

Wetting and Autophobicity of a Polymer Melt on a Network of Itself

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ABSTRACT: Wetting properties of thin films of a polymer melt on top of a network formed by irradiation cross-linking of an identical melt were studied. The permeability of the network and its wettability as a function of the extent of cross-linking were characterized by nuclear reaction analysis, atomic force microscopy, contact-mechanics measurements of the adhesion energy, and light microscopy. As the degree of cross-linking increased, we observed a crossover from complete to partial wetting, followed by a second crossover back to complete wetting at higher cross-link densities. We suggest that the first crossover is a manifestation of entropy-induced autophobicity arising from the brush-like nature of the cross-linked surface, while the second originates from surface roughening induced by the cross-linking.

Introduction

The wettability of cross-linked polymer networks plays a key role in their usage in high-technology applications, ranging from permeable membranes in artificial kidneys¹ to materials in the aeronautic industry.² The permeability of the network distinguishes its surface from that of an ideal solid and gives rise to unique effects: In a number of systems it was observed that the wettability of the surface is determined by the ability of the liquid to penetrate into the network. Such is the case of a polymer melt which is put into contact with a surface covered by a transient network of a densely grafted polymer brush.^{3–6} When the melt and the brush are of similar chemical structure, entropy considerations limit the penetration of the melt chains into the brush, leading to partial wetting. This phenomena is known as *autophobicity*.^{7–10} Another deviation from the ideal solid case is introduced by the cross-linking process itself. Surface fluctuations that were present at the liquid/vacuum interface at the time of cross-linking are “frozen” by the process of cross-linking. This additional surface roughness may also affect the wetting behavior.¹¹

We report here a study on the wetting of a polymeric network by a thin film of a (non-cross-linked) melt of the same polymer. The network was formed by cross-linking a polymer melt layer on a solid support, using ion-beam radiation. A second thin film of the non-cross-linked melt was then spread on top of this network, forming a bilayer. Cross-link-induced autophobicity has recently been reported.¹² Here we extend this to a comprehensive investigation of the factors underlying this effect. We use several complementary experimental methods to characterize the permeability of the network, its surface characteristics, and its wettability by the non-cross-linked polymer. We interpret our results in terms of an entropy-driven dewetting model, combined with simple considerations of the effect of cross-linking-induced roughness on the spreading coefficient at the melt/network interface.

Experimental Section

1. Materials. Random copolymers, in which the monomers are structurally analogous to ethylene and butene-1 mono-

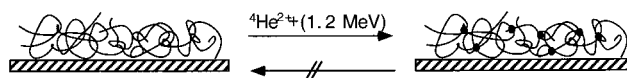


Figure 1. Schematic representation of the cross-linking process. In a nonreversible process bonds in the polymer chains are broken, leading to a random recombination of the dangling bonds and the formation of C–C bonds between different chains. In this way a three-dimensional network is formed.

mers, were synthesized by anionic polymerization as described in detail elsewhere.^{13,14} The materials were kindly donated by Dr. L. J. Fetters. The mean microstructure was $[(C_4H_8)_{0.14}-(C_2H_3(C_2H_5)_{0.86})_N]$, and an identical but partly deuterated analog where 40% of the H are replaced by ²H (henceforth designated h86 when protonated and d86 when deuterated) was also used. We used highly monodisperse samples ($M_w/M_N < 1.08$), with weight-averaged molecular weight $M_w = 8.5 \cdot 10^4$, which corresponds to a degree of polymerization $N = 1520$; the glass transition temperature is $T_g = -36$ °C. Polished silicon wafers (P-type, (100) oriented, 6–13 Ω/cm were obtained from the Institute of Electronic Materials Technology Warsaw). The toluene used was analytical grade, purchased from either Frutarom or Merck.

2. Sample Preparation. Thin polymer films in the thickness range of 150–500 nm were prepared by spin casting from toluene solutions onto gold-covered silicon wafers. Film thickness was controlled by the concentration and the spinning rate. The films were thoroughly dried and then cross-linked by exposing them to a uniform flux of high energy (1.2 MeV) α particles (⁴He) from a Van de Graaff accelerator under a fixed angle $\alpha = 15^\circ$ between sample and beam (see Figure 2). The ion penetration depth was always larger than the sample thickness in order to get a uniformly irradiated layer. The cross-linking density of the polymers was controlled by varying the exposure time t and thus the overall fluence (typical values are 10^{13} to 10^{15} ions/cm²). The use of irradiation for inducing cross-linking in polymers was already described in early works of Charlesby and Lawton et al.^{15–17} The process is nonreversible and involves the formation of C–C interchain bonds, thus creating a three dimensional network (Figure 1). A thin film of polymer was spin cast on a piece of freshly cleaved mica and then transferred, using a jig as recently described,¹⁴ on top of the cross-linked substrate film. The bilayer samples were then annealed for varying time intervals and temperatures in sealed glass ampules under vacuum ($5 \cdot 10^{-3}$ Pa) in order to prevent degradation. The stability of the ovens used in these experiments was ± 1 °C. After annealing, the samples

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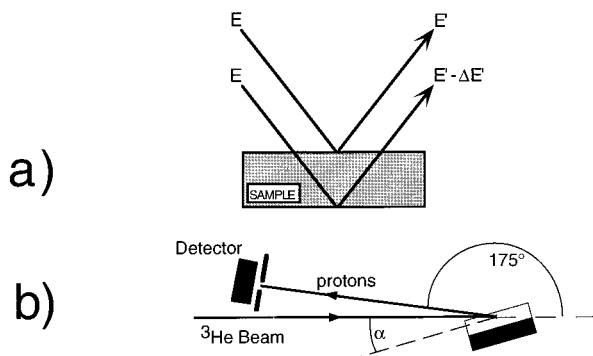
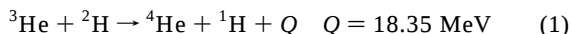


Figure 2. The geometry of the proton-NRA setup used for depth profiling the interdiffused polymer layers: (a) A magnified scale of the sample. The energy loss $\Delta E'$ of the protons reveals the depth at which the reaction occurred. (b) The use of proton-NRA enables us to achieve a resolution at the polymer/air surface of up to 4 nm HWHM; the angle α between beam and sample was typically in the range 8–14°.

were quenched rapidly to a temperature (< -80 °C) below the glass transition temperature and stored at this temperature until measured.

