

## Wetting of Substrates with Phase-Separated Binary Polymer Mixtures

Jan Genzer and Edward J. Kramer

*Department of Materials Science and Engineering and the Materials Science Center, Cornell University, Ithaca, New York 14853-1501*

(Received 10 March 1997)

We investigate a wetting reversal transition in thin films of two-phase mixtures of poly(ethylene-propylene) (PEP) and its deuterated analog (dPEP) on substrates covered by self-assembled monolayers (SAM) whose surface energy,  $\gamma_{\text{SAM}}$ , is tuned by varying the SAM composition. As  $\gamma_{\text{SAM}}$  increases from 21 to 24 mJ/m<sup>2</sup>, a transition from a dPEP/PEP/dPEP/SAM to a dPEP/PEP/SAM structure occurs at increasing  $T_C - T$ , where  $T_C$  and  $T$  are the critical and transition temperatures, respectively. The dependence of  $T$  on  $\gamma_{\text{SAM}}$  is predicted by a simple model from surface and interfacial energies of PEP/dPEP. [S0031-9007(97)03445-5]

PACS numbers: 61.25.Hq, 68.10.-m, 68.45.Gd, 83.80.Es

The behavior of phase-separated polymer mixtures has been the subject of much theoretical and experimental work in the past few years. Upon quenching into the unstable region of the phase diagram, critical mixtures of  $A$  and  $B$  polymers phase separate into  $A$ -rich and  $B$ -rich coexisting phases. In the bulk, the concentration fluctuations that govern the phase separation process are random. As a result, the final morphology consists of mutually interconnected  $A$ -rich and  $B$ -rich domain structures that coarsen slowly with time [1]. However, in thin films the situation changes drastically. The presence of additional interfaces, i.e., mixture/surface and mixture/substrate, causes the directions of the compositional waves in the mixture close to the interfaces to be modified such that the resultant domains are oriented parallel to these interfaces [2–5]. Hence the phase morphology and its time evolution in thin, phase-separated polymer films is governed by an interplay between phase-separation processes and interactions of the  $A$ -rich and  $B$ -rich polymer phases with the air and with the substrate. While the air surface will always prefer the low surface energy (say, the  $A$ -rich phase), the substrate interfacial preference can change from the  $A$ -rich phase to the  $B$ -rich phase if the nature of the substrate surface changes [3–5] or, for a constant substrate surface, as the composition of the  $A$ -rich phase changes [2]. Thus, if the properties of the substrate surface can be tuned sensitively, it may be possible to observe a transition from a two-layer structure ( $A$ -rich/ $B$ -rich/substrate) to a three-layer one ( $A$ -rich/ $B$ -rich/ $A$ -rich/substrate) as the polymer mixture is cooled from the critical temperature.

In this Letter we demonstrate experimentally that this possibility can be realized using phase-separated mixtures of poly(ethylene-propylene) (PEP) and its deuterated analog (dPEP) deposited on substrates covered with self-assembled monolayers (SAM) composed of blends of thiols with hydrophobic and hydrophilic end groups. In agreement with previous experiments [4], the mixture/air interface is always found to be enriched by the dPEP-rich phase. However, depending on the composition of the

SAM, either a dPEP-rich or a PEP-rich phase wets the mixture/SAM interface. The transition from dPEP-rich to PEP-rich (dPEP-poor) phase at the mixture/SAM interface takes place at a particular composition of the SAM or, for SAM's in a suitable composition range, it takes place at a particular annealing temperature. We will refer to such a transition as a three-layer to two-layer transition. By carrying out such experiments at different temperatures in the two-phase region, the phase diagram of three-layer to two-layer transitions is generated.

