

## Autophobic Behavior of Polymers at the Melt–Elastomer Interface

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Received April 12, 1999; Revised Manuscript Received July 21, 1999

**ABSTRACT:** The wetting behavior at the interface of athermal polymer–elastomer couples was investigated experimentally. Using end-linked poly(dimethylsiloxane) (PDMS) elastomers as model substrates and PDMS liquids of different molecular weights, we observed a crossover from complete to partial wetting. This behavior is analogous to the phenomenon of “wetting autophobicity” at the interface between polymer melts and polymer brushes and may originate from entropic effects. The shape of the substrate at the autophobic regime was profiled by optical phase interference microscopy and found to be undistorted, unlike the theoretical predictions. We suggest that the steady-state configuration of the melt–elastomer interface may be that of “pseudo partial wetting”.

### Introduction

Wetting properties of soft, elastomeric surfaces are affected by their ability to deform under the moderate action of interfacial forces and by their permeability to liquids. The resulting interfacial behavior has important practical implications in applications ranging from adhesives and synthetic membranes<sup>1</sup> to biocompatible implants and more.

An elastomer may be formed by chemically cross-linking a polymer melt. Model networks result from end-linking of chains, leading to the formation of a network or a “rubber” with well-defined molecular weight between cross-link points.

The wetting behavior of elastomers was investigated by Carre and Shanahan.<sup>2</sup> In particular, they described the response of soft solids to the action of the surface tension at the solid–liquid–vapor (SLV) contact line. Recently, Leibler et al.<sup>3</sup> pointed out the analogy between the wetting behavior of elastomers and densely tethered polymer brushes. In particular, they suggested that *wetting autophobicity*, which is the term used to describe incomplete wetting of a substrate by a chemically identical liquid, may be observed at the interface between an elastomer and a polymer melt due to entropic interactions.

Wetting autophobity at the interface between a densely tethered polymer brush and an athermal liquid (defined by the value of the Flory interaction parameter,  $\chi = 0$ ), as a function of the molecular weight of the liquid, was described by Leibler et al.<sup>4</sup> and later by Shull.<sup>5,6</sup> They suggested that the onset of a positive interfacial tension at the substrate–melt couples is a manifestation of two opposing tendencies: melt chains (of polymerization index  $P$ ) tend to penetrate into the grafted layer in order to gain transitional entropy, while the brush (or elastomer) chains (of polymerization index  $N$ ) oppose the penetration which results in their swelling and consequential loss of conformational (elastic) entropy due to stretching. At equilibrium, very short chains ( $P \ll N$ ) are expected to fully penetrate into the brush, leading to complete wetting, while long chains ( $P \gg N$ ) only penetrate to a typical depth  $\lambda$ .  $\lambda$  provides a measure of the melt–brush interfacial depth and is related to the brush–melt interfacial tension  $\gamma_{bm} \propto kT/(\lambda a)$ , where  $kT$  is the thermal energy and  $a$  is a

molecular length scale, typically some angstroms.<sup>4</sup> Wetting autophobicity is observed in the regime of  $\gamma_{bm} > 0$ .

Several experimental observations of wetting autophobicity at the brush–melt interface were reported in the past few years,<sup>8–11</sup> most of them in good agreement with the theoretical predictions. Recently Kerle et al.<sup>10,11</sup> described the observation of a related phenomenon: dewetting of thin films of a polymer melt on top of a cross-linked network of the very same polymer. They found that the delicate balance of entropic interactions is modified by surface roughness, leading to an unexpected reentrant wetting transition.

Leibler et al.<sup>4</sup> also predicted the interfacial profile at the autophobic regime. They suggested that a droplet of a partially wetting polymer melt will lead to an elastic deformation of the substrate at the SLV contact line, due to the action of the vertical component of the melt interfacial tension,  $f_0 = \gamma_{lv} \sin \theta$ . The distortion is expected to scale as  $f_0/\mu_0$ , where  $\mu_0$  is the bulk shear modulus of the tethered chains, in a manner similar to that of chemically *incompatible* droplet and a deformable elastomer.<sup>12</sup>

To our knowledge, the profile of the contact line at the interface of athermal couples, such as the elastomer–melt interface, was not measured before. We suggest that the equilibrium profile in this case may differ from that of chemically incompatible couples: as the entropic penalty of bulk deformation is comparable to the entropic penalty of (elastic) surface deformation, the delicate balance of entropy may lead to an equilibrium shape, in which both bulk and surface deformations are minimized.

In the following we report a study of the wetting behavior of thin films of polymer melts on top of a cross-linked polymeric substrate of similar chemical composition (an athermal system). We investigate the wetting transition as a function of the melt molecular weight, for two PDMS substrates of similar values of surface energy and roughness, which differ by the average molecular weight between cross-links and the resulting shear modulus. Thus, we are able to focus on the role of molecular weight in determining the wetting behavior at the elastomer–melt interface and examine the validity of “brush” models to the description of wetting behavior of elastomers.

