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Self-Assembled Thin-Film Blends by Polymer Codeposition: Poly(ethylene oxide) and Poly(methyl methacrylate)

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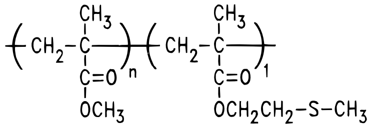
ABSTRACT: Two-component self-assembled films have been fabricated by codeposition of sulfur-derivatized poly(methyl methacrylate) (S-PMMA) and poly(ethylene oxide) (PEO). The unique surface morphology which results has been investigated by polarized infrared spectroscopy, contact angle measurements, and ellipsometry. In this binary blend, a coexistence of both PEO crystalline domains and an amorphous blended matrix was observed. Further investigation revealed that the PEO chains in the crystalline regions were oriented preferentially with their helical axes normal to the substrate surface.

Introduction

With the growing interest in self-assembled (SA) monolayers of long-chain organic compounds, and more recently polymers, has come the challenge of combining two components into organized, ultrathin films for patterned assembly. Two-component systems are known to form during preparation of Langmuir−Blodgett films. In fact, McConnell et al.[1] have observed striking patterns of domain formation using fluorescence microscopy. These patterns result because of thermodynamically driven phase separation on the microscopic scale, with the size and shape of the patterns being determined by the relative concentrations of the two components.

Very little work has been done on patterned self-assembled polymer films. However, numerical simulations on AB copolymers adsorbed on chemically heterogeneous surfaces (Balazs et al.[2]) suggest that a nonrandom spatial distribution of polymer units on a surface can be induced when there is a strong interaction between one of the components (A or B) and certain surface sites. Experimental studies on thiols by Whitesides et al.[3] provided a compelling argument in favor of surface segregation by chain length. Their contact angle measurements suggest that domains of long chains and short chains form separately in adjoining regions. The spatial segregation results in the longer chain ends collapsing to cover the shorter chain domains.

Recently,[4] polymers which self-assemble have been investigated as an alternative to the uniform-length thiols[5] and trichlorosilanes[6] which form quasi-crystalline arrays on the substrate surface. The attractiveness in using polymers for self-assembly is that they can be totally amorphous and, depending on their chemical structure, will have a glass transition temperature (T_g) which can be varied. High-T_g polymers like the sulfur-derivatized PMMA (PMMA-*n*) previously studied[4] will self-assemble on metallic surfaces to form an ultrathin (10−40 Å) glassy film. On the other hand, preliminary studies[7] on a similarly derivatized poly(dimethylsiloxane) (PDMS) indicate that, because of its low T_g, self-assembled films on gold are rubbery and exhibit significant chain mobility at room temperature. The ability to modify the surface texture simply by changing the chemical architecture, and hence the T_g, is particularly attractive since the surface topography, and hence the tribological properties, will also change.



$$\left(CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}\right)_n\left(CH_2-\overset{CH_3}{\underset{\underset{OCH_2CH_2-S-CH_3}{C=O}}{C}}\right)_1$$

Figure 1. Chemical formula of sulfur-derivatized PMMA (PMMA-*n*). $n = 10$ in this study.

Initial studies[4] of self-assembled PMMA-*n* came about because of the simplicity of its chemical structure and the observed tenacity with which it chemisorbed to metals. These studies indicated that it formed ultrathin films (10−40 Å) depending on the density of derivatized side chains and the solution concentration. Some displacement of the initial polymer was noted in samples which contained a low concentration of “sticky” side chains. A further result suggested that the films were extremely porous, allowing a second short-chain linear thiol molecule to easily penetrate the polymer film and form organized domains on the surface. This significant porosity of the SA films was a motivating factor for the current study.

It is the purpose of this work to report the results obtained from codeposition studies in which two compatible polymers dissolved in solution are chemisorbed to a gold surface as an ultrathin film. PMMA-10, studied previously, was codeposited with its compatible partner, semicrystalline poly(ethylene oxide) (PEO), to form a blended thin film which exhibits a unique surface morphology.

