

Negative Excess Interfacial Entropy between Free and End-Grafted Chemically Identical Polymers

Günter Reiter and Rajesh Khanna

Institut de Chimie des Surfaces et Interfaces, CNRS, 15, rue Jean Starcky, B.P. 2488, 68057 Mulhouse Cedex, France

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We measured the temperature dependence of the interfacial tension between free melt and end-grafted chemically identical polymers. The excess interfacial entropy (ΔS_{MB}) was found to be extremely small and negative. This is in sharp contrast to the case of liquid surfaces and interfaces between different liquids, where ΔS_{MB} is usually much larger and positive, i.e., molecules at such surfaces and interfaces have a higher degree of freedom than in the bulk. A quantitative comparison with theoretical predictions revealed large differences which we attribute to the finite compressibility of the polymer melt, not yet taken into account by theory.

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Thermodynamic properties of molecules at interfaces determine (among others) adhesion, mixing, and wetting behavior of materials, but may show different characteristics than in the bulk [1–7]. Such differences become especially intriguing when they originate from alterations in entropy only, as is often the case in polymeric systems. Dissimilar polymeric liquids usually do not mix, and form an interface between them. The interfacial tension γ , and similar is valid for their surface tensions, is given as $\gamma = \Delta H - T\Delta S$. ΔH and ΔS represent the difference in enthalpy and entropy (per unit area) before and after contact of the liquids, respectively. The excess interfacial entropy (ΔS) as a function of pressure (P) and temperature (T) is defined as $\Delta S(P, T) \equiv -[\partial\gamma(P, T)/\partial T]$. The enthalpic contribution originates mostly from nonfavorable interactions, e.g., due to dispersion forces at the segment level. Experimentally [8–12], γ as well as the surface tension of pure organic liquids are usually found to decrease with increasing temperature, implying positive values of ΔS . At elevated temperatures, γ may even disappear for weakly incompatible liquids due to the gain in entropy of mixing.

It is also possible to create an interfacial tension between identical molecules. This phenomenon has been termed autophobicity [9], i.e., a liquid drop does not spread out on a surface of the same liquid. Autophobicity may also be found for polymeric liquids [13–18], in particular when polymers are attached to a surface, e.g., by permanently grafting these molecules at one end to the substrate. This limits the number of possible configurations of the polymers. Theoretically [19–22] one expects a reduction of the interfacial entropy rather than an increase when a melt penetrates a grafted polymer layer (= polymer brush). The penetration and the wettability of grafted or adsorbed polymers by the melt of identical molecules are quite important phenomena by themselves in the context of adhesion and friction or the compatibilization of polymer blends using block copolymers. In particular, it is relevant to know if wettability, adhesion, or compatibility

improve (positive ΔS) or get worse (negative ΔS) at elevated temperatures.

For our experiments, we have chosen the polydimethylsiloxane (PDMS) melt-brush system [23]. In contrast to the expectations of early experiments [10], silicone molecules do show autophobic behavior. Details of sample preparation have been presented in [23]. The viscosity of the melt ($M_w = 308\,000$ g/mol) at room temperature was $\eta = 1000$ Pa s. The brush molecules had a molecular weight of 8800 g/mol and were end grafted at a density of 0.44 ± 0.04 nm⁻² onto pretreated silicon wafers which do not allow for adsorption of PDMS [23]. The thicknesses of the melt (between 20 and 500 nm) and the grafted layers (about 6 ± 0.5 nm) were measured by ellipsometry. Temperature (T) was varied with a hot stage directly under an optical microscope. We measured the contact angle (θ) to determine the values of γ .

θ was obtained from the dark rings in Fig. 1 caused by interference of light reflected at the surface of the droplet and at the substrate/droplet interface. The height difference between consecutive rings equals half of the wavelength (λ) of the light used times the refractive index (n) of PDMS. Thus, the distance (r) between the first two rings defines θ : $\tan\theta = \lambda/(2nr)$. Alternatively, θ was determined by measuring the diameter (D) of the droplet and assuming that the drop has a spherical shape. For small θ , the number (m) of rings defines θ : $\theta = 2m\lambda/(2nD)$. Note that at 130 °C, the rings are closer and D is smaller indicating that θ increased. Small deviations from the circular shape can be related to small pinning effects [24]. For a few droplets, we have successfully compared our results for θ obtained from the equations described above with values obtained by using atomic force microscopy (AFM), allowing us to determine the three-dimensional droplet shape with nanometer precision. The precision of both approaches to determine θ is comparable for the small values of the present study.