3. Characterization of the System. 3.1. Nuclear Reaction Analysis. Interdiffusion experiments were carried out in order to characterize the properties of the cross-linked matrix. Proton Nuclear Reaction Analysis (proton-NRA)^{18,19} was used to probe the depth-distribution profiles of deuterated marker chains. In this method a monoenergetic ^3He beam is incident at low angle on the polymer sample and undergoes the following reaction:



From the energy spectrum of the emitted protons (Figure 2) and the known energy losses and reaction cross section, the concentration profile $\phi(z)$ of the deuterated chains is directly measured, as function of depth (the underlying idea being that the energy of the emerging reaction products when they reach the detector is a function of the depth within the sample at which the reaction occurred). The spatial resolution of the method depends on the incident energy of the ^3He beam, the angle between beam and sample, and the depth within the sample. It is highest at the sample surface. The technique yields a spatial resolution of 4 nm HWHM at the polymer/air interface for an incoming ^3He energy of 700 keV and an angle $\alpha = 8^\circ$ between beam and sample¹⁹ (see Figure 2b) and stays better than approximately 25 nm HWHM for depths up to 600 nm for an incoming beam with energy 1.2 MeV and $\alpha = 14^\circ$.

3.2. Atomic Force Microscopy (AFM). We used AFM to study the surface features of the polymer films.^{20,21} The measurements were performed on 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 (manufacturer's specification). Contact angles of polymeric droplets were also measured by AFM. As the typical dimensions of the measured features are in the range of some tens of nanometers and the characteristic angles are rather small ($< 10^\circ$), tip size and shape did not present any difficulties.²² To prevent penetration of the AFM tip into the soft, liquid polymer film, we cross-linked the films prior to scanning by exposing them to the ion beam for a short time ($t < 16$ s).²³

3.3. Surface Energy Measurements. The surface energy of the cross-linked layers was determined via contact-mechanics measurements. The experiments are based on the Johnson–Kendall–Roberts (JKR) model of contact mechanics²⁴ which describes the relation between the load and distortion arising when two macroscopic bodies are forced into close contact. The experiments were carried out in the laboratory of Prof. M. Tirrell at the University of Minnesota. In the experimental setup, a given displacement is imposed on a spherical cap of cross-linked polydimethylsiloxane (PDMS) in contact with the

flat surface of a cross-linked polyolefin film. Both the load (P) and the radius (a) of the contact area between the sphere and the flat surface are monitored. A typical experiment consists of a loading sequence in which the spherical cap is compressed at progressively higher loads against the flat surface, followed by an unloading sequence in which the cap is again progressively pulled away from the surface.²⁵ The values of P and a are monitored during the cycle and analyzed according to the JKR equation

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

where K is the elastic modulus, R is the radius of the undeformed sphere, and W is the reversible work of adhesion. The curvature radius of the cap is measured independently. The interfacial energy γ_1 is given by $W = 2\gamma_1$ for symmetrical contacts (i.e. lens material the same as the flat material), and by $W = 2(\gamma_1\gamma_2)^{1/2}$ for asymmetrical contacts, where the surface energies of the two components are γ_1 and γ_2 . The basis of eq 2 is the balance of attractive energy exerted through the adhesive contact, producing a deformation that tends to increase a and a counteracting elastic energy that tends to reduce a .

Results

1. Visual Inspection. In the first set of experiments thin layers of deuterated polyolefin (d86) were spin-coated on gold-covered silicon wafers to form homogeneous thin layers of about 500 nm thickness. These substrate layers were then cross-linked by exposing them to the ion beam for different time intervals which correspond to different ion fluences. A second layer of d86, with a characteristic thickness of 300 nm was floated on top, thus creating a bilayer. The bilayers were annealed under vacuum ($5 \cdot 10^{-3}$ Pa) for 12 h at a temperature of 120 °C. Figure 3 presents a series of samples in which the substrate layer was cross-linked for different time intervals. Whereas the polyolefin films that are on top of a layer that was not cross-linked at all (a) or a layer cross-linked for 44 s (d) show a smooth, unruptured surface, macroscopic holes are clearly visible in the films on top of the matrices which were cross-linked for 8 s (b) and 24 s (c). The micrograph of the 8 s cross-linked sample (b) shows a polygonal pattern of droplets, which is typical for the final state of a dewetted film.^{3–6} We observe that cross-linking the matrix for time intervals in the range between 8 s and 1 min induces a gradual monotonic transition from partial to complete wetting. Above a cross-linking time of ca. 40 s, the top layer of the polyolefin melt remains as a uniform film which completely wets the matrix, as can be seen in Figure 3d.

2. Characterization of the Cross-Linked Polymer Layer. To characterize the structure and permeability of the cross-linked polyolefin, we carried out two sets of diffusion experiments: (1) diffusion of free polymer chains into the cross-linked substrate served as a probe for the permeability of the network to the non-cross-linked melt and (2) diffusion of chains out of the cross-linked substrate into the overlying melt of free chains was used to characterize the cross-linking density and the fraction of free chains entangled with the network.