Experimental Method

A. Materials. PMMA-*n* is a copolymer of methyl methacrylate (MMA) and sulfur-derivatized MMA as shown in Figure 1. The relative ratio of MMA to sulfur-derivatized MMA used in this study was 10 to 1, designated PMMA-10. The PEO number-average molecular weight was 25 000 amu and that of PMMA-10 was about 89 000 amu. The solvent for these two polymers was CH_2Cl_2 (analytical grade) and was used as supplied.

Microscope glass slides (75 mm × 25 mm) were cleaned by immersion in an oxidative sulfuric acid solution. The substrates were then rinsed in deionized water, degreased in 2-propanol vapor, and dried under a warm nitrogen flow. A 200 Å adhesion layer of chromium and 2000 Å layer of Au were deposited on the substrates by thermal evaporation in a

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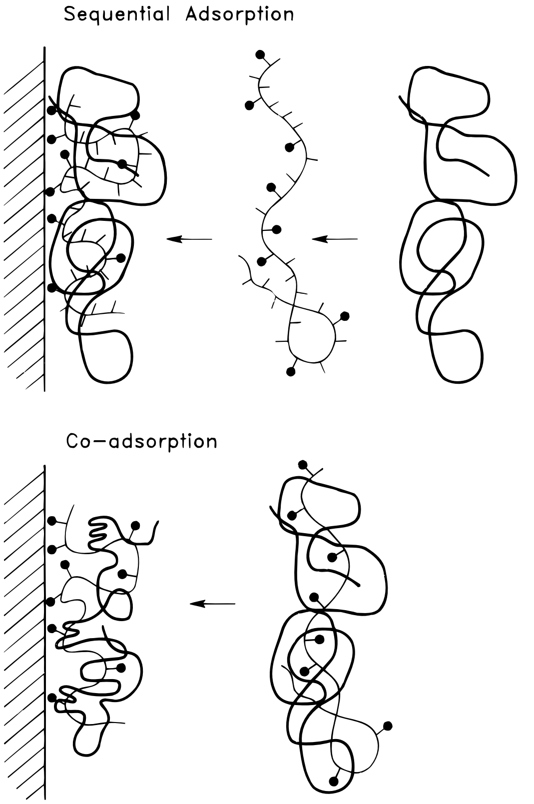

Figure 2. Schematic representation of sequential and codeposition of polymers from solution onto a substrate.

vacuum chamber. Deposition rates were 2−3 Å/s for Cr and 8−10 Å/s for Au. Substrates were immersed in solution within minutes of removal from vacuum.

B. Blend Formation. Two-component films on gold were formed by two methods, sequential deposition and codeposition (Figure 2). For the sequential deposition, the fresh gold-coated glass microscope slide was immersed in a solution of 0.1 mg/mL PMMA-10 in CH_2Cl_2 for 20−24 h. The glass slide was then removed from the solution, rinsed with solvent, and blown dry with a stream of nitrogen. The dipping procedure was then repeated in the second polymer solution (0.1 mg/mL PEO). In the codeposition procedure, the gold substrate was immersed in a 0.1 mg/mL blend solution (1:1 PMMA-10:PEO). The deposition time was again 20−24 h. Coated substrates were then rinsed with solvent and dried with nitrogen. Alternatively, films were made by dropping the dilute blend solution directly onto the Au substrate and allowing the solvent to evaporate (solution cast).

C. Spectroscopic Measurements. Samples were placed immediately in the FTIR instrument after drying and were kept under vacuum (≃5 mTorr) for 2 h before acquiring spectral data. The gold substrates were transferred immediately from the evaporator to polymer solutions or to the FTIR for measurement as reference. Infrared spectra were taken with an IBM/Bruker Model 98 evacuable FTIR using a grazing incidence external reflection attachment (incident angle 81−83°). The spectra were collected at a resolution of 4 cm^{-1}, and 8000 scans (approximately 4 h each for sample and reference) were coadded to achieve the desired signal-to-noise ratio. Water vapor was subtracted from the resultant spectra as necessary.