For real time determination of θ during dewetting [Fig. 1(b)] we used the following equation, based on

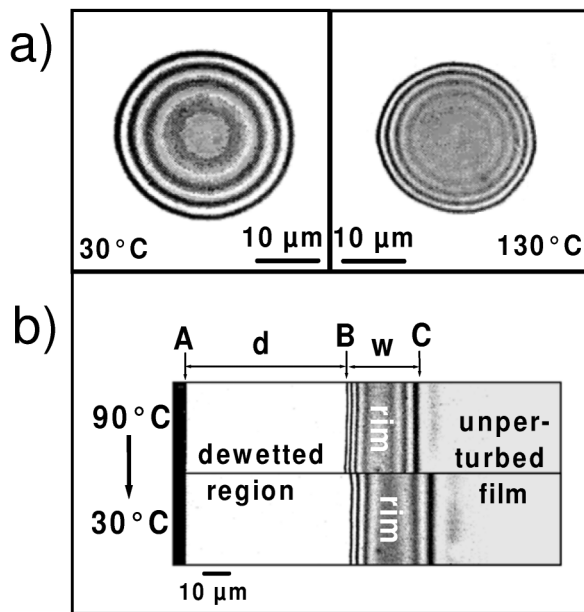


FIG. 1. Typical optical micrographs used for the determination of contact angles (θ) for the studied melt-brush system. (a) Droplet, obtained by dewetting, photographed at 30 and 130 °C, respectively. The change in θ and the interfacial tension (γ_{MB}) between melt and brush after 1 h equilibration at 130 °C are: $\Delta\theta = 2.3 \pm 0.2$ deg and $\Delta\gamma_{MB} = +30 \pm 1.3$ $\mu\text{N}/\text{m}$. (b) Retracting contact line in autophobic dewetting of a 150 nm thick film. Note that during the reduction of the temperature from 90 to 30 °C, which took about 10 min, the dewetted distance (d) did not change much ($\Delta d = 2.1 \pm 0.5$ μm). In contrast, the width of the rim (w) increased significantly ($\Delta w = 4.3 \pm 0.5$ μm). These changes correspond to $\Delta\theta = -1.1 \pm 0.2$ deg and $\Delta\gamma_{MB} = -14 \pm 0.6$ $\mu\text{N}/\text{m}$.

mass conservation [23]: $dh = Cw^2\theta$. Here, d , w , and h are the dewetted distance, the width of the rim, and the thickness of the unperturbed film, respectively. The constant C , accounting for the asymmetric shape of the rim, has been found to be 0.1 [25]. θ was also obtained from the distance (f) between consecutive interference fringes: $\tan\theta = \lambda/(2nf)$. We want to emphasize that the ways we used to determine θ allowed us to detect very small values (in fact, the absolute precision is best at the smallest values) and very small relative changes of $\theta(T)$.

We first looked at small droplets [Fig. 1(a)] resulting from an autophobic dewetting process of a thin film of PDMS on a layer of end-grafted PDMS molecules [23]. In a second set of experiments we also measured θ in real time during the retraction of this film [Fig. 1(b)]. In both cases, we observed an increase of θ when we increased T as can be clearly seen, either via the spacing of the interference fringes (a smaller spacing reflects higher contact angle) or via the width of the rim or the diameter of the drop which both decrease with increasing T .

Quantitatively, we present the changes of $\theta(T)$ for two samples (drop A and drops B and C, respectively) selected from a set of about 20 independent experiments in Fig. 2,

both for increasing and decreasing T . Two important features have to be noticed. First, $\theta(T)$ increased about linearly, and second, we observed contact angle hysteresis. The latter has to be attributed to small heterogeneities of the grafting density of the brush leading to small variations in the interfacial tension which, in turn, may lead to pinning of the contact line [24]. Such pinning effects were probably also responsible for the fluctuations of θ around mean values given by the dotted lines. Our experiments suggest that the contact line had to move over heterogeneities differing by at maximum up to 15 $\mu\text{N}/\text{m}$, a small pinning force (per unit length) indeed.

From $\theta(T)$ we determined the interfacial tension $\gamma_{MB}(T)$ between the melt and the brush for different temperatures using the following relation (based on Young's equation and assuming that the melt and the brush have about the same surface tension [8,19]):

$$\gamma_{MB}(T) = \gamma_{LV}(T)[1 - \cos\theta(T)]. \quad (1)$$

For the temperature dependence of the surface tension of the melt (γ_{LV}) we used the results found by Sauer and Dee [8]: $\gamma_{LV} = C_1 + C_2T$ with $C_1 = 22.05$ mN/m and $C_2 = -60$ $\mu\text{N}/\text{m}^\circ\text{C}$.