2.1. Diffusion of Free Chains into the Cross-Linked Substrate. For this set of experiments we used a bilayer configuration in which the first layer is typically a 250 nm thick film of hydrogenated polymer (h86). The films were spin cast on the gold-coated silicon wafers and then cross-linked by exposing the

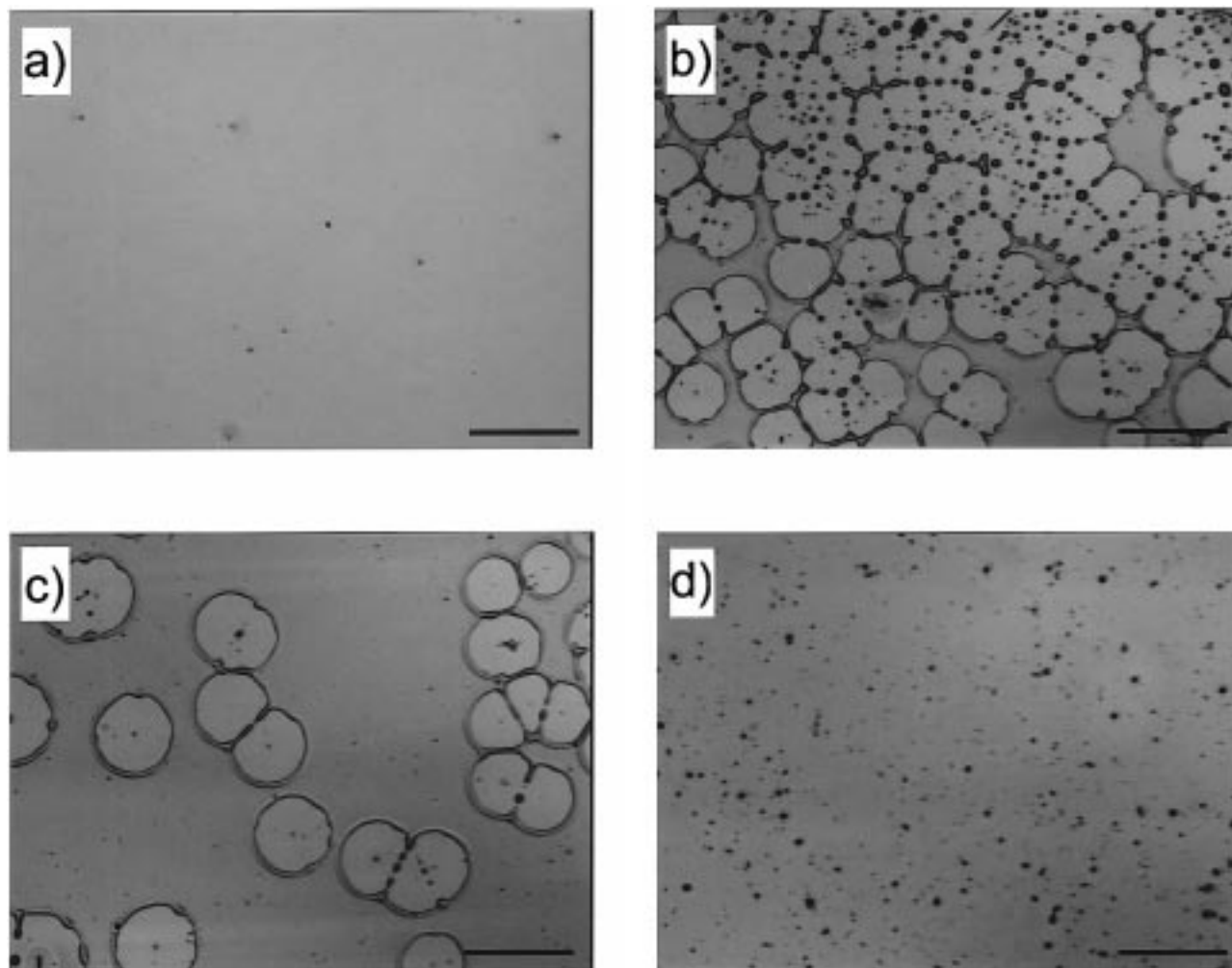


Figure 3. Images of bilayers where the matrix was either not cross-linked (a) or cross-linked for (b) 8 s, (c) 24 s, and (d) 44 s, following annealing under vacuum ($5 \cdot 10^{-3}$ Pa) for 12 h at $T = 120$ °C. The scale bar is 100 μm . With increasing cross-linking density the formation of holes ceases. The film on top of the 44 s sample stays flat and homogenous (characteristic of complete wetting).

samples for different time intervals ($t = 0$ s, 8 s, 16 s, and 1 min) to the beam. A second layer of deuterated polymer (d86) was similarly spin cast on mica and floated onto the h86 film. The thickness of the overlay film was 120 nm. The bilayers were annealed under vacuum ($p = 5 \cdot 10^{-3}$ Pa) for 12 h at $T = 80$ °C. Concentration–depth profiles of these samples taken with NRA are shown in Figure 4. In the case of the non-cross-linked h86 layer (Figure 4a), the annealing time of 12 h is sufficient for complete interdiffusion of the two polymer layers. This is consistent with the work of Losch et al.,²⁶ who measured a self-diffusion coefficient of $D = 2.3 \cdot 10^{-15}$ cm²/s for the system h86/d86 at a temperature of $T = 23.5$ °C. An extrapolation of this self-diffusion coefficient according to the WLF relation,²⁷ which describes well the variation of D for this couple,²⁶ results in a self-diffusion coefficient $D \approx 10^{-13}$ cm²/s for $T = 80$ °C. We find that a cross-linking time as short as 8 s (b) suppresses significantly the interdiffusion of free chains into the cross-linked matrix. Samples annealed much longer than 12 h at $T = 80$ °C showed indications of rupturing and dewetting. Depth profiling with NRA does not yield useful information for this kind of sample, as the lateral inhomogeneity becomes too large. This marked influence of cross-linking on the interdiffusion rate between free and cross-linked polymer was already reported by other authors.^{28–30} Cross-