D. Thickness Measurements. A Rudolph Research Auto-El ellipsometer (6328 Å, 70° angle of incidence) was used to determine film thicknesses. A refractive index of 1.5 was used for the blended film. Varying this parameter from 1.40 to 1.60 changed the calculated thickness by 1−2 Å (±1 or 2 Å). Using this method, film thicknesses for the immersed samples varied from 25 to 40 Å. The cast samples ranged from 2000 to 8000 Å thick.

Results and Discussion

In this study, two chemically dissimilar polymers that have been described as compatible in the amorphous state at room temperature[8] were investigated. It is generally accepted that PMMA and PEO are miscible in the melt.[9,10] Several authors have presented evidence that PEO and PMMA are compatible in the amorphous phase at temperatures near the melting temperature.[11−13] Li and Hsu[14] used differential scanning calorimetry (DSC) to show a single T_g for blends (0−100% PEO) formed by quenching from the melt to liquid nitrogen temperature. In other studies[11,15] involving both quenched and solution-cast films, the PEO spherulite growth rate and degree of crystallinity were reduced by increasing the amount of PMMA in the blend. The melting temperature for PEO was depressed in these mixtures as well.[12,14] For films solution cast from mixtures less than 50% PEO, phase separation into a PEO-rich (80% PEO) and a PMMA-rich (20% PEO) phase was observed.[14] Silvestre et al.[13] combined SAXS and DSC to show that in solution-cast films of PEO blended with atactic-PMMA and syndiotactic-PMMA, one homogeneous amorphous phase was present; this amorphous region underwent phase separation in blends of PEO with isotactic-PMMA. The conclusion reached in all these studies is that PEO and PMMA are at least partially miscible in solution-cast films for most compositions. Further, the compatibility of these two polymers has been shown to be affected by processing, stereoregular content, and composition.

PEO, a semicrystalline polymer and PMMA-10, an amorphous sulfur-derivatized polymer, produce a semicrystalline mixture when the proportion of PEO exceeds[8] 20 wt %. For the concentration used in this study (50 wt % PEO), the two-component system is expected to be composed of amorphous blended regions with some crystalline regions made up entirely of PEO. The assumption of miscibility with PMMA in the amorphous state is not necessary for the type of orientational analysis presented here since we are focusing on the crystalline component of PEO.

As shown previously,[4] sulfur-derivatized PMMA (PMMA-10) will self-assemble on metallic surfaces to form an amorphous, isotropic, ultrathin (20−25 Å) glassy film. Under the experimental conditions used here, PMMA-10 forms a continuous monolayer over the entire surface of the gold.[4] This conclusion was drawn by observing the change in contact angle with measured film thickness. For films found to be 15 Å or thicker, the constant contact angle suggests that the surface coverage is complete. The films were shown to be quite porous by performing a secondary adsorption experiment using a fluorinated amide thiol.[5] The amount of the fluorinated material adsorbed was equivalent to approximately 50% of a well-ordered monolayer while none of the PMMA-10 was lost. The semifluorinated amide thiol formed domains at the surface due to thermodynamic incompatibility between fluorocarbons and hydrocarbons and the availability of unoccupied surface sites on the gold substrate. The continuity at the free surface of the PMMA-10 was preserved as shown by contact angle measurements.[4] This was possible since the fluorinated molecule was smaller than the film thickness and resided only at the gold surface, not at the polymer/air interface.