Special attention is given to the investigation of the shape of the elastomer surface at the autophobic regime, as a function of the substrate shear modulus (characterized by JKR-type experiments) and the permeability of the liquid (measured by the degree of swelling). We use a nonperturbative technique, optical phase interference microscopy (OPIM), for 3-dimensional imaging of the surface profile. We find that the shape of the droplet–substrate contact line differs from that predicted by theory.<sup>4</sup>

## Experimental Section

**1. Materials.** Vinyl-terminated poly(dimethylsiloxane) (PDMS) of two molecular weights, 5530 and 11 400 g/mol, were purchased from United Chemical Technologies Inc., Bristol, PA. Monodisperse (polydispersity index  $M_w/M_n \leq 1.1$ ) PDMS melts of molecular weights 700 g/mol (designated PDMS 0.7K), 2400 g/mol (PDMS 2.4K), 6000 g/mol (PDMS 6K), 11 000 g/mol (PDMS 11K), and 31 500 (PDMS 31K) were purchased from Polymer Source Inc., Canada. PDMS of  $M_w$  49 000 (PDMS 49K) and  $M_w/M_n$  of 1.1 was purchased from American Polymer Standards Corp. The glass transition temperature of PDMS is  $T_g = -123$  °C.

**2. Sample Preparation.** Model networks were formed by end-linking in the bulk, vinyl-terminated PDMS chains with tetrafunctional silane cross-linker, in the presence of Pt catalyst, at a stoichiometric ratio, following the procedure described by Gottlieb and co-workers.<sup>13,14</sup> Samples for wetting experiments were of typical dimensions  $0.5 \times 0.5 \times 1$  cm<sup>3</sup>. Wetting experiments were performed by placing microdroplets (a diameter of 20–150  $\mu\text{m}$ ) of PDMS liquids on top of the cross-linked PDMS matrix and, for all molecular weights, also by spin casting directly from the melt, on different substrates, thin layers in the thickness range 0.5–1  $\mu\text{m}$ . The contact angles measured in the first set of experiments are known as “advancing angles” while those measured after dewetting of the spin-cast films exhibit “receding angles”. The wetting behavior of the different series was monitored for 2–3 weeks at room temperature ( $23 \pm 1$  °C) by optical microscopy and OPIM.

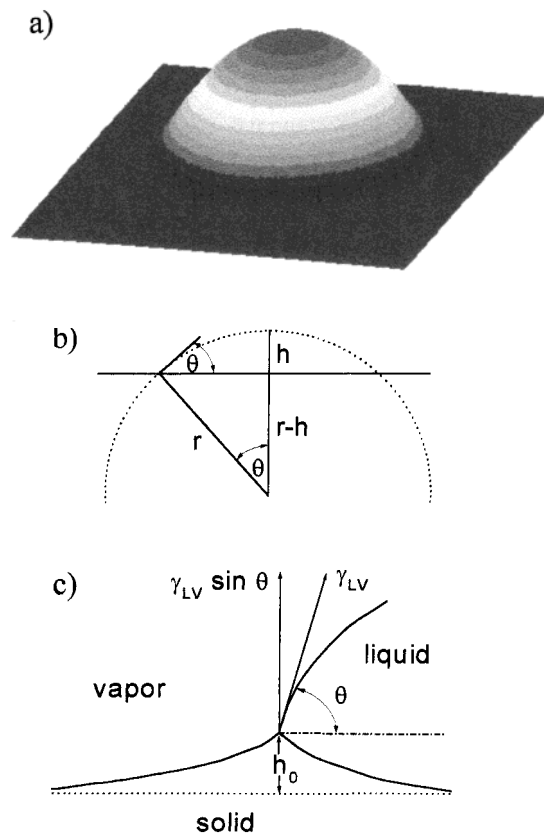
In one set of experiments the elastomers were extracted prior to their use in wetting experiments: the elastomers were immersed in heptane, a good solvent for the PDMS, for 3 weeks, drawn out of the liquid, and dried under vacuum for about 2 days.

Spherical caps for JKR measurements were prepared by depositing the standard reaction mixture on fluorinated glass slides. (The glass slides were coated by 1H,1H,2H,2H-perfluorodecyltrichlorosilane (16584) by Lancaster Synthesis, England.)

**3. Characterization Methods. 3.1. Light Microscopy.** Light microscopy in the reflectance mode (Zeiss, SV11, coupled to a CCD camera) was used to monitor the samples, under ambient conditions.

**3.2. Optical Phase Interference Microscopy (OPIM).** Scanning white-light interference microscopy (OPIM, New View 200, Zygo) was used for profiling surfaces. In this technique the sample surface is scanned along the perpendicular axis, while a CCD camera is monitoring the generated interference patterns. A computerized algorithm (“frequency domain analysis”) is used for transforming the information into a quantitative 3-D image. The technique offers a subnanometer resolution in the vertical direction combined with a lateral resolution and a field of view which depend on the optical setup. In our apparatus the lateral resolution is of 0.64  $\mu\text{m}$ , and the largest field of view is of  $280 \times 220$   $\mu\text{m}^2$ .