linking for longer time periods leads to a progressively less penetrable matrix for the marker chains (parts c and d). A comparison of the 1 min cross-linked sample (d) and a sample frozen immediately after creating the bilayer shows no differences. The marker chains are no longer able to penetrate into the cross-linked matrix. This indicates that the crossover from penetrable to nonpenetrable matrix has already occurred by the time the matrix was cross-linked for 1 min. Control experiments carried out at elevated annealing temperatures ($T > 160$ °C) and longer annealing periods ($t > 7$ d) show no interdiffusion of tracer chains into matrices with cross-linking times equal or above 1 min.

2.2. Diffusion of Substrate Chains into the Overlying Melt of Free Chains. A bilayer configuration complementary to that described in the previous section was used to study the diffusion out of the cross-linked matrix. Thin films of d86 were spin cast to a thickness of about 250 nm and cross-linked for time intervals of $t = 8$ s, 16 s, and 1 min. Following this a second layer of h86 (thickness 125 nm) was floated on top to form a bilayer that was annealed for 12 h at $T = 80$ °C under vacuum ($p = 5 \cdot 10^{-3}$ Pa). NRA was used to measure the resulting concentration–depth profiles (Figure 5). We compare the diffusion-broadened profiles with a reference profile of the nonannealed bilayer (dotted line, Figure 5). We see that after 8 s cross-

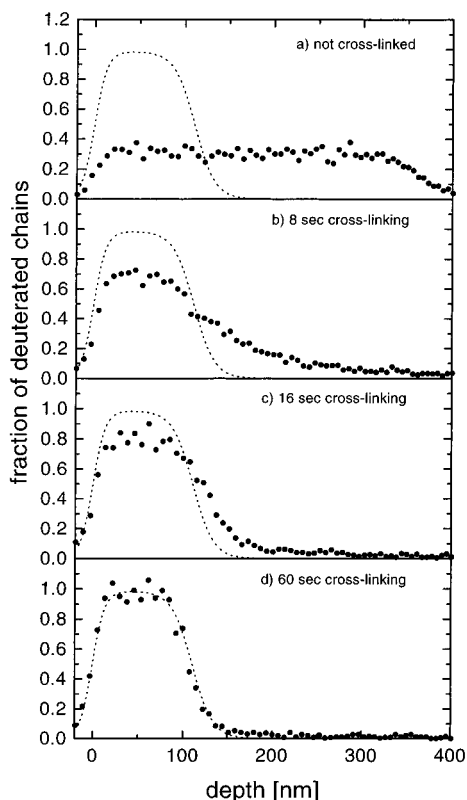


Figure 4. Volume fraction versus depth profiles of d86 melt on cross-linked h86 layers after annealing under vacuum ($5 \cdot 10^{-3}$ Pa) for 12 h at $T = 80^\circ\text{C}$, as determined by NRA. A non-cross-linked control sample (a) shows complete interdiffusion, resulting in a homogenous distribution of d86 over the entire depth of the film. Also shown are depth profiles for samples cross-linked for (b) 8 s, (c) 16 s, and (d) 1 min. The dotted line corresponds to the depth profile of a non-cross-linked sample frozen ($T < -80^\circ$) immediately following the creation of the bilayer (i.e. an unannealed sample).

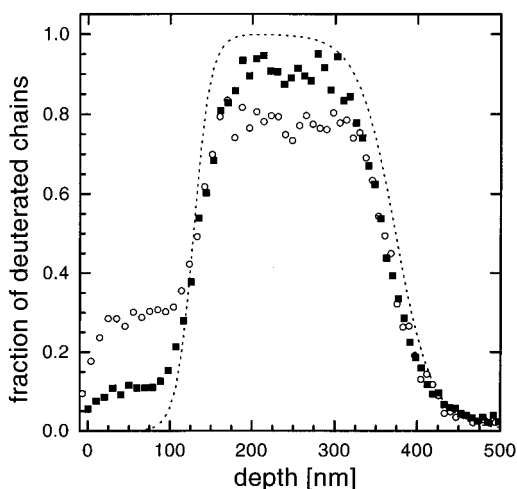


Figure 5. Volume fraction versus depth profiles of cross-linked d86 layers covered by h86 melt after annealing under vacuum ($5 \cdot 10^{-3}$ Pa) for 12 h at $T = 80^\circ\text{C}$, as recorded by NRA. The amount of d86 chains diffusing out of the matrix drops significantly when going from an 8 s cross-link time (open circles) to a 16 s cross-linking time (filled squares). The dotted line corresponds to the depth profile of a non-cross-linked sample frozen ($T < -80^\circ$) immediately following the creation of the bilayer (i.e. an unannealed sample).

linking (○) some d86 chains diffused out and were replaced with free h86 chains. A rough estimate of the mean cross-linking density may be made from the