The reflection IR spectrum ($E_\perp$) of PMMA-10 adsorbed onto Au can be seen in Figure 3. The characteristic peaks which identify this material are[4] ν(C=O) near

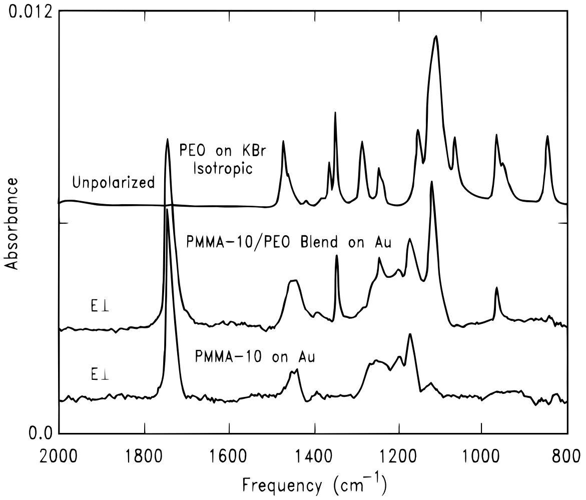

Figure 3. Reflection IR spectrum ($E_\perp$) of S-PMMA adsorbed onto Au surface (lower trace); reflection IR spectrum ($E_\perp$) of PEO:S-PMMA (1:1) self-assembled film (middle trace); IR spectrum (unpolarized) of room temperature semicrystalline PEO (upper trace).

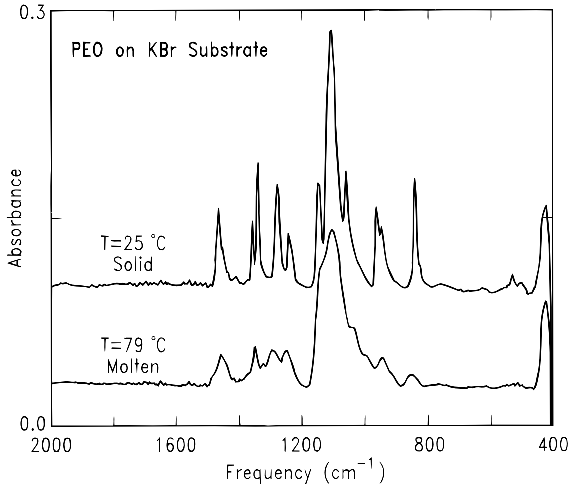

Figure 4. IR spectra of room temperature semicrystalline (upper) PEO and its high-temperature melt (lower).

1740 cm^{-1}, $\delta(CH_2)$ near 1450 cm^{-1}, and stretching and bending vibrations of the methacrylate side chain[16,17] which appear from 1250 to 1180 cm^{-1}. These signature vibrational features may be used to verify the presence of adsorbed PMMA-10.

Attempts to obtain an IR spectrum of a thin adsorbed film of PEO were unsuccessful. This is because PEO does not adsorb onto the Au surface from the solution or it physisorbs so weakly that rinsing with solvent completely removes it from the surface. This was established by immersing the Au-coated substrate in the PEO solution as described in the experimental section and noticing the absence of PEO in the IR spectrum. For reference, the characteristic spectra of PEO in the isotropic semicrystalline and melt forms obtained from bulk samples are shown in Figure 4.

Since PEO is a morphologically interesting semicrystalline polymer, it has been the subject of many detailed IR and Raman spectroscopic studies and its band assignments in both the melt and solid state are well understood.[14,18,19] The conformation in the solid state is a 7/2 helix, and as such, the IR bands can be assigned to either the A_2 (transition moment parallel to the helical axis) or E (transition moment perpendicular to the helical axis) symmetry species. As shown in Figure 4, a number of medium to strong bands (see Table 1) are present in the crystalline state. The most prominent feature is the strong doublet at 1107/1061 cm^{-1}, which has been attributed to CO stretching mixed with a small amount of CH_2 rocking in the latter peak. Of moderate intensity is the 1342 cm^{-1} CH_2 wagging vibration whose intensity is sensitive to the conformational order as shown by the lower melt spectrum. The spectrum of the molten PEO is included as a reasonable approximation to the amorphous state since the morphology of PEO/PMMA blends consists of PEO crystallites coexisting with an amorphous blend of PEO and PMMA.[11−15] A planar zigzag modification of PEO not normally present without mechanical deformation[20] has previously been observed and the assignment of the characteristic bands made by Tashiro and Tadokoro,[20] who combined IR experiments with wide-angle X-ray diffraction structure verification. As expected, these vibrations are not present in the bulk spectrum shown in Figure 4.