In this study we used the technique for profiling surfaces and for measuring contact angles of microdroplets. In Figure 1 we present a three-dimensional OPIM image of a liquid droplet (a) and an analysis of the contact angle formed by the droplet on top of a rigid, nondeformable substrate (b) and a soft deformable substrate (c).



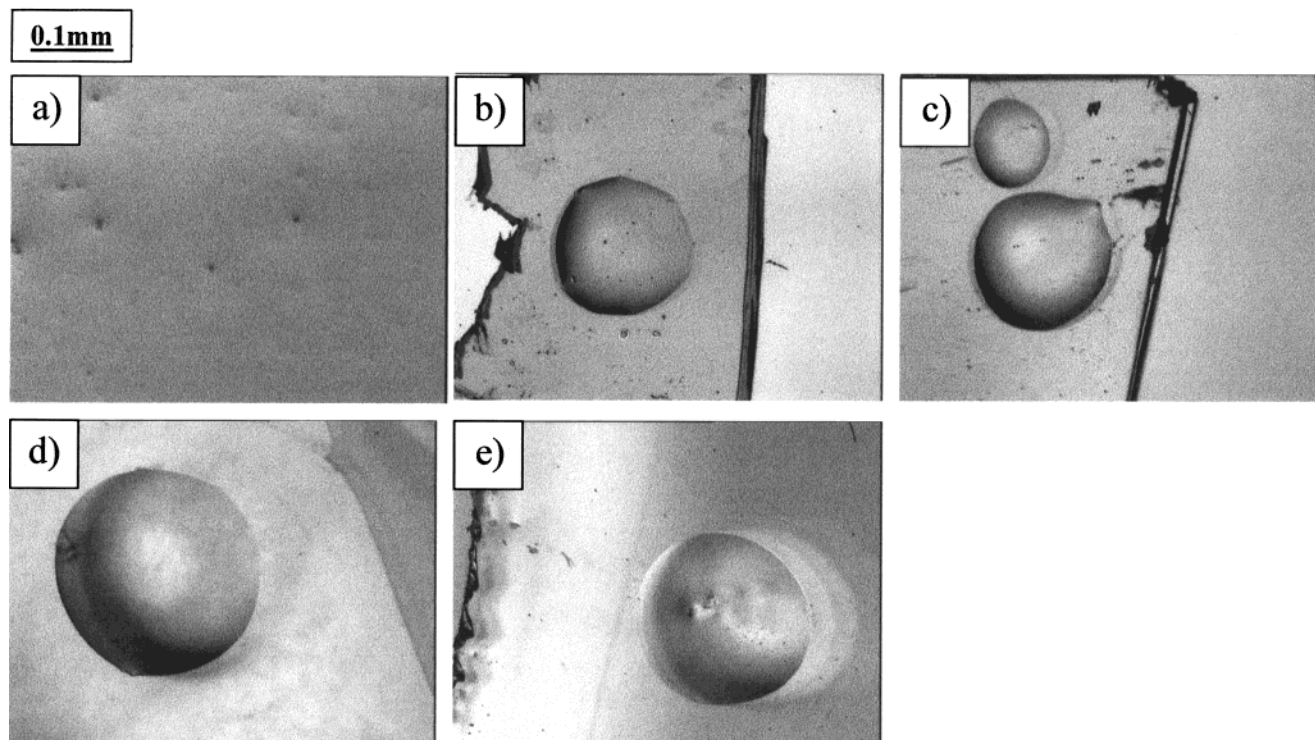
**Figure 1.** An OPIM image and analysis of liquid droplets. (a) A liquid droplet on top of a rigid, nondeformable substrate. The diameter of the droplet is  $120 \pm 5$   $\mu\text{m}$ , and the height is 4  $\mu\text{m}$ . (b) For a nondeformable substrate the contact angle is calculated from the ratio between the radius of the droplet ( $r$ ) and the height of the droplet ( $h$ ) following the geometrical relation  $\cos \theta = 1 - h/r$ . (c) In the case of a soft substrate the vertical component of the liquid vapor surface tension,  $\gamma_{LV} \sin \theta$ , may lead to local deformation of the substrate. The vertical displacement is characterized by the maximal height,  $h_0$ , measured from the undeformed baseline.