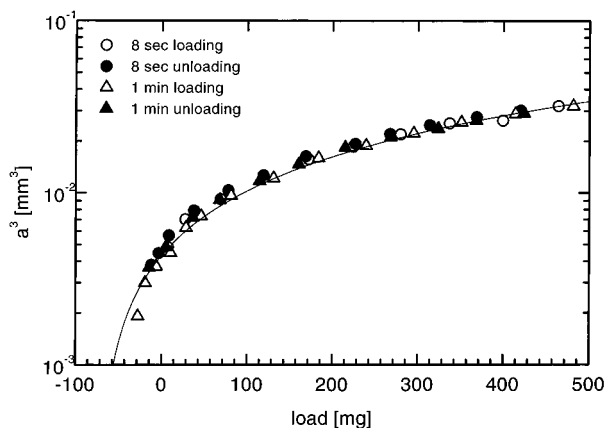


Figure 6. JKR-type measurements of samples cross-linked for 8 s (circles) and 1 min (triangles). The solid lines are from eq (2) with appropriate values of W . The surface energy determined from these measurements is in both cases 28 ± 1 mJ/m².

fraction of chains in the cross-linked substrate that remain free (i.e. non-cross-linked) to diffuse out. Using a Poisson distribution as a model and neglecting possible chain scission, such an estimate yields an expectation value of ca. 2 cross-link points per chain. As the degree of cross-linking is increased, the number of chains free to diffuse out of the cross-linked substrate film decreases. Analysis of the concentration depth profile of the sample cross-linked for 16 s (■) gives an expectation value ca. four cross-link points per chain. By the time the matrix was cross-linked for 1 min (not shown), essentially all d86 chains were trapped in the matrix.³¹

3. JKR Measurements. Figure 6 presents results of two different JKR experiments in which the same PDMS lens²⁵ was used to probe the surface energy of the two films of cross-linked d86. One film was cross-linked for 8 s (circles), the other film for 1 min (triangles). To determine the surface energy of the polyolefin films, we first measure the reversible work of adhesion (W) between two PDMS lenses (yielding γ_1). Then one of the lenses is used for probing the adhesion energy of all the cross-linked layers. The value of W from these experiments is then used to determine the surface energy γ_2 of the cross-linked substrates according to the relation $W = 2(\gamma_1\gamma_2)^{1/2}$.³² We find that the surface energy of samples which were cross-linked for different times is similar and corresponds to $\gamma_2 = 28 \pm 1$ mJ/m² (in line with literature values³³).

4. Surface Roughness Measurements by AFM.

Figure 7 shows typical AFM scans for samples cross-linked for (a) 8 s and (b) 8 min on equal scales. It is clearly observed that the characteristic wavelength of the height fluctuations of the surface decreases as we go from the 8 s cross-linked sample to the 8 min cross-linked sample while their amplitude increases correspondingly. We also observe that the rms (root mean square) value of the roughness increases with increasing cross-linking density. In Figure 7c we present the surface roughness, derived by AFM measurements, as a function of the cross-linking time. From an average rms value of 10.5 Å for the 8 s cross-linked sample, the roughness rises quasi-linearly to 19 Å after 8 min cross-linking. A possible explanation is that the surface roughness arises from weak attractive interactions between the cross-link points, as they are expected to be slightly incompatible with the bulk of the non-cross-