Table 1. Crystalline PEO Bands and Their Assignment

PEO	polarization	assignment[a]
1467 s	∥	$\delta(CH_2)$
1455 s	∥	$\delta(CH_2)$
1413 vw	⊥	$w(CH_2)$
1360 s	⊥	$w(CH_2)$
1342 s	∥	$w(CH_2)$
1280	⊥	$t(CH_2)$
1241 m	∥	$t(CH_2)$
1235 sh	⊥	$t(CH_2)$
1148 s	⊥	$\nu(CO)$
1107 vs	∥	$\nu(CO)$
1061 s	⊥	$\nu(CO) + r(CH_2) + \nu(CC)$
962 s	∥	$r(CH_2) + \nu(CH_2)$
948 s	⊥	$r(CH_2) + \nu(CC)$
842 s	⊥	$r(CH_2) + \nu(CO)$
531 vw	∥	$\alpha(CCO) + r(CH_2)$

[a] Reference 18. ν = stretch, r = rock, δ = scissors, w = wag, t = twist, α = bend.

Comparing a thin cast film of pure PEO with the bulk spectrum, both ∥ and ⊥ bands are observed as all orientations are possible. However, relative changes in the ratio of ∥ and ⊥ (to the helical axis) bands of PEO can be induced by annealing a cast film.[22,23] This indicates that the cast films are not in equilibrium; certain crystallite orientations are more stable than others and their nucleation and growth is thermally activated. Using cast films of PEO an order of magnitude thinner than those studied previously,[22,23] we have seen similar changes on annealing. As the film anneals, it changes from relatively isotropic to one with some degree of preferred chain orientation. The effect is more pronounced in the thinner films, suggesting that this phenomenon is caused by the presence of the surface or interface. However, even in very thin films, both ∥ and ⊥ components are present no matter how long the annealing time; that is, complete orientation has not been observed upon annealing a cast film of pure PEO.

When a gold-coated glass slide is immersed in a 1:1 solution of PEO:PMMA-10, both PEO and PMMA-10 are found in the spectrum (shown in Figure 3). Since PEO and PMMA are compatible in the solvent and concentrations used here, we might expect the two polymers to be associated. This entanglement with the sulfur-derivatized polymer is responsible for binding PEO to the surface. (PEO has no special affinity for Au itself as mentioned above.) The removal of PEO by rinsing could happen in codeposited films if the two polymers were not entangled sufficiently to withstand the flow of solvent. By comparing the intensities of the signature peaks of PMMA-10 in the blend spectrum with those of the single-component film, it can be seen that the amount of PMMA-10 in the film is nearly that of a full monolayer. The amount of PEO in the film cannot be determined by this method since we were unable to produce a complete monolayer of PEO as a reference due to its lack of adhesion to the substrate.

Of particular interest in the two-component films is the fact that the PEO crystalline portions are not oriented randomly. This can be seen by comparing the adsorbed spectrum in Figure 3 with that of the bulk solid isotropic spectrum (upper trace). On the contrary (Table 1), only those bands representing A_2 vibrations which have a change in dipole moment parallel to the 7/2 helical axis (1342, 1241, 1107, and 962 cm^{-1}) are observed in the adsorbed blend spectrum. The fact that these bands are the only ones observed in the polarized $E_\perp$ experiment[21] indicates that the PEO chains in the crystalline regions are oriented with their helical axes normal to the gold surface.