**3.3. JKR-Type Measurements.** The elastic modulus  $K$  and the intrinsic surface energy  $\gamma$  (calculated from the reversible work of adhesion  $W$ , via the relation  $W = 2\gamma$ ) of the cross-linked networks were determined by JKR-type measurements.<sup>15</sup> The experiments were carried out in the laboratory of Prof. M. Tirrell at the University of Minnesota. In the experimental setup,<sup>16</sup> using a sphere–sphere geometry, a given displacement is imposed on a spherical cap of cross-linked PDMS (of undeformed radius  $R_1$ ), in contact with another cap ( $R_2$ ). In a typical experiment<sup>17</sup> both the load ( $P$ ) and the contact radius of the spheres ( $a$ ) are monitored during a loading and unloading sequence and analyzed according to the JKR equation<sup>15</sup> (where  $R$  is the geometric mean radius of curvature of the two lenses)

$$a^3 = (R/K)\{P + 3\pi RW\sqrt{6\pi RWP + (3\pi RW)^2}\} \quad (1)$$

The bulk elastic modulus measured by the JKR experiments is related to the Young modulus,  $E$ , by the relation  $K = 2E/3(1 - \nu^2)$  where  $\nu$  is the Poisson ratio. For an incompressible elastomer, the static shear modulus,  $\mu_0$ , is  $1/3E$ , the Poisson ratio is  $1/2$ , and  $K = 4\mu_0$ .<sup>18</sup>

**3.4. Atomic Force Microscopy (AFM).** The surface roughness was characterized by AFM. The measurements were performed by a Topometrix TMX2010 Discoverer system with etched silicon tips on cantilever (Nanoserver) of spring constant  $k$  ranging between 0.1 and 0.3 N/m and a tip size of 15 nm (as specified by the manufacturer).



**Figure 2.** Optical micrographs of PDMS films, spin-coated on top of a cross-linked PDMS network (PDMS 5530), following 5–7 days incubation at room temperature ( $23 \pm 1$  °C). Initial film thickness is in the range of  $1 \mu\text{m}$ . (a) to (e) present PDMS films of different molecular weights. (a) A thin PDMS 0.7K is stable and does not evolve with time. Thin films of PDMS 6K (b), 11K (c), 31K (d), and 49K (e) dewet into droplets on top of the cross-linked PDMS substrate.

**3.5. Swelling Experiments.** Swelling experiments were performed by immersion of a small volume ( $0.5 \text{ cm}^3$ ) of the PDMS elastomers in PDMS melts, of different molecular weights, for a month, at room temperature. The networks were weighted prior to immersion in the liquid, and after being drawn from the liquid, following the removal of excess liquid.

## Results

**1. Wetting Behavior.** In Figure 2 we present optical micrographs of five different samples, formed by spin-coating substrates of the cross-linked PDMS 5530 elastomer by PDMS melts of different molecular weight. The pictures were taken after equilibration at room temperature for a few days: (a) PDMS 0.7K, (b) PDMS 6K, (c) PDMS 11K, (d) PDMS 31K, and (e) PDMS 49K. We observe that PDMS 0.7K completely wets the elastomer, forming a homogeneous thin film with no distinguishable features. Thin films of the higher molecular weight PDMS liquids are observed to dewet into droplets of a finite contact angle, on top of the elastomer. Microdroplets that were laid on top of the elastomer showed similar behavior: while the PDMS 0.7K spread spontaneously on the substrate, droplets of the higher molecular weight equilibrated into a finite contact angle.

The wetting behavior at the interface of the cross-linked PDMS 11 400 is presented in Figure 3. Five different samples, all made of cross-linked PDMS 11 400, were prepared by spin-coating the elastomer by a thin film of PDMS melt of a specific molecular weight: (a) PDMS 0.7K, (b) PDMS 6K, (c) PDMS 11K, (d) PDMS 31K, and (e) PDMS 49K. We observed that in this case both PDMS 0.7K and PDMS 6K form stable films while the higher molecular weight melts dewet. Again, pre-laid microdroplets exhibited a similar behavior: the PDMS 0.7K and PDMS 6K spread, while droplets of the higher molecular weights melts formed finite contact angles.