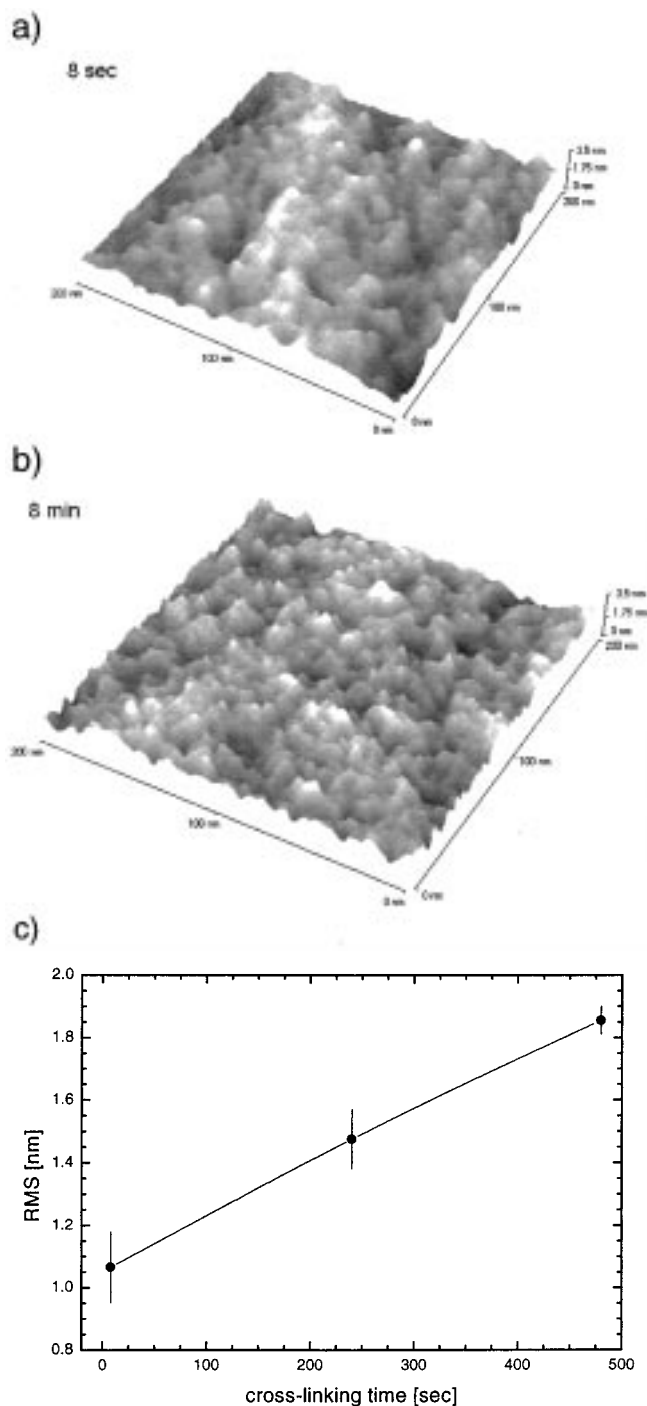


Figure 7. AFM topography scans of h86 films cross-linked for (a) 8 s and (b) 8 min on the same xyz-scale. The characteristic wavelength of the height fluctuations of the surface clearly decreases for increasing cross-linking time. An analysis of the surface roughness shows (in c) that the rms value rises roughly linearly with cross-linking time.

linked segments. Such attraction may weakly segregate the cross-links, resulting in an inhomogeneous (i.e. roughened) surface structure.

5. Dependence of the Contact Angle on the Cross-Linking Density. Contact angles were measured by AFM. As the dewetted polymer film is liquid even at room temperature, it can easily wet the AFM tip, thus preventing stable feedback and imaging, making any analysis of the contact angle impossible. By exposing the dewetted sample once again to high-energy α radiation we were able to take topography scans of

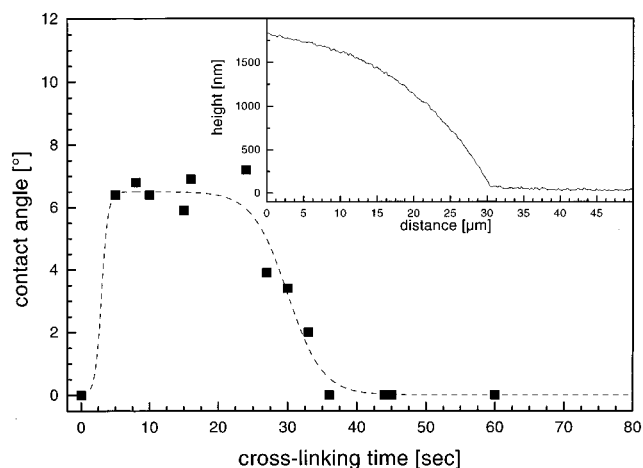


Figure 8. Contact angles of h86 on top of h86 matrices cross-linked for different times as measured by AFM. The dotted line is a guide to the eye. The inset shows a typical cross section through an AFM topography scan of a dewetted sample (24 s cross-linking time). The angle between dewetted polymer and matrix can easily be derived from such a scan.

the polymer droplets in a cross-linked state. The cross-section of the contact area of a polymer drop and the substrate can then be utilized to determine the contact angle between polymer and substrate.²³ Control measurements carried out with optical phase modulated interference microscopy gave contact angles closely comparable to the AFM results. Figure 8 (inset) presents a typical cross-section. On the right side we observe the exposed surface of the cross-linked matrix. At a distance of ca. 30 μm one can clearly see the drop rising. The contact angles were derived by constructing the tangent to the drop shape at the point of intersection and measuring the angle between this line and the baseline (linear fit through the data right of the sphere). In Figure 8 (main) we show the contact angles for samples cross-linked in the range $t = 0$ s to 1 min, determined as described above. Samples with a contact angle of 0° showed a flat, homogenous surface as the polymer melt wetted the matrix completely. The contact angle rises very sharply from 0° to a value of ca. 7° in the initial 4 s.³⁴ Up to a cross-linking time of ca. 24 s the contact angle stays on a constant level and decays with further cross-linking time. At a cross-linking time of 36 s the film already stays smooth and no longer dewets. Control measurements carried out on samples annealed for 7 days did not show a further increase in the contact angles.

Discussion

The central finding of the present study is that wetting of a cross-linked polymer substrate by a melt of chemically similar chains, spread on top of it, depends on the degree of cross-linking. When the substrate polymer is not cross-linked, we observe the expected full interdiffusion and complete wetting by the overlaid melt. As the substrate chains are progressively cross-linked we note correspondingly lower extents of interdiffusion, together with partial wetting of the substrate by the non-cross-linked melt, and measure contact angles of up to 7°. At yet higher cross-linking densities, interdiffusion between the substrate and the unentangled melt is completely suppressed, and we observe that the substrate is once again fully wetted by the overlying melt.

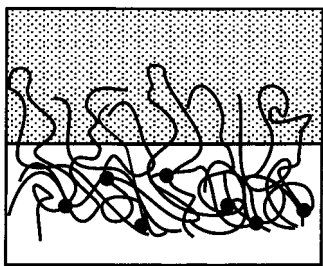


Figure 9. Schematic representation of the interfacial area between the two polymer layers (shaded layer is the free melt film). Chain ends and loops are pinned by the cross-links within the matrix, forming a brush-like surface. With increasing cross-linking density both the effective length of tethered (i.e. cross-linked) loops and tails and the mean area per loop or tail are reduced.

We may ask whether this unusual wetting behavior is a result of chemical changes introduced at the substrate surface by the cross-linking process itself. The JKR experiments provide a measure of the substrate surface energy, and the data shown in Figure 6 reveal clearly that any changes in the surface energy introduced by the cross-linking are insignificant and are of a magnitude smaller than the experimental uncertainty of $\pm 1 \text{ mJ/m}^2$. The absence of hysteresis between loading and unloading curves implies that no interpenetration of the PDMS into the substrate polymer occurs (i.e. there is no entropic component to the interaction as discussed below) and that the constant surface energies measured therefore reflect the essentially constant value of the energies at the polymer–air interface at different cross-linking levels. These results are also consistent with other measurements that we carried out on the effect of different extents of cross-linking on the polyolefin surface energies, using X-ray photoelectron spectroscopy, surface raman spectroscopy, and sessile-drop contact angle measurements (to be published). These different approaches all indicate little or no change in surface chemical composition over the range of cross-linking of the present study.