Smooth and well-characterized substrates are necessary prerequisites for accurate control of the interactions at the mixture/substrate interface. Such substrates can be fabricated by depositing SAMs of end-functionalized alkanethiols onto gold [6]. If two thiols having different end groups are coadsorbed on the Au surface, the surface energy of the resultant SAM is related to the ratio of the two thiols in the SAM blend. The extent to which the SAM surface energy changes depends on the character of the thiol end groups. When the difference between the polymer/SAM interactions for both phase-separated phases is not substantial, such as in isotopic polymer mixtures, one expects that by varying the surface energy of SAM one can induce either the  $A$ -rich or the  $B$ -rich phase to wet the substrate. The SAM substrates were produced as follows. Thiol solutions (concentration  $\sim 1$  mM) were prepared by codissolving 16-mercaptohexadecanoic acid, HS(CH<sub>2</sub>)<sub>15</sub>COOH (courtesy of G. Whitesides, Harvard University), and 1-octadecanethiol, HS(CH<sub>2</sub>)<sub>17</sub>CH<sub>3</sub> (Aldrich), in tetrahydrofuran. The mole fraction,  $x$ , of HS(CH<sub>2</sub>)<sub>15</sub>COOH in the HS(CH<sub>2</sub>)<sub>17</sub>CH<sub>3</sub> + HS(CH<sub>2</sub>)<sub>15</sub>COOH blend ranged from 0 to 1. The substrates for the SAMs were produced by evaporating a layer of Au ( $\sim 1500$  Å thick) onto Si wafers covered with a layer of Cr ( $\sim 150$  Å thick). The latter served as an adhesion promoter for Au. The SAMs were prepared by exposing the Au-covered Si wafers to thiol solutions for 24 h at room temperature. After adsorption, the SAM monolayers were washed in tetrahydrofuran and dried with nitrogen. The surface energies

of the SAM monolayers,  $\gamma_{\text{SAM}}$ , were evaluated using the geometric mean approximation (GMA) from the measurements of the advancing contact angle,  $\theta$ , of deionized water and methylene iodide [7]. The resultant values of  $\gamma_{\text{SAM}}$  are plotted in the inset of Fig. 1. The data show that, by increasing  $x$  from 0 to 1,  $\gamma_{\text{SAM}}$  is increased from  $\sim 20$  to  $81 \text{ mJ/m}^2$ . The values of the critical surface energies of SAMs,  $\gamma_{\text{SAM},c}$ , were determined from Zisman plots [8]. These were generated by measuring  $\theta$  using a series of homologous alkanes [9] on SAMs with  $x$  ranging from 0 to 0.4. At each  $x$  the differences between  $\gamma_{\text{SAM}}$  and  $\gamma_{\text{SAM},c}$  were found to be less than  $1 \text{ mJ/m}^2$ . This result confirmed the applicability of GMA in evaluating  $\gamma_{\text{SAM}}$  for substrates with low  $x$ . Later in this Letter we show that, within the investigated temperature range, the three-layer to two-layer transitions are observed on SAMs with  $\gamma_{\text{SAM}} < 25 \text{ mJ/m}^2$ , which corresponds to  $x < 0.4$  [10].

The PEP and dPEP polymers were prepared by hydrogenating and deuterating, respectively, anionically polymerized 1,4-polyisoprenes [11]. The degrees of polymerization of both polymers,  $N$ , were  $\sim 2280$ , which leads to an upper critical solution temperature,  $T_C$ , of  $\sim 93^\circ\text{C}$  [12]. Thin films ( $\sim 4000 \text{ \AA}$  thick) of critical dPEP/PEP mixtures (50/50  $v/v$ ) were spin coated from toluene solutions onto glass-microscope slides, floated onto a bath of deionized water and picked up with the SAM covered substrates. The samples were annealed in vacuum at four different temperatures below  $T_C$ , namely, at 23, 44, 66, and  $75^\circ\text{C}$  for various times ranging from four days ( $75^\circ\text{C}$ ) to three weeks ( $23^\circ\text{C}$ ). The annealing times were chosen such that the samples reached equilib-

rium [13]. After annealing, the samples were quenched by immersion into a bath of liquid nitrogen to preserve the structure. Conventional forward recoil spectrometry (FRES) was then used to measure the volume fraction profiles of dPEP and PEP in the samples [14].

Figure 1 shows the volume fraction profiles of dPEP in critical dPEP/PEP mixtures on SAMs with  $x \approx 0.28$  (open circles) and  $x \approx 0.30$  (solid circles) annealed at  $44^\circ\text{C}$  for 110 h. The volume fractions of dPEP in the dPEP-rich and the PEP-rich coexisting phases are 0.710 and 0.315, respectively [13]. Figure 1 shows that, in both samples, a dPEP-rich phase is present at the mixture/air interface, in agreement with previous experiments [4,13,15]. This behavior is expected because the surface energy of dPEP is lower than that of PEP [15]. However, depending on the substrate, either a dPEP-rich or a PEP-rich phase is present at the mixture/SAM interface. Namely, for SAMs with  $x \leq 0.28$ , the mixture/SAM interface is wet by the dPEP-rich phase, and for SAMs with  $x \geq 0.30$ , the mixture/SAM interface is wet by the PEP-rich phase. The transition from the dPEP-rich phase at the mixture/SAM interface (three-layer structure) to the PEP-rich phase at the mixture/SAM interface (two-layer structure) thus occurs for SAMs with  $0.28 < x < 0.30$ , which corresponds to  $22.4 < \gamma_{\text{SAM}} < 23.5 \text{ mJ/m}^2$ . The crossover from the three-layer to two-layer structure was monitored at three additional annealing temperatures below  $T_C$ . The results are presented in the form of the phase diagram of three-layer to two-layer transitions shown in Fig. 2.