**Table 1. Bulk and Surface Characteristics of the Cross-Linked PDMS Elastomers**

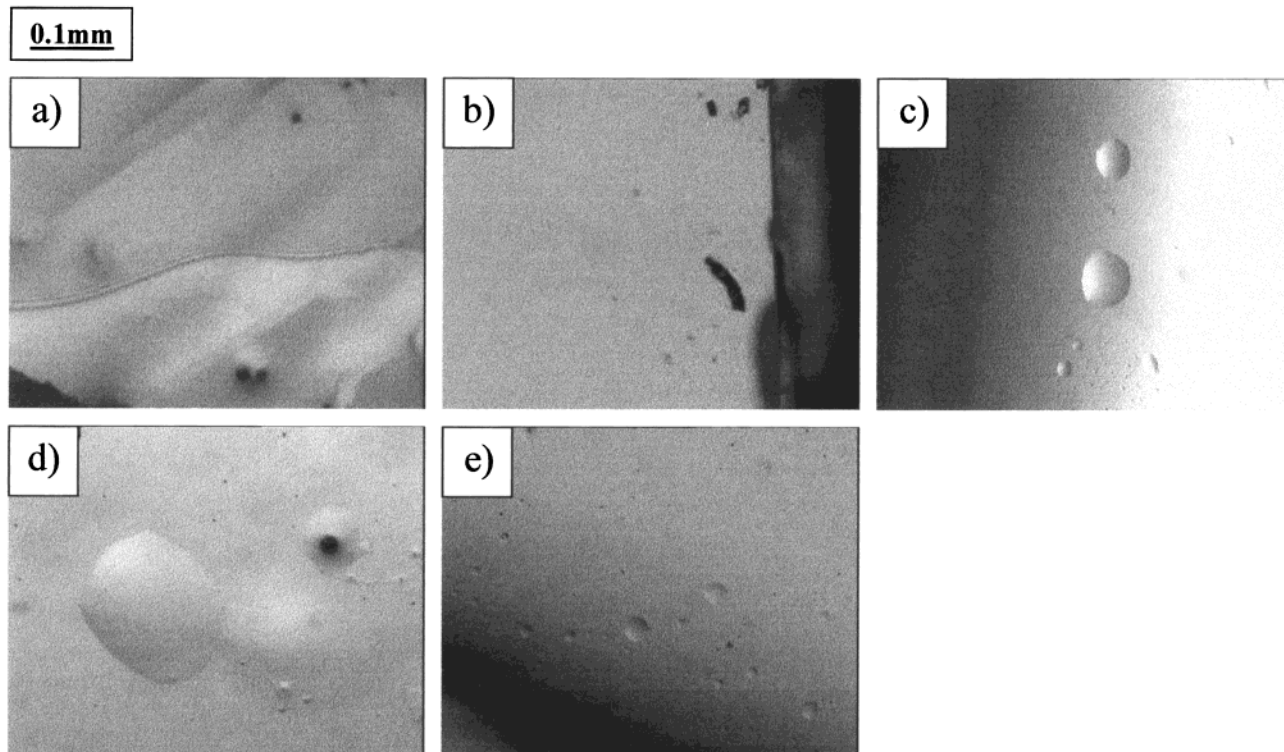
	bulk elastic modulus $K$ (MPa) measured by JKR	surface energy (dyn/cm) $\gamma = W^{1/2}$ measured by JKR	rms roughness (nm) measured by AFM (over area of $5 \mu\text{m}^2$ )
cross-linked PDMS 5530	$1.8 \pm 0.05$	$22 \pm 2$	2
cross-linked PDMS 11 400	$0.9 \pm 0.05$	$22 \pm 2$	2

**2. Roughness, Elastic Modulus, and Surface Energy of the Elastomers.** The bulk elastic modulus of the elastomers and the surface energy as measured by JKR-type experiments and the root-mean-square (rms) roughness of the surface as characterized by AFM are summarized in Table 1.

We observe that the two types of cross-linked elastomers differ in their bulk properties while having similar surface characteristics: the bulk and shear elastic modulus of PDMS 5530 is about twice as high as that of the PDMS 11 400, while the rms roughness of both networks is of a similar value of less than  $\approx 2$  nm and their surface energy is  $\gamma \approx 22$  dyn/cm.

**3. Swelling Experiments.** We measured the degree of swelling of the cross-linked networks, in PDMS melts of different molecular weight. We summarize the results in Table 2. Our findings suggest that the degree of swelling, and the related permeability of the network toward the melt, strongly depends on the ratio between the inter-cross-link molecular weight and the melt molecular weight: both matrices are highly swollen by the oligomeric PDMS (PDMS 0.7K and PDMS 2.4K) and are almost impermeable to the high molecular weight PDMS 49K. The degree of swelling by melts of intermediate molecular weights depends on the elastomer





**Figure 3.** Optical micrographs of PDMS films, spin-coated on top of a cross-linked PDMS network (PDMS 11 400), following 5–7 days incubation at room temperature ( $23 \pm 1$  °C). Initial film thickness is in the range of  $1 \mu\text{m}$ . (a) to (e) present PDMS films of different molecular weights. (a, b) Thin films of PDMS 700 and 6K are stable and do not evolve with time. Thin films of (c) PDMS 11K, (d) 31K, and (e) 49K dewet into droplets on top of the cross-linked PDMS substrate.

**Table 2. Degree of Swelling (vol %) of Cross-Linked PDMS in PDMS Melts**

	PDMS 0.7K	PDMS 2.4K	PDMS 6K	PDMS 11K	PDMS 30K	PDMS 49K
cross-linked PDMS 5530	200	161	30	17	7	5
cross-linked PDMS 11 400	275	200	47	8	6	3

**Table 3. Contact Angles (deg) of Dewetted PDMS Droplets (Receding Angles) on Top of Cross-Linked PDMS Substrates**

	PDMS 0.7K	PDMS 6K	PDMS 11K	PDMS 31K	PDMS 49K
cross-linked PDMS 5530	wetting	$\theta = 10.5 \pm 0.5$	$\theta = 11 \pm 0.5$	$\theta = 11 \pm 0.5$	$\theta = 10 \pm 0.5$
cross-linked PDMS 11 400	wetting	wetting	$\theta = 4 \pm 0.5$	$\theta = 4 \pm 0.5$	$\theta = 6.2 \pm 0.5$

and decays with the melt molecular weight. These results are in agreement with the theoretical predictions of the interaction between athermal melts and polymeric elastomers.<sup>19</sup>