The origin of the dewetting of the cross-linked substrate by the chemically similar but non-cross-linked melt must therefore lie elsewhere. A good starting point for discussing the initial crossover from complete to partial wetting revealed by our experiments is to consider the change in the Helmholtz free energy due to a change of unit area by the (nonvolatile) wetting liquid spread on top of a nonpenetrable dry surface^{35,36}

$$f_{\text{dry}} - f_{\text{wet}} = \gamma_{\text{SV}} - (\gamma_{\text{SL}} + \gamma_{\text{LV}}) \equiv S \quad (3)$$

Here f_{dry} and f_{wet} are the energies per unit area of the dry surface and of the surface when covered by the liquid, γ_{SV} , γ_{SL} and γ_{LV} are the surface tensions respectively at the solid/vapor, solid/liquid, and the liquid/vapor interfaces, and S is the spreading coefficient. Complete wetting is expected for the case of $S > 0$ (since in that case the energy of the dry surface is higher than that of the wetted surface), whereas in the case of $S < 0$ partial wetting follows.

In the system described in our experiments, the substrate is not an ideal smooth solid but rather a penetrable network, and the liquid is a polymer melt. Once cross-linking is induced in the substrate polymer, the chains at the surface behave—as suggested in the drawing in Figure 9—as an array of loops and tails attached by the cross-links to the bulk of the substrate

film. Such a surface phase may be thought of as a melt “brush” in the sense that it consists of an array of tethered chains which may extend normal to the surface when swollen by any added free chains. In order to describe the wetting properties of such a surface structure by a non-cross-linked polymer melt, we need to consider the additional interactions which affect the free energy balance. As suggested in our earlier brief report,¹² it is convenient to consider such interactions in the framework of a recent theoretical treatment (by Leibler et al.⁸) of the wetting of a polymer melt brush by a polymer melt. This model analyzed the wetting behavior of a polymer melt of degree of polymerization P (P -mer) on top of a melt brush of densely grafted N -mers with identical monomers (i.e. athermal conditions). The basic idea of the model is to consider the swelling of the melt brush by the overlying free melt. In order to determine if the equilibrium state is complete wetting or partial wetting, the theory compares the gain of melt translational entropy, which leads to swelling of the underlying brush, with the loss of conformational entropy due to the stretching of the tethered chains. Enthalpic interactions are neglected by the model, which is reasonable in view of the chemical identity of the monomers and—in relation to our experiments—the negligible changes in the substrate surface chemistry introduced by the cross-linking. In practice, the conditions of our study do not exactly match the model assumptions. Thus, the model is restricted to the case where the density Σ^{-1} of the grafted layer (Σ = area per brush chain) is high enough that even in the absence of a wetting solvent the chains are stretched; in addition, the brush chains in the model are monodispersed and are all tails rather than tails and loops as in our cross-linked surfaces. Nonetheless, more recent calculations by Shull¹⁰ suggest that the essential ideas of the simple Leibler model carry over even for the case of a “brush” formed—as in our case—by polydispersed, end-attached tails and loops. In what follows, therefore, we discuss our findings in terms of this simple model, though in view of the only-approximate match between model assumptions and actual experimental conditions we do not carry the quantitative comparisons too far.

In the absence of significant enthalpic interactions, the free-melt/cross-linked-substrate interfacial energy is dominated by the entropy balance. Qualitatively, one expects that for short P -mers and long N -mers the brush will be solvated and complete wetting is favored. The other extreme favors partial wetting only. The important parameter turns out to be the ratio between the chain length of the melt (N) and the effective chain length of the surface structure (P). This ratio controls the relative importance of the translational entropy gained by the free chains, as they penetrate into the brush, and the conformational entropy lost by the tethered chains which have to stretch further. Leibler et al. derived an approximate expression for the energy change f_L associated with the interpenetration of the P -mer melt into the N -mer brush per unit area of contact between them, given by

$$f_L \approx k_B T [A/\lambda a - B\lambda/Pa^3] \quad (4)$$

where a is the statistical segment length and $\lambda = (12/\pi^4)^{1/3} (Na\Sigma)^{1/3}$ is the characteristic penetration depth of the P -mer melt into the N -mer brush. A and B are

constants of order unity. This is the main result of the model, describing the formation of a new interface, of width λ , which depends on the chain length of the tethered chains. The two terms in the square brackets correspond, respectively, to the loss of configurational entropy due to swelling of the N -mer brush induced by interpenetration of the P -mer liquid and to the gain in translational entropy by the P -mer chains due to this interpenetration. For $f_L < 0$ interpenetration of the brush by the melt is favored, and wetting occurs. For $f_L > 0$, dewetting is favored. The crossover from complete wetting to partial wetting, known as "auto-phobicity", takes place at a value of $P = P^*$, given by

$$P^* \cong (\lambda/a)^2 \cong (N \sum a^2)^{2/3} \quad (5)$$

Complete wetting in the Leibler model is expected for $P \ll P^*$ and partial wetting for $P > P^*$. We note again that while the details of the Leibler model do not tally exactly with our system, we expect any treatment of entropy-controlled interactions to result in a form analogous to eq 4; for this reason we may use it as a valid basis for our discussion.