For the increasing temperature direction we found, based on a linear regression: $\gamma_{MB}(T) = C_3 + C_4T$ with $C_3 = 73 \pm 4$ $\mu\text{N}/\text{m}$, $C_4 = 0.47 \pm 0.05$ $\mu\text{N}/\text{m}^\circ\text{C}$ for droplet A and $C_3 = 90 \pm 3$ $\mu\text{N}/\text{m}$, $C_4 = 0.40 \pm 0.03$ $\mu\text{N}/\text{m}^\circ\text{C}$ for droplets B and C, respectively. Although the values for C_3 are different in the decreasing temperature direction due to hysteresis, the values for C_4 are almost identical.

Within experimental uncertainties due to contact angle hysteresis and systematic errors in the contact angle measurements, all our experiments indicate that, extrapolating our results to lower temperatures, γ_{MB} tends to zero at absolute zero temperature. Noting that $C_4 = -\Delta S_{MB}$, $C_3(T = -273^\circ\text{C}) \approx 0$ N/m implies that the interfacial tension is of purely entropic origin, corroborating that the pretreated wafers do not allow for enthalpic interactions (e.g., adsorption).

The excess surface entropy ΔS_{surf} of PDMS was found to be positive and of the order of +60 $\mu\text{N}/\text{m}^\circ\text{C}$ [8]. Here, for the excess interfacial entropy ΔS_{MB} between PDMS brush and PDMS melt, we found a value about 2 orders of magnitude lower. Furthermore, and even more importantly, the value of ΔS_{MB} was *negative*, meaning that from the entropy point of view it is better to keep melt and brush separated than to bring them in contact, although both consist of chemically identical molecules.

We also checked that our observations hold for moving contact lines. In Fig. 3 we show the temporal (t) evolution of $d(T, t)$, $\theta(T, t)$, and $\gamma_{MB}(T, t)$ during the retraction of the film shown in Fig. 1(b). Qualitatively and even quantitatively we observe the same behavior for γ_{MB} as in Fig. 2. Pinning effects become highly visible when the contact line moved only slowly at lower temperatures and

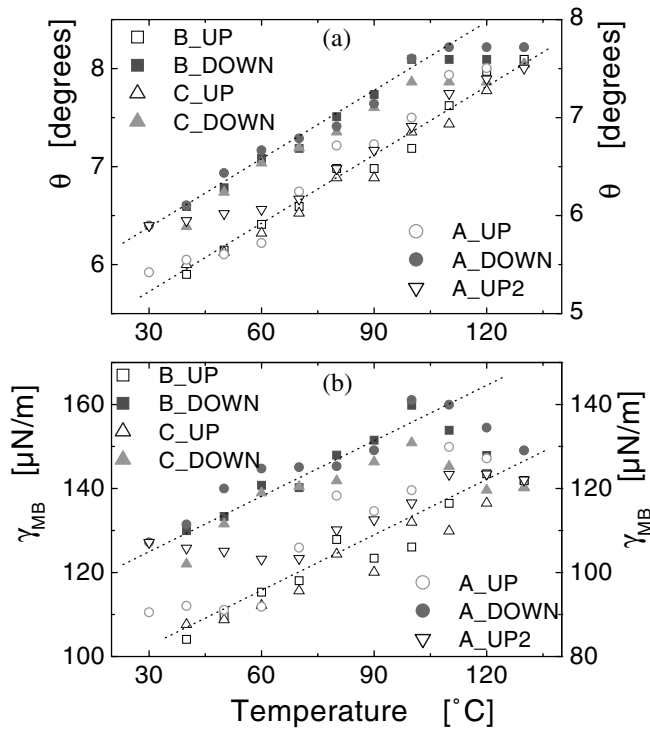


FIG. 2. Influence of temperature (T) on contact angle (θ) and interfacial tension (γ_{MB}) for three (A, B, C) PDMS droplets with diameters between 20 and 50 μm residing on PDMS brushes. (a) θ and (b) γ_{MB} as a function of increasing (open symbols) and decreasing (full symbols) T . The droplets were equilibrated at each temperature until no further changes could be detected. Usually this took about 5 min. Because of slight differences in the absolute values, we had to use different y axis (left axis for droplets B and C). The dotted lines serve as guides to the eye. Note the pronounced hysteresis and the fluctuations around the dotted lines, which we attribute to contact line pinning.

later times. It is certainly worth mentioning that systematic dewetting experiments [23] showed that the melt is slipping on the brush during the dewetting process. Thus, we do not expect a difference between dynamic and static contact angles [25], as verified in our experiments [23].