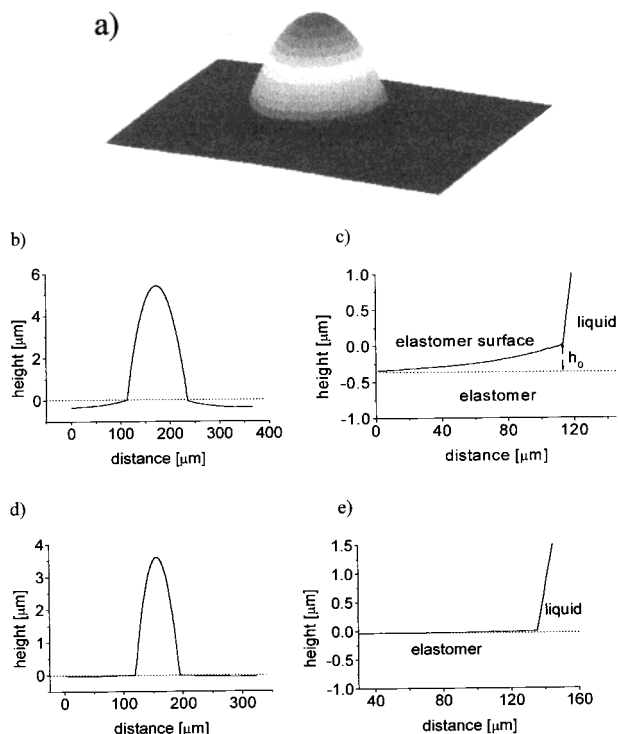
**4. Contact Angles and Surface Profiling.** OPIM was used for determination of the contact angles of both the dewetted droplets and the pre-laid microdroplets. In Table 3 we summarize the contact angle values of the dewetted samples (“receding angles”). Similar measurements of the pre-laid microdroplets (“advancing angles”) yielded values comparable (within the experimental error) to those presented in Table 3.

We observed that the volume of laid droplets decreased with time: a fast initial decrease in volume over a period of days was followed by a very slow decrease over weeks. We note that the PDMS liquids used in this study are nonvolatile.<sup>20</sup>

Using OPIM we profiled the interface. We found that the shape of the elastomer surface, especially at the vicinity of the SLV contact line, depends strongly on annealing time: freshly laid droplets, as well as dewetted droplets measured less than 2 days after formation, are observed to induce deformation of the substrate at the contact line. In Figure 4a,b we present an OPIM scan and a height–distance cut through a fresh droplet

of PDMS 11K on top of the cross-linked PDMS 5530. The maximal height of the distortion,  $h_0$ , is found to be (Figure 4c)  $0.34 \mu\text{m}$ ; the vertical displacement decays to about half its maximal value after a distance of  $28 \mu\text{m}$ . A calculation based on the theoretical predictions<sup>12</sup> gives  $h_0 \approx 0.55 \mu\text{m}$  and a decay length of  $40 \mu\text{m}$  for  $\gamma = 22 \text{ dyn/cm}$ ,  $\theta = 10.5^\circ$ , and  $\mu_0 \approx 7.2 \text{ MPa}$ . After 4 days of annealing at room temperature we observe that the profile of the substrate at the vicinity of the droplet has changed dramatically (Figure 4d,e): the deformation has vanished, and the surface profile corresponds to that observed on a nondeformable substrate. The contact angle of the droplet has not changed (within the experimental scatter). Similar behavior was observed for droplets of the different PDMS melts: typical values of  $h_0 \approx 0.3\text{--}0.5 \mu\text{m}$  and a decay length in the range  $20\text{--}50 \mu\text{m}$  were measured for fresh droplets of the different  $M_w$  melts. For each of the samples, the deformation disappeared after a few days of annealing, and a nondeformed surface in contact with a liquid droplet was observed.

We also followed the wetting behavior of the other elastomer, PDMS 11 400, in contact with PDMS melts of the different molecular weights. We found that the initial distortion relaxed after a few days of annealing



**Figure 4.** OPIM images of liquid PDMS 11K droplet on top of cross-linked PDMS 5530 substrate: (a) a three-dimensional image of a fresh droplet, (b) a height–distance cut through the droplet and the cross-linked PDMS substrate, (c) a magnified view of the contact line showing a distortion with a height of  $h_0 = 0.34 \mu\text{m}$  and a decay distance of  $28 \mu\text{m}$ . The measured contact angle is  $10 \pm 0.5^\circ$ . (d) The same droplet following 4 days of annealing at room temperature: the volume of the droplet has decreased, while the contact angle did not change significantly ( $11 \pm 0.5^\circ$ ). (e) A magnified view of the contact line shows a nondistorted surface.

at room temperature and that the typical height of the initial distortion was  $h_0 \approx 1 \pm 0.2 \mu\text{m}$  with a decay length of  $60 \pm 20 \mu\text{m}$  independent of the molecular weights of the liquid droplets.