The preferentially oriented blend result may also be obtained by solution casting. This is interesting since the films are much thicker in this case (2000−8000 Å). Since the cast blend films were similar in thickness to the cast PEO films, the different orientation behavior can be directly compared. Thin PEO films change orientation upon annealing but never show the extent of orientation observed in the thin cast films without annealing. It follows that the interaction between PEO and PMMA in the film is in part responsible for the unique orientation observed.

Preferential orientation may also be achieved by solution casting a 1:1 blend of PEO and PMMA that has not been derivatized with the sulfide groups. This indicates that the orientation effect is not solely caused by the presence of the sulfide linkages. Li and Hsu,[14] who pointed out the importance of sample preparation on determining morphology, obtained isotropic films by solution casting blends of PEO and PMMA. It is important to note that their films were much thicker than the ones being considered here and hence the isotropic spectrum of the bulk may have masked any orientation that may have occurred at the 100 nm scale. However, these results make it clear that the dimensions of the film, or the presence of a surface or interface, have a definite effect on the morphology of a blended film of PEO and PMMA.

In an attempt to determine if this unique surface topography can be produced by sequential deposition, a PMMA-10 adsorbed film sample was immersed in the PEO solution for 24 h. Interestingly enough, the PEO does not entangle with the adsorbed PMMA-10. Because the PEO could not be incorporated into an already adsorbed film, this method could not be used to form blended samples.

It is of interest to determine the origin of the preferred orientation in the blend monolayer and cast films. The annealing behavior of a thin cast film of PEO indicates that the surface and/or interface plays a role. However, no annealing is required for complete orientation of PEO in the blended film and this condition was never reached in pure PEO films. Hence the association of the two polymers and the resulting surface nucleation probably cause the peculiar anisotropy of the PEO crystallites. Certainly entanglement of the two polymers is responsible for binding PEO to the surface. The fact that polymer molecules oriented parallel to the substrate can be seen in very thick cast films of the blend reaffirms the contribution of the surface and/or interface to the orientation mechanism. Neither a surface/interface effect nor the association of two compatible polymers can fully explain the behavior of PEO crystallites in the blended films.

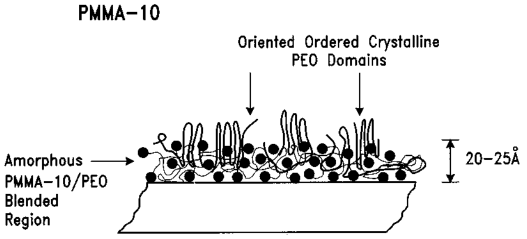

Figure 5. Schematic representation of film architecture in self-assembled blended film.

Combining the PEO crystallite orientation information obtained from polarized IR spectroscopy and the ellipsometric thickness of 31−37 Å of the PMMA-10/PEO adsorbed blended film, it is possible to depict schematically the unique morphology obtained in this thin-film blend. As shown in Figure 5, there is a coexistence between an amorphous component of blended PMMA and PEO and crystallites of PEO embedded in this amorphous matrix. In this illustration, the surface "roughness" caused by the crystallites has been exaggerated. We have no information on the lateral extent of the PEO crystalline domains or whether or not they protrude from the surface. The intriguing result is that the PEO chains within the crystallites perferentially orient with their helical axes normal to the surface. It is interesting to note that the translational repeat unit of PEO is 17.2 Å, indicating that, at the measured thickness (≃31−37 Å), the crystallites contain at most two translational repeat units. The general applicability of this result is currently under investigation using other two-component self-assembed systems, and preliminary results on a PMMA-10/PVF_2 blend are encouraging.

