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Surface Segregation in Polymer Blends of Minimal Difference in the Components Surface Free Energy

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SUMMARY: One of the most remarkable features of polymeric materials is the phenomenon of surface segregation in polymer blends whose components surface energies are similar in magnitude. Herein, we contribute to this field by considering (i) surface phase behavior in *stereochemically asymmetric* polymer blends and (ii) determination of the sign and magnitude of surface energy (γ) difference for a pair of polymers differing only *slightly* in their γ values. Specifically, we present experimental results obtained on the blends of isotactic and syndiotactic poly(methyl methacrylate) (i-PMMA/s-PMMA blends), revealing that the syndiotactic macromolecules segregate to both the polymer–air and polymer–solid (glass) interface, expelling their isotactic counterparts. Also, the contact angle results and their analysis by the use of Lifshitz-van der Waals/acid-base approach are presented for PMMA and polystyrene (PS), which reveal that the surface free energy of PS is 1.5 ± 1.1 mJ/m^2 *higher* than that of PMMA.

Introduction

Surface segregation in polymer blends whose components surface energies are similar in magnitude is one of the most intriguing features of multicomponent polymer systems. Since small molecule mixtures do not segregate under this condition, the phenomenon appears to originate from *micro-structural* factors associated with the large size of polymer chains. Till now, three major factors have been recognized: conformational entropy, packing effects, and cohesive energy. However, the role of each factor in determining surface segregation remains to be a matter of essential controversy and discussion[1-3]. On the experimental side, the progress in this field seems to be hampered by (i) a lack of appropriate model systems and (ii) non-availability of precise data on the components surface energy. The first limitation is due to the fact that, practically, the condition of similar surface energy of components is hard to attain. Actually, the only model system, which has been studied experimentally, is a mixture of linear and branched polyolefins[1,3]. Recently, we proposed a system which may represent a step forward in the search for appropriate models[4]. The idea is to consider a mixture of two tactic forms of the same polymer. Since the stereochemical versions are built with the same

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monomer unit and, thus, chemically identical, the condition of equal surface energy is satisfied. As an example of such *stereochemically asymmetric* polymer blends, we consider mixtures of isotactic and syndiotactic poly(methyl methacrylate) (i-PMMA/s-PMMA blends). The lack of precise data on the γ values of blend components is due to the fact that no direct method of measuring solid surface energy has been found to date. Indirect methods are based on certain assumptions and have certain limitations. Therefore, the comparison of surface energy data for a pair of polymers differing only *slightly* in their γ values requires a great care. We address this problem by considering the sign and magnitude of surface energy difference between PMMA and polystyrene (PS) from contact angle measurements.

Surface Segregation in i-PMMA/s-PMMA Blend Films

The blend films were cast from mixtures of i-PMMA (91% *mm* triads, $M_n = 47 \times 10^3$, $M_w/M_n = 4.24$) and s-PMMA (75% *rr* triads, $M_n = 62 \times 10^3$, $M_w/M_n = 3.37$) in benzene on chromic acid-cleaned glass substrates by slowly evaporating the solvent at 25 °C in a dust-free environment. The residual solvent was removed by drying films on the substrates at 75 °C for 10 h in a clean oven. The films were then scored around the edges and floated onto the surface of double-distilled water, from which they were picked up, blotted with filter paper and stored over desiccant until required. The blend films were in the thickness range 9–12 μm, uniform to within 1 μm over the whole film area (ca. 20 cm^2). The surface composition of the blends was studied by attenuated total reflection Fourier transform (ATR-FTIR) spectroscopy and contact angle measurements.

Table 1. Water contact angles on homopolymer and blend films of i-PMMA and s-PMMA and surface volume fraction of s-PMMA ($\varphi_S^{\text{s-PMMA}}$) derived from these contact angle data.

i-PMMA/s-PMMA	Contact angle		$\varphi_S^{\text{s-PMMA}}$	
	air side	glass side	air side	glass side
0/100	72.2	60.1	–	–
25/75	72.1	60.4	0.99	0.94
50/50	72.6	60.5	1.0	0.92
75/25	69.6	62.3	0.62	0.56
100/0	66.4	65.1	–	–

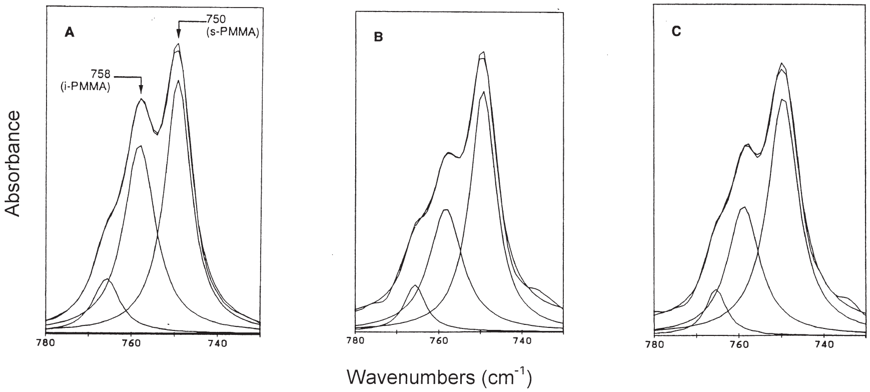

Fig.1: FTIR transmission (A) and ATR-FTIR spectra in the 700-800 cm^{-1} region of 50/50 i-PMMA/s-PMMA blend film. The ATR-FTIR spectra were obtained with the air facing side (B) and glass facing side (C) of the film.