In a different set of experiments we used the cross-linked networks that were extracted prior to the wetting experiments. When fresh droplets of nonwetting melt were laid upon the matrix, the substrate was distorted, as in the case of the unextracted networks. Upon annealing at room temperature, the deformation disappeared. We explain the significance of that observation in the discussion.

## Discussion

In the study presented here we characterized the wetting behavior of cross-linked polymeric networks in contact with polymer melts of a similar chemical composition. We investigated the different regimes of complete and partial wetting as a function of the melt and matrix molecular weight and profiled the shape of the interface in the regime of incomplete wetting. The central finding of this work is related to the shape of the substrate at the autophobic regime: we find that the profile of the elastomer at the vicinity of a melt droplet is flat and undeformed (once a steady state is reached), unlike the theoretical predictions.<sup>3,4</sup> The transition from a distorted to a flat surface profile provides, we believe, an insight into the dewetting process and the final configuration of the dewetted liquid. We come back to this point after discussing the significance of the observed transition from complete to partial wetting.

The substrates used by us were end-linked PDMS elastomers of two different molecular weights. The cross-linking procedure results in the formation of elastomers that differ by the inter-*cross*-link molecular weight and the consequential values of the bulk elastic modulus but have similar values of surface roughness and surface energy. As was pointed out by the study of Kerle et al.,<sup>10,11</sup> surface roughness may dominate over the molecular weight dependence of the wetting behavior in athermal systems. Because of the use of an experimental system in which the variation of the inter-*cross*-link molecular weight of the substrate is decoupled from the variation of surface roughness, we are able to compare our observations with theoretical models.

Using the theoretical terms to describe the experiments, in our system an elastomer of inter-*cross*-link  $M_w(N)$  is brought into contact with a thin liquid film of  $M_w(P)$ . The values  $P$  and  $N$  correspond to intermediate chain length values of both the tethered chains and the melt. For this regime it was shown recently<sup>21,22</sup> that the transition from complete to incomplete wetting as a function of  $P$  is expected to occur at  $P \approx N^{2/3}$ . It was also suggested<sup>22</sup> that the wet-to-dry transition (swollen-to-nonswollen brush) is not equivalent to the transition from complete-to-partial wetting and should occur at lower values of  $P$ . Thus, a regime of complete wetting of a partially swollen brush is expected.<sup>22</sup>

The experimental findings are in line with the theoretical predictions for the wetting behavior at the brush–melt interface. In particular, we observe the onset of entropy-driven autophobic behavior at the elastomer–melt interface as a function of the melt molecular weight. The transition occurs, for each of the substrates, at around  $N = P$  (Table 2), and the observed contact angles (at the regime of partial wetting) depend on the inter-*cross*-link molecular weight, with values below  $11^\circ$ . This value is somewhat higher than the value of  $6^\circ$  reported by Mourran et al.<sup>4</sup> and the values of  $\theta < 4^\circ$  reported by Liu<sup>7</sup> et al. for a droplet of a polymer melt on top of a polymer brush. We also find that the degree of swelling of the cross-linked matrix varies with the melt molecular weight from over 200% for  $N \gg P$  to less than 5% for  $N < 2P$ .

Our observations support the suggested analogy between the wetting behavior of the brush–melt and rubber–melt<sup>2</sup> interfaces and their description as “entropic springs”. Yet, a few discrepancies exist between the experimental observations and the theoretical predictions: while the observed transition from complete to partial wetting takes place at around  $N = P$ , the transition from significant to negligible swelling of the network is shifted to higher values of the melt,  $N < 2P$ . Thus, while theory predicts the existence of a regime of complete wetting of a partially swollen brush,<sup>23</sup> we observe a regime of partial wetting of a swollen elastomer. We also do not observe the expected dependence of the contact angle on the molecular weight of the  $P$  chains, for each of the substrates.