Conclusions

By codeposition of a self-assembling polymer (S-PMMA) and compatible partner (PEO), an ultrathin blended film with a unique morphology was formed. The blended amorphous regions serve to anchor the two polymers to the substrate surface; the crystalline regions are anisotropic with the helical axes preferentially assuming an orientation perpendicular to the substrate. Cast films of the blend yielded the same crystallite orientation even though the film thicknesses were much greater in this case. The association of the two polymers in solution appears to be partially responsible for this final film architecture since crystallites in cast films of the semicrystalline polymer (PEO) by itself are randomly oriented. The unique orientation of PEO crystallites was duplicated in cast films of blends of PEO and PMMA (no sulfide linkages) as well. This further points to the association of the two polymers in solution and their confinement in thin films as contributing factors for the specificity of the crystalline orientation. The change in orientation of a thin cast film of PEO upon annealing indicates that the presence of a surface or interface is also important in determining the morphology of this polymer. Hence the small film dimensions and the interaction of the two polymers in the blended film are apparently both necessary conditions for achieving the special orientation of PEO crystallites.

Sequential deposition of a blended film failed as the two polymers did not entangle at room temperature once the first component had adsorbed to the gold surface. The PEO, which has no special affinity for gold, was removed during the rinse procedure.

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References and Notes

(1) Klinger, J. F.; McConnell, H. M. *J. Phys. Chem.* **1993**, *97*, 2962.
(2) Balazs, A.; Gempe, M.; Zhou, Z. *Macromolecules* **1991**, *24*, 4918.
(3) Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1993**, *9*, 1766.
(4) Lenk, T. J.; Hallmark, V. M.; Rabolt, J. F.; Haussling, L.; Ringsdorf, H. *Macromolecules* **1993**, *26*, 1230.
(5) Lenk, T. J.; Hallmark, V. M.; Hoffmann, C. L.; Rabolt, J. F.; Castner, D. G.; Erdelen, C.; Ringsdorf, H. *Langmuir* **1994**, *10*, 4610.
(6) Ulman, A. *An Introduction to Ultrathin Organic Films: From Langmuir−Blodgett to Self-Assembly*; Academic Press, Inc.: Boston, 1991.
(7) Tsao, M.-W.; Hoffmann, C. L.; Rabolt, J. F.; Hausseling, L.; Ringsdorf, H., work in progress.
(8) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley & Sons: New York, 1989.
(9) Sanchez, J. C. *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press, Inc.: New York, 1978.
(10) Martuscelli, E.; Demma, G.; Rossi, E.; Segre, A. C. *Polymer* **1983**, *24*, 266.
(11) Calahorra, E.; Cortazar, M.; Guzman, G. M. *Polymer* **1982**, *23*, 1322.
(12) Liberman, S. A.; Gomes, A. De S.; Macchi, E. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2809.
(13) Silvestre, I. C.; Cimmino, S.; Martuscelli, E.; Karasz, F. E.; MacKnight, W. J. *Polymer* **1987**, *28*, 1190.
(14) Li, X.; Hsu, S. L. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1331.
(15) Martuscelli, E.; Canetti, M.; Vicini, L.; Seves, A. *Polymer* **1982**, *23*, 331.
(16) Havriliak, S., Jr.; Roman, N. *Polymer* **1966**, *7*, 387.
(17) Nagai, H. *J. Appl. Polym. Sci.* **1963**, *7*, 1697.
(18) Yoshihara, T.; Tadokoro, H.; Murahashi, S. *J. Chem. Phys.* **1964**, *41*, 2902.
(19) Matsuura, H.; Miyazawa, T. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1798.
(20) Tashiro, K.; Tadokoro, H. *Rep. Prog. Polym. Phys. Jpn.* **1978**, *XXI*, 417.
(21) Greenler, R. G. *J. Chem. Phys.* **1966**, *44* (1), 310.
(22) Rao, G. R.; Castiglioni, C.; Gussoni, M.; Zerbi, G.; Martuscelli, E. *Polymer* **1985**, *26*, 811.
(23) Marcos, J. I.; Orlandi, E.; Zerbi, G. *Polymer* **1990**, *31*, 1899.
(24) Mores, W.; Hoffmann, C.; Rabolt, J. F., work in progress.

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