In Fig. 2 we plot  $\gamma_{\text{SAM}}$  as a function of the annealing temperature (bottom axis) and the volume fraction of PEP-rich phase at the coexistence,  $\phi_{\text{PEP,coex}}$  (top axis). At constant temperature,  $\phi_{\text{PEP,coex}}$  is the same regardless whether the dPEP-rich or PEP-rich phase wets the mixture/SAM interface. The open and solid circles in Fig. 2 represent the three-layer and two-layer structures, respectively, as determined from the FRES experiments. The solid line is a guide to the eye. The results in Fig. 2 show that with decreasing the quench depth ( $T \rightarrow T_C$ ) the three-layer to two-layer transition takes place at lower values of  $\gamma_{\text{SAM}}$ .

The free energies of the three-layer and two-layer structures,  $F_3$  and  $F_2$ , respectively, can be estimated from

$$F_3 = \gamma_{\text{SAM/dPEP}} + 2\gamma_{\text{SAM/dPEP}} + \gamma_{\text{dPEP}}, \quad (1a)$$

$$F_2 = \gamma_{\text{SAM/PEP}} + \gamma_{\text{PEP/dPEP}} + \gamma_{\text{dPEP}}, \quad (1b)$$

where  $\gamma_{\text{SAM/dPEP}}$  and  $\gamma_{\text{SAM/PEP}}$  are the interfacial energies of the dPEP-rich and PEP-rich phases and the SAM, respectively,  $\gamma_{\text{PEP/dPEP}}$  is the interfacial energy between the dPEP-rich and PEP-rich phases, and  $\gamma_{\text{dPEP}}$  is the surface energy of the dPEP-rich phase. From Eqs. (1a) and (1b) we see that the three-layer structure will be the preferred configuration when  $\gamma_{\text{SAM/PEP}} - \gamma_{\text{SAM/dPEP}} > \gamma_{\text{PEP/dPEP}}$ , whereas the two-layer structure will exist when  $\gamma_{\text{SAM/PEP}} - \gamma_{\text{SAM/dPEP}} < \gamma_{\text{PEP/dPEP}}$ . These relations

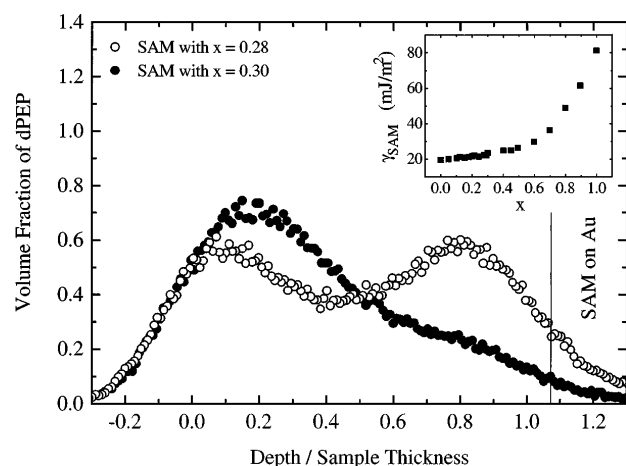


FIG. 1. Volume fraction profiles of dPEP in critical dPEP/PEP mixtures  $\sim 4000 \text{ \AA}$  thick annealed at  $44^\circ\text{C}$  for 110 h at SAMs with  $x \approx 0.28$  (open circles) and  $x \approx 0.30$  (solid circles). The depth coordinate of the dPEP volume fraction profiles has been normalized by the total sample thickness. The mixture/air and mixture/SAM interfaces are located at depths equal to 0 to 1, respectively. The inset shows the dependence of the surface energy of SAM,  $\gamma_{\text{SAM}}$ , on the molar fraction of  $\text{HS}(\text{CH}_2)_{15}\text{COOH}$  in the  $\text{HS}(\text{CH}_2)_{17}\text{CH}_3 + \text{HS}(\text{CH}_2)_{15}\text{COOH}$  blend,  $x$ .