We now attempt to interpret our results in the framework of the theoretical description of the autophobic behavior of a polymer melt-brush system [19–22]. The interfacial tension between the brush and the melt can be determined as (assuming incompressibility of the liquids)

$$\gamma_{MB}(T) = \frac{3}{8} \frac{kT}{\zeta a} = -T\Delta S_{MB}. \quad (2)$$

Here, k is the Boltzmann constant, a ($= 0.5$ nm) is the statistical size of a polymer segment [23], and ζ is the interpenetration depth given by

$$\zeta \sim \frac{3}{8} \frac{k}{\Delta S_{MB} a} \sim \frac{1}{2} (Na\Sigma)^{1/3}. \quad (3)$$

Here, N gives the number of segments of the grafted polymer and Σ^{-1} is the number of polymers grafted per unit area. From Eq. (3) and the measured values of

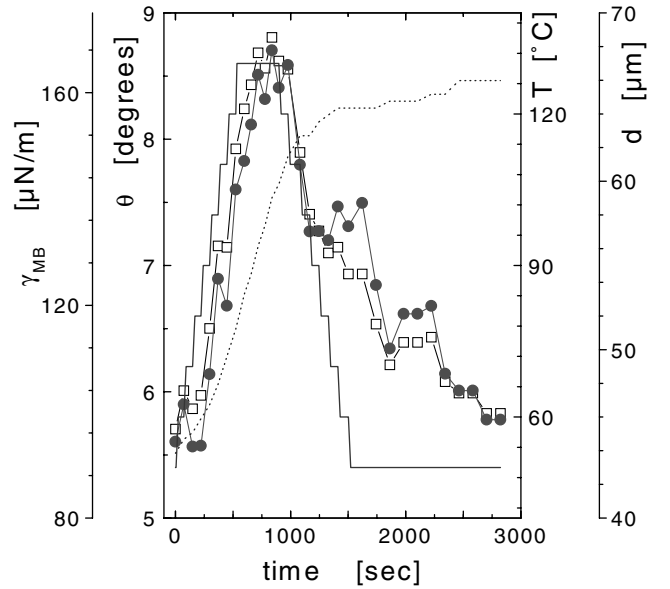


FIG. 3. Influence of temperature (T) on contact angle (θ) and interfacial tension (γ_{MB}) during autophobic dewetting of a 150 nm PDMS film on a PDMS brush. The variation of T and the dewetted distance (d), θ , and γ_{MB} are represented by the full and dotted lines, and filled and open symbols, respectively. Note that contact-line pinning (expressed by fluctuations in γ_{MB}) was more pronounced for low dewetting velocities at times >1000 sec.

$\Delta S_{MB} = -0.4 \mu\text{N/m}^\circ\text{C}$ we obtain $\zeta \sim 25$ nm. This value is about $4\times$ the thickness of the grafted monolayer. Consequently, theory predicts that the system is *not* autophobic for such small values of ΔS_{MB} , opposite to our observations. From complementary experiments [23] we know that the melt penetrates only about 1 nm into the brush. According to Eqs. (2) and (3), theory expects for $\zeta \sim 1$ nm the following values at room temperature: $\gamma_{MB} \sim 3$ mN/m and $\Delta S_{MB} \sim -10 \mu\text{N/m}^\circ\text{C}$. As a possible source for a lowering of the absolute value of ΔS_{MB} we propose that thermal expansion, reflecting the finite compressibility of a polymer melt, has to be taken into account in Eqs. (2) and (3). Theory does not yet include such a positive contribution to ΔS_{MB} resulting from the lower density and, consequently, larger number of possible configurations of the polymer chains at higher temperatures. We note that previous experiments [13,14,17,18] have focused on the N and Σ dependence of ζ and not on the T dependence. Because of the $\frac{1}{3}$ power [see Eq. (3)], such measurements lack sensitivity. Consequently, deviations from theoretical predictions are small and could erroneously be attributed to inaccuracies in the determination of, e.g., Σ .

Our experiments proved that the autophobic effect in our melt-brush system is of entropic origin and becomes more pronounced with increasing temperature. No enthalpic contributions could be detected, as expected from theory and implicitly assumed in the interpretation of previous experiments. Most importantly, however, we demonstrated

that theoretical treatments to date are *not* able to describe the experimental results quantitatively.

As a general conclusion we note that γ for two chemically different species in contact can exhibit two opposing trends as a function of temperature. On the one hand, where enthalpic factors dominate we expect a diminution of γ . If entropy controls the behavior, then we may even observe the opposite trend. However, such is possible only if an additional parameter comes into play. This may be the interaction with a substrate or the chemical connection of two different molecules as in block copolymers. If enthalpic and entropic contributions are present, e.g., a polymer on top of a brush of a weakly incompatible polymer or in block copolymer melts, we thus can expect the superposition of an enthalpy-caused decrease and an entropy-caused increase of γ with T . This can lead to phenomena such as a transition from partial wetting to wetting and back to partial wetting or the transition from a disordered to an ordered to again a disordered phase [26] as temperature is increased.

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