The water contact angles observed on the homopolymer and blend films are listed in Table 1. It can be seen that the s-PMMA film has substantially greater contact angle at the air side as compared to the glass side, while the contact angle on the i-PMMA film is nearly the same on both sides and intermediate between those of s-PMMA film. This effect of the contacting medium and the tacticity of polymer on the water wettability of PMMA has been studied and explained in detail elsewhere[5,6)]. Briefly, s-PMMA macromolecules adopt a highly amphiphilic surface conformation which allows for selective surface exposure of nonpolar or polar functional groups, whereas the conformational structure of i-PMMA does not allow for such a behavior. Consequently, in the film casting process, the syndiotactic polymer minimizes its *interfacial* free energy by exposing the energetically favorable functionality, whereas the isotactic polymer does not. The difference in the wettability of the two tactic forms of PMMA makes it possible to apply contact angle measurements to probe the surface composition of i-PMMA/s-PMMA blends. Thus, for example, the fact that blends consisting 25 and 50% of i-PMMA have the contact angle values practically equal to those of the pure s-PMMA (Table 1) indicates that both the air-side and the glass-side surfaces of these blends are composed almost totally of s-PMMA. From the contact angle results it is possible to estimate the fractional coverage of the blend surface by s-PMMA, $\varphi_S^{\text{s-PMMA}}$, from the Cassie equation. The $\varphi_S^{\text{s-PMMA}}$ values obtained by the use of this approach are listed in Table 1. The data show clearly that all the blends studied surface segregate favoring the syndiotactic component at both surfaces. This finding is supported by the results of ATR-FTIR spectroscopy. As an example, Fig. 1 shows the ATR-FTIR and transmission spectra for the

50/50 blend film. The bands at 750 and 758 cm^{-1} are purely due to the syndiotactic and isotactic components, respectively[6]. It can be seen that, in comparison with the transmission spectrum, the relative intensity of the syndiotactic peak to the isotactic peak is increased in the ATR spectra for both the air-side and the glass-side surface. This indicates that the blend film contains a surface excess of s-PMMA at both surfaces.

As shown elsewhere[4,6], the phenomenon of surface enrichment by the s-PMMA in the solvent-cast i-PMMA/s-PMMA blends is a direct consequence of the high surface activity of s-PMMA and the non-surface-active behavior of i-PMMA described above. The surface segregation of the blends occurs during casting as preferential s-PMMA adsorption at the polymer–air and polymer–glass interfaces. The driving force for segregation is the lowering of *interfacial* free energy that occurs when nonpolar groups of the surface-active polymer concentrate at the polymer–air interface and polar groups concentrate at the polymer–glass interface. The surface-active syndiotactic macromolecules thus segregate both to the air-side and to the glass-side surfaces, expelling their non-surface-active isotactic counterparts. This finding strongly suggests that the difference in the surface activity associated with peculiarities of the individual conformational characteristics of components is an important micro-structural factor of surface segregation in polymer blends – a conclusion that had not previously been available.

While the surface segregation appears to be driven primarily by the difference in the surface activity of the components, it is likely that second-order factors, such as conformational entropy, packing effects, and cohesive energy, also contribute to the segregation process by either counteracting or promoting the tendency of the surface-active component to occupy the surface. This is manifested in the contact angle data (Table 1) displaying the dependence of the surface s-PMMA content on the polarity of contacting medium and on the bulk composition of blend. Elucidation of these secondary effects (which would require a detailed study of concentration profiles as a function of solvent quality and its evaporation rate, annealing conditions, etc.) is beyond the scope of the present paper.

The Sign and Magnitude of Surface Energy Difference between PS and PMMA from Contact Angle Measurements

In recent years, several papers on PS-PMMA block copolymers[7,8] and PS/PMMA blends[9,10] have demonstrated the strong tendency for the PS component to segregate at the polymer–air interface. This has been ascribed to the lower surface energy of PS (γ_{PS}) as compared to that of PMMA (γ_{PMMA}). In order to evaluate precisely the surface energy of these polymers, we employed the measurement of contact angle in conjunction with the Lifshitz-van der Waals/acid-base approach. Unlike previous treatments of contact angle on polar solids, this method appears to describe accurately the hydrogen-bonding interactions at the solid–liquid interfaces and to predict reliable values of the surface energy[11,12)]. The method yields the solid surface energy (γ_{S}) as the sum of the two components, $\gamma_{\mathrm{S}}^{\mathrm{LW}}$ and $\gamma_{\mathrm{S}}^{\mathrm{AB}}$ (i.e., $\gamma_{\mathrm{S}} = \gamma_{\mathrm{S}}^{\mathrm{LW}} + \gamma_{\mathrm{S}}^{\mathrm{AB}}$), associated with Lifshitz-van der Waals (LW) interactions and acid-base interactions (AB) respectively. The component $\gamma_{\mathrm{S}}^{\mathrm{AB}}$ is a combination of the electron-acceptor (γ_{S}^{+}) and the electron-donor (γ_{S}^{-}) parameter of the surface energy: $\gamma_{\mathrm{S}}^{\mathrm{AB}} = 2(\gamma_{\mathrm{S}}^{+}\gamma_{\mathrm{S}}^{-})^{1/2}$. The relationship between the equilibrium contact angle θ and the surface tension components of liquids and solids is given by the modified Young–Dupré equation

