a) b) c)

Figure 5. Optical micrographs of a solution sample 1 in cyclohexanone during solvent evaporation while subjected to an applied field of 3 kV/cm. (a) Fluid solution showing elongated phases, some of which are in the process of ejecting smaller droplets. (b) About 20 min after Figure 5a, showing pearl chains. Note that the domains are somewhat elliptical, indicating that they are experiencing deformation by the applied field. (c) About 30 min later, showing pearl chains of spheres. The PEO domains retract presumably due to the increasing interfacial tension during solvent evaporation.

constant sphere radius, according to eq 1. Here σ is the

$$E_{\mathrm{DF}} = 600\left(\frac{\pi\sigma}{\epsilon_1 R_0}\right)^{1/2}\left[\frac{\epsilon_1}{\epsilon_1 - \epsilon_2} - G\right]H_1 \qquad (1)$$

interfacial tension, R_0 is the initial radius of the sphere, ϵ_1 and ϵ_2 are the dielectric constants of the matrix and dispersed phases, respectively, and G and H_1 are functions of γ. Preliminary experiments with the binary PS/PEO blend (sample 1) indicate that elongated PEO domains first form during casting from cyclohexanone in an electric field, and these begin to break up into smaller entities as solvent evaporates (Figure 5a). The smaller entities then form pearl chains (Figure 5b) and retract[12] (Figure 5c) during the later stages of solvent evaporation. It is important to note that interfacial tension is expected to increase as solvent is removed, and the break up of elongated domains may be the result of this increase, leading to stabilization of spheres vs elongated phases.[13] Moriya et al.[1] also observed that elongated PEO phases in PEO/PS *melts* may become unstable and break up to form pearl chains. These observations are also reminiscent of the disintegration of threads of a molten polymer in a molten matrix of another, a phenomenon known as a Rayleigh instability.[14] It is also observed that if the threads are too short they retract into spheres.[12]

The added block copolymer in our samples can encourage the formation of elongated phases in two ways. First, the interfacial tension may remain low even as solvent evaporates, allowing a low field for elongation (see eq 1) to prevail. Second, the lower interfacial tension can help to retard the breakup of the elongated phases. Elongated liquid phases or "threads" (e.g., induced in a shear flow) in immiscible mixtures are susceptible to sinusoidal disturbances which lead to break up into droplets.[15] This is driven by the interfacial tension between the components. Surfactants are known to decrease the rate of thread disintegration.[15] Interestingly, it has recently been reported[14] that a diblock copolymer can increase the stability of the molten polymer threads in another polymer matrix due to a reduction in interfacial tension. We therefore suggest that the elongated phases which form initially during casting of sample 4 (Figure 4b) can be stabilized toward disintegration into smaller phases by the block copolymer.

In summary, we have shown that elongated PEO phases are found in ternary PS/PEO/PS-*b*-PEO films cast in an electric field and containing ca. 4% by weight PS-*b*-PEO. It is believed that the elongated domains are initially formed more easily and are stabilized toward breakup as a result of a lowering of the interfacial tension between PEO and PS. These elongated phases are not observed in the absence of diblock copolymer even at much higher applied fields.

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References and Notes

(1) Moriya, S.; Adachi, K.; Kotaka, T. *Polym. Commun.* **1985**, *26*, 235.

(2) Venugopal, G.; Krause, S.; Wnek, G. E. *J. Polym. Sci., Part. C: Polym. Lett.* **1989**, *27*, 497.

(3) Venugopal, G.; Krause, S.; Wnek, G. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31* (1), 377.

(4) O'Malley, J. J.; Marchessault, R. H. *Macromol. Synth.* **1972**, *4*, 35. However, following on the work of Marie et al.[5a] and Barker and Vincent,[5b] diphenylmethylpotassium was used in place of cumylpotassium to initiate the polymerization. The block copolymer was isolated and purified by precipitation in hexane and extraction with methanol. The molecular weight and dispersity of the PS segment were determined by GPC from a methanol-quenched aliquot of the living PS intermediate. The PEO content of the copolymer was determined from ^{1}H NMR spectra using the ratio of the phenyl hydrogens in the styrene block to the PEO hydrogens. The M_w of the styrene block was found to be 115 000 with a polydispersity of 1.3. The M_n (number-average molecular weight) of the PEO block was calculated to be approximately 27 000 on the basis of the PEO content from NMR. The copolymer was dissolved in tetrahydrofuran, precipitated in hexane, decanted, suspended in methanol, and filtered prior to its use in our experiments.

(5) (a) Marie, P.; Lengelser, J. P.; Gallot, Y. *Makromol. Chem.* **1982**, *183*, 261. (b) Barker, M. C.; Vincent, B. *Colloids Surf.* **1984**, *8*, 289.

(6) Ruska, S. W. *Microelectronics Processing*; McGraw-Hill: New York, 1987; p 114.

(7) We consistently refer to "applied electric field", as the actual electric field strength is uncertain due to the presence of solvent and polymer covering the electrodes.

(8) Hashimoto, H.; Fujimura, M.; Hashimoto, T.; Kawai, H. *Macromolecules* **1981**, *14*, 844.

(9) It also seems that the same effect is responsible for the decrease in the size of pearl-chained spheres formed in films cast in the field and containing block copolymer (Figures 1b–3b).

(10) In the work of Moriya,[1] it was shown that the average phase size had decreased after application of the electric field. Although this may seem contrary to our results, coalescence processes and phase-separation kinetics may be making a comparison between our results and Moriya's study difficult.

(11) Garton, C. G.; Krasucki, Z. *Proc. R. Soc. London A* **1964**, *280A*, 211. The Gaussian system (cgs·esu) of units is used in the equation, where a factor of 300 is necessary for conversion from Stat·volts to volts (mks). A reviewer noted that the relationship between field strength and material parameters could be equally well represented (via dimensional analysis) by the equation $E = (\sigma/R_0)^{1/2}(f(\epsilon_1,\epsilon_2,\gamma)$. The electric field strength is a direct function of the square root of both the interfacial tension and the inverse of the initial domain radius.

(12) Carierre, C. J.; Cohen, A.; Arends, C. B. *J. Rheol.* **1989**, *33* (5), 681.

(13) Both deformation and breakup depend on the viscosities of the matrix and the minor phase. See: Moriya, S.; Adachi, K.; Kotaka, T. *Langmuir* **1986**, *2*, 155; **1986**, *2*, 161.

(14) Elemans, P. H. M.; Janssen, J. M. H.; Meijier, H. E. H. *J. Rheol.* **1990**, *34* (8), 1311.

(15) Carroll, B. J.; Lucassen, J. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 1228.

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