We now focus on the observed shape of the interface, at the autophobic regime, and in particular on the transition from an initially deformed to an undeformed contact line. We observe that at early times, before reaching a steady state with respect to dewetting, the SLV contact line of liquid droplets on top of the elastomer is deformed, and the deformation height follows the expected relation  $h_0 \approx \gamma_{lv} \sin \theta / \mu_0$  for the two elastomers. With time, each of the droplets becomes

smaller in size, the deformation is released, and neighboring droplets tend to coalesce. The steady state is that of an undeformed surface on top of which rest a small number of liquid droplets. As the liquid is nonvolatile, size reduction of droplets may result from permeation into the matrix, leading to local swelling, or from the formation of a subdroplet film, on top of the matrix. In the first scenario we would expect a higher rather than a lower distortion, as it is known that swelling of polymeric matrices reduces the effective bulk shear modulus of a cross-linked matrix.<sup>18</sup>

The liquid may yet have an indirect effect on the elasticity of the matrix: permeation of the melt into the matrix may extract un-cross-linked chains and thus increase the local shear modulus of the network. To explore this possibility, we performed a series of experiments in which the networks were thoroughly extracted in heptane prior to forming the contact between the PDMS melt and the matrix. We found that the wetting transition, the contact angles of the dewetting melt, and the shape of the contact line at steady state were similar to those observed at the interface of the nonextracted networks. We may thus conclude that neither swelling of the network nor leaching of un-cross-linked chains is the origin of the observed phenomenon.

We suggest that it is the second scenario, in which a thin film spreads around the dewetted droplets, which finally leads to relaxation of the distorted contact line: due to the spreading of a thin liquid layer, the SLV contact line is replaced by a liquid–vapor contact plane, and a liquid layer that cannot support an elastic distortion covers the substrate. While we cannot observe directly the formation of a thin surface film, the presence of a liquid film on top of the elastomer is consistent with the observed course of the dewetting process: as mentioned before, the dewetting of precoated melt films proceeds via the formation of microdroplets which collect into a small number of macroscopic droplets. The process leads to a “single droplet” steady-state morphology, which differs from the polygonal patterns of droplets observed in other cases of dewetting.<sup>24,25</sup> The single droplet morphology corresponds to a minimum in the surface free energy and is achieved, we believe, by flow of liquid via the surface film. Similar steady-state morphology is attained by the different route taken by the pre-laid droplets: as mentioned before, we observe that the volume of these droplets reduces while the initial distortion of the substrate is removed, and the contact angles sustain their initial value.

A surface morphology in which a single liquid drop coexists with a flat film of finite (and small) thickness is known as “pseudo partial wetting”. This type of wetting morphology was described by Brochard et al.<sup>26</sup> for the case of simple liquids, by Shull<sup>6</sup> for polymer melts in contact with polymer brushes, and for the general case by Sharma and Khanna.<sup>27</sup> The model is based on the description of the interfacial energy,  $\Delta G$ , of a thin film of thickness  $h$ , as a sum of long-range van der Waals (vdW) interactions and short-range interactions represented by the spreading coefficient,  $S$

$$\Delta G = -A/12\pi h^2 + S \exp(-h/L) \quad (2)$$

where  $L$  is a typical correlation length ( $R_g$  for polymers) and  $A$  is the effective Hamaker constant which describes the vdW interactions at the solid–liquid interface. In our system the Hamaker constant favors wetting,<sup>28</sup> while the spreading coefficient attains a negative value

at the autophobic regime due to entropic interactions, as described above.<sup>4–6</sup> Sharma and Khanna<sup>27</sup> demonstrated that, in the case of a negative value of  $S$ , the free energy as described in eq 2 leads to instability of very thick films, resulting in pseudo-partial wetting. According to the model, a clear signature of a dewetting process, leading to pseudo-partial wetting, is the initial formation of isolated circular droplets, followed by the formation of an equilibrium flat film around the droplets and merger of neighboring droplets into a single drop coexisting with an underlying film.

To summarize, we suggest that wetting autophobicity at the melt–elastomer interface leads to pseudo-partial wetting in which bulk and surface elastic (entropic) terms are balanced and minimized.

## Conclusions

To conclude, the wetting behavior of the melt–elastomer interface in athermal couples depends on the ratio between the inter-cross-link molecular weight of the network and that of the melt, in close analogy to the case of polymer brushes. The transition from complete to partial wetting is observed at lower melt molecular weights than those leading to complete expulsion of melt chains from the matrix.

The steady-state morphology of the substrate at the autophobic regime is characterized by a flat surface, which is not distorted in the vicinity of the droplets. We believe that, unlike the theoretical predictions, a triple SLV contact line, as expected for “partial wetting”, does not exist in this system. Rather, at equilibrium, a thin liquid film surrounds the droplets and removes the elastic distortion of the interface, resulting in a wetting configuration known as “pseudo-partial wetting”. We suggest that in the case of athermal systems, and a soft, deformable surface, this configuration corresponds to a lower free energy state than that of partial wetting.

**Acknowledgment.** We thank Yafa Yagen and Moshe Gottlieb for their help with the PDMS elastomers, Afra Ritzl for carrying the JKR measurements, and Matt Tirrell for enabling her to use his laboratory. We thank Tobias Kerle for illuminating discussions. The generous support of the Wolfson Family Charitable fund, The U.S.–Israel Binational Science Foundation (BSF, Grant No.95-147), and the Minerva Foundation (in the frame of the “Reimund Stadler Minerva Center for Mesoscale Macromolecular Engineering” at the Ben-Gurion University) are acknowledged with gratitude.

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MA990555I