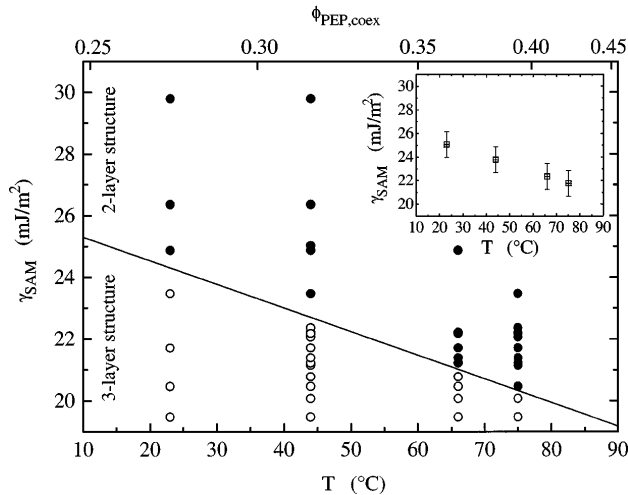


FIG. 2. Phase diagram of three-layer to two-layer transitions at the dPEP/PEP mixture/SAM interface for mixtures annealed at four different temperatures below  $T_C$ . The results are plotted in the form of the surface energy of the SAM substrate,  $\gamma_{SAM}$ , as a function of temperature (bottom axis) and the volume fraction of PEP-rich phase at the coexistence,  $\phi_{PEP,coex}$  (top axis). The open and solid circles represent the three-layer and two-layer structures, respectively. The solid line is a guide to the eye. The inset shows the positions of the three-layer to two-layer transition calculated using the model described in the text.

indicate that the transition between the three-layer and two-layer structures takes place whenever the driving force for segregation of the dPEP-rich phase at the mixture/SAM interface ( $\gamma_{SAM/PEP} - \gamma_{SAM/dPEP}$ ) balances the energy penalty associated with an additional interface in the bulk between the two coexisting phases ( $\gamma_{PEP/dPEP}$ ). Because the relevant experimental quantity we measure is  $\gamma_{SAM}$ , we next try to relate  $\gamma_{SAM/PEP} - \gamma_{SAM/dPEP}$  to  $\gamma_{SAM}$  via a simple model.

Dupré showed that  $W_{sl}$ , the work of adhesion at the solid/liquid interface, is related to the surface energies of the solid and liquid,  $\gamma_s$  and  $\gamma_l$ , respectively, and the interfacial energy at the solid/liquid interface,  $\gamma_{sl}$ , via  $W_{sl} = \gamma_s + \gamma_l - \gamma_{sl}$  [16]. Later, Good and Girifalco proposed that  $W_{sl}$  can be approximated by a geometric mean of  $\gamma_s$  and  $\gamma_l$  [17],  $W_{sl} = 2\Phi(\gamma_s\gamma_l)^{0.5}$ , where  $\Phi$  is a correction factor for intermolecular interactions. If the interactions between the solid and liquid are alike,  $\Phi = 1$ . On the other hand, for disparate solid/liquid interfacial interactions,  $\Phi < 1$ . A combination of Dupré's and Good and Girifalco's equations leads to a useful relation that provides the means of estimating  $\gamma_s$ . For the case of thin films of dPEP-rich and PEP-rich phases, respectively, on SAM monolayers, the above treatment yields

$$\gamma_{SAM} + \gamma_{dPEP} - \gamma_{SAM/dPEP} = 2\Phi_{dPEP}(\gamma_{SAM}\gamma_{dPEP})^{0.5}, \quad (2a)$$

$$\gamma_{SAM} + \gamma_{PEP} - \gamma_{SAM/PEP} = 2\Phi_{PEP}(\gamma_{SAM}\gamma_{PEP})^{0.5}. \quad (2b)$$

By subtracting Eq. (2a) from (2b), and assuming that  $\Phi_{dPEP} = \Phi_{PEP} \approx 1$ , we arrive at

$$\begin{aligned} & (\gamma_{PEP} - \gamma_{dPEP}) - (\gamma_{SAM/PEP} - \gamma_{SAM/dPEP}) \\ & = 2\gamma_{SAM}^{0.5}[\gamma_{PEP}^{0.5} - \gamma_{dPEP}^{0.5}]. \end{aligned} \quad (3)$$