$$\gamma_{\mathrm{L}}(1+\cos\theta) = 2\sqrt{\gamma_{\mathrm{S}}^{\mathrm{LW}}\gamma_{\mathrm{L}}^{\mathrm{LW}}} + 2\sqrt{\gamma_{\mathrm{S}}^{+}\gamma_{\mathrm{L}}^{-}} + 2\sqrt{\gamma_{\mathrm{S}}^{-}\gamma_{\mathrm{L}}^{+}} \tag{1}$$

where the subscript "L" denotes the surface energy components and parameters of the test liquids. Thus, from contact angle measurements with three test liquids, the solid surface energy can be determined by solving a system of three equations in the form of eq 1. If the solid surface is monopolar ($\gamma_{\mathrm{S}}^{-} \approx 0$ or $\gamma_{\mathrm{S}}^{+} \approx 0$), measurements with two test liquids suffice to determine the solid surface energy.

Table 2. Surface energy components and parameters (in mJ/m^2) and static contact angles (in deg) for the test liquids on PS and PMMA.

					contact angle	
liquid	γ_{L}	$\gamma_{\mathrm{L}}^{\mathrm{LW}}$	γ_{L}^{+}	γ_{L}^{-}	PS	PMMA
water (**W**)	72.8	21.8	25.5	25.5	80	69
glycerol (**GL**)	64.0	34.0	3.9	57.4	71	67
diiodomethane (**DM**)	50.8	50.8	0.70	0	–[a)]	29
tetrabromoethane (**TBE**)	49.7	49.7	0.75	0	28	25

[a)] Contact angle could not be measured because the solid surface was attacked by the liquid.

The values of the surface energy components and parameters of the test liquids used in this study are listed in Table 2. Given also in Table 2 are the values of contact angles for the test liquids observed on the free (air-side) surfaces of the PMMA and PS films. The values of the total surface energy and its LW and AB components and parameters obtained for the PMMA and PS surfaces are summarized in Table 3. As it can be seen, the average over the four γ_S values is 38.6 (standard deviation ±0.5) and 40.1 (± 0.7) mJ/m^2 for PMMA and PS respectively, i.e., the surface energy of PMMA is 1.5 ± 1.1 mJ/m^2 *lower* than that of PS. The obtained values of γ_{PMMA} and γ_{PS} as well as the sign of surface energy difference do not agree with those reported by van Oss *et al.*[12)] ($\gamma_{PMMA} = 42.7$ and $\gamma_{PS} = 42.0$ mJ/m^2, $\gamma_{PMMA} > \gamma_{PS}$). As shown elsewhere[13)], the reason is that these authors have ignored the weak acidic character of *virtually* apolar halogenated liquids in their treatment of contact angle data and, consequently, overestimated the γ_S^{LW} component of the polymers. The associated systematic error in the γ_S^{LW} value should be substantially higher for PMMA, because the γ_S^- parameter of the PMMA surface is markedly greater than that of the PS surface (Table 3); hence, the erroneous sign of surface energy difference. Our finding leads us to a conclusion that the surface segregation of PS at the free surfaces of PS-PMMA block copolymers and PS/PMMA blends, reported in recent publications[7–10)], cannot be explained on the basis of general surface energy considerations.

Table 3. Surface energy components and parameters (in mJ/m^2) obtained from the contact angle data in Table 2 for the free surfaces of PMMA and PS.

polymer	liquids	γ_S^+	γ_S^-	γ_S^{AB}	γ_S^{LW}	γ_S
PMMA	W–GL–DM	0.00	16.2	0.00	38.6	38.6
	W–GL	0	16.1	0	39.4	39.4
	W–DM	0	16.6	0	38.4	38.4
	GL–DM	0	18.8	0	38.1	38.1
	mean (SD)		16.9 (±1.1)		38.6 (±0.5)	38.6 (±0.5)
PS	W–GL–TBE	0.00	6.5	0.00	40.0	40.0
	W–GL	0	6.5	0	41.2	41.2
	W–TBE	0	6.9	0	39.9	39.9
	GL–TBE	0	8.8	0	39.4	39.4
	mean (SD)		7.2 (±0.9)		40.1 (±0.7)	40.1 (±0.7)

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