As previously discussed, at the three-layer to two-layer transition,  $\gamma_{SAM/PEP} - \gamma_{SAM/dPEP} = \gamma_{PEP/dPEP}$ . The values of  $\gamma_{PEP/dPEP}$  were determined by using the formula proposed by Tang and Freed [18]. This formula reproduces the result of Helfand and Tagami [19] in the limit of infinite molecular weight and has been verified by Shull using self-consistent field calculations [20]:

$$\gamma_{PEP/dPEP} = k_B T a \rho_0 (\chi/6)^{0.5} \left[ 1 - \frac{1.8}{\chi N} - \frac{0.4}{(\chi N)^2} \right]^{1.5}. \quad (4)$$

In Eq. (4),  $k_B$  is Boltzmann's constant,  $T$  is the absolute temperature,  $a$  is the segment length of the polymers,  $\rho_0$  is the monomer number density,  $N$  is the degree of polymerization, and  $\chi$  is the interaction parameter on the coexistence curve between dPEP-rich and PEP-rich phases given by  $\chi = 0.16/T - 4.6 \times 10^{-4}$  [13]. The values of  $\gamma_{PEP/dPEP}$  were generated using  $a = 8 \text{ \AA}$ ,  $\rho_0 = 0.0077 \text{ \AA}^{-3}$ , and  $N = 2280$ .

The symbols in the inset of Fig. 2 denote the values of  $\gamma_{SAM}$  calculated using Eq. (3), based on values of  $\gamma_{PEP/dPEP}$  from Eq. (4), and  $\gamma_{PEP} - \gamma_{dPEP}$  determined from  $\Delta\gamma$ , the values of the surface energy difference between PEP and dPEP as a function of the composition of PEP/dPEP mixtures reported by Norton and co-workers [15]. In the calculations we used  $\gamma_{PEP} = 30.6 \text{ mJ/m}^2$  at  $25 \text{ }^\circ\text{C}$  and  $-d\gamma/dT \approx 0.052 \text{ mJ/m}^2 \text{ K}$  [21]. The error bars denote the uncertainty in the transition values of  $\gamma_{SAM}$  based on the assumption that the values of  $\gamma_{PEP}$  are known to within  $\pm 1 \text{ mJ/m}^2$ . The agreement between the measurement (main part of Fig. 2) and the calculation (inset of Fig. 2) is excellent, particularly at small  $\phi_{PEP,coex}$ . At larger  $\phi_{PEP,coex}$  the small deviations between the measured and calculated  $\gamma_{SAM}$  may be caused by the assumption that  $\Delta\gamma$  does not change with temperature. Although the variation of  $\Delta\gamma$  with temperature is not expected to be large [15], it is evident from Eq. (3) that even a small decrease in  $\Delta\gamma$  and thus  $\gamma_{PEP} - \gamma_{dPEP}$  with increasing temperature could bring the calculated  $\gamma_{SAM}$  closer to the experimental values.

In this Letter we have demonstrated that the ultimate phase morphology in thin polymer films can be controlled by suitably adjusting the polymer/substrate interactions and/or the annealing temperature. This control may be exploited in a number of ways. For example, microcontact printing can be used to fabricate a lateral pattern of compositionally different SAMs on the substrate surface. A phase-separated polymer mixture cast on such surfaces may then produce phase structures that are modulated laterally at one temperature but disappear

at another one. One could also explore the phase morphologies that will form if the temperature is changed from above the three-layer to two-layer transition to below it at various stages in the spinodal decomposition process. It seems likely that interesting new morphologies may result.

This research was supported by the Division of Materials Research, NSF Polymers Program, under Grant No. NSF-DMR92-23099. The use of the Central Facilities of the Cornell Materials Science Center for the ion beam analysis funded by the NSF-DMR-MRSEC program is acknowledged. We are greatly indebted to F. S. Bates (University of Minnesota) for supplying PEP and dPEP, G. Whitesides (Harvard University) for donating HS(CH<sub>2</sub>)<sub>15</sub>COOH, and B. Sauer (DuPont) for providing the values of the surface energy of PEP. J.G. thanks C. Franck (Cornell University) for useful discussions.

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