The spreading coefficient S defined in eq 3 for an impermeable solid surface now needs to be modified to take account of f_L :

$$S = f_{\text{dry}} - (f_{\text{wet}} + f_L) \quad (6)$$

If we replace the subscripts for liquid (L), solid (V), and vapor (V) in eq 3 by melt, brush (the cross-linked substrate), and air, respectively, we have, on substituting for f_L in eq 5,

$$S = -\gamma_{\text{air/melt}} + \gamma_{\text{air/brush}} - \gamma_{\text{brush/melt}} - k_B T [A/\lambda a - B\lambda/Pa^3] \quad (7)$$

To understand the changes in the wetting behavior it is important to appreciate the relative magnitude of the terms appearing in eq 7. The largest terms by far in eq 7 are those involving either the air/melt or the air/brush interfaces ($\gamma_{\text{air/melt}}$ and $\gamma_{\text{air/brush}}$, respectively), which are dominated by the incompatibility of polymer and air (each has a magnitude on the order of $k_B T/a^2$). However, in the absence of cross-linking the magnitudes of $\gamma_{\text{air/melt}}$ and $\gamma_{\text{air/brush}}$ are clearly identical, while $\gamma_{\text{brush/melt}}$ is zero, so wetting occurs. The term in square brackets is applicable only once cross-linking has commenced, so that a brush-like structure of tethered loops and tails is formed. To first order, as revealed also by the JKR and other measurements described above, the magnitudes of $\gamma_{\text{air/melt}}$ and $\gamma_{\text{air/brush}}$ remain closely similar even once cross-linking takes place, while $\gamma_{\text{brush/melt}}$ must remain very small. The term in square brackets, while not large compared with either $\gamma_{\text{air/melt}}$ or $\gamma_{\text{air/brush}}$ (the magnitude of either term in the square brackets is on the order of $k_B T/N^{1/2}a^2$, which is much smaller than $k_B T/a^2$ since $N \gg 1$), must then dominate the energy balance and the sign of S in eq 7.

As cross-linking progresses the effective mean size N of the tethered loops and tails in the brush-like substrate layer becomes progressively smaller than P , while at the same time the effective density Σ^{-1} of the tethered chains increases. This decreases the value of λ , and the first term in the square brackets in eq 7 dominates. This makes S negative, leading from the complete wetting (at no cross-linking or very weak cross-linking) to the partial wetting regime, as indeed observed in the

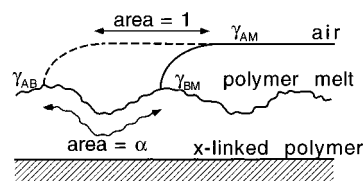


Figure 10. Schematic representation of the effect of roughness on the spreading parameter. When the liquid layer, whose surface is smooth, spreads by unit area, both the area exposed by the substrate and the liquid/substrate interface change by an area α (subscripts A, B, and M stand for air, brush, and melt).

experiments, and is the explanation for the first (complete-to-partial) cross-link-induced wetting transition.

As cross-linking proceeds to higher values, the decrease in the effective size N and increase in the effective tethering density Σ^{-1} is monotonic (resulting in ever smaller values of the interpenetration parameter λ). There is therefore no reason on the basis of the Leibler model to expect the transition back to the complete wetting regime (the *re-entrant* transition) which is observed at the higher cross-link densities. Rather, we suggest that the origin of this re-entrant wetting transition is due to another feature of the system, as revealed by the AFM scans of the bare surface of the cross-linked matrix. We observed (Figure 7) that the surface roughness increases monotonically with the cross-linking density. It is known that surface roughness has a substantial affect on the wetting properties of surfaces¹¹ as it increases the surface area which is exposed to air by a factor α , where $\alpha \equiv$ (actual surface area)/(geometric surface area). The effect on the spreading parameter is illustrated schematically in Figure 10: when the liquid layer (whose surface is smooth) spreads by unit area, both the area exposed by the substrate and the area of the liquid/substrate interface change by an area α . By inspection (as noted long ago¹¹) this immediately modifies eq 3 to the form

$$S = f_{\text{dry}} - f_{\text{wet}} = \alpha\gamma_{\text{SV}} - (\alpha\gamma_{\text{SL}} + \gamma_{\text{LV}}) \quad (8)$$

so that eq 7 now becomes

$$S = -\gamma_{\text{air/melt}} + \alpha(\gamma_{\text{air/brush}} - \gamma_{\text{brush/melt}}) - \alpha k_B T [A/\lambda a - B\lambda/Pa^3] \quad (9)$$

Equation 9 assumes that the entropy term in square brackets remains unchanged by the roughness. This is probably a simplification, but as we shall see, it makes little difference to the overall balance once surface roughening occurs. Since there is no longer a cancellation between the terms in $\gamma_{\text{air/melt}}$ and $\gamma_{\text{air/brush}}$ in eq 9, we now expect the dominant effect on S to be due to the difference ($\alpha\gamma_{\text{air/brush}} - \gamma_{\text{air/melt}}$). Since both $\gamma_{\text{air/melt}}$ and $\gamma_{\text{air/brush}}$ are almost equal but are much larger than the other terms in eq 9, at growing magnitudes of the roughness α , this difference soon swamps all other effects and makes $S > 0$, i.e. complete wetting once again. This roughening then is the origin of the re-entrant wetting transition observed at the higher cross-linking densities. In fact it may be shown that for an extent of cross-linking proportional to the radiation time t [i.e. $N \propto (1/t)$] and a roughness increase ($\alpha - 1$) proportional to t , eq 9 can indeed lead to a prediction of re-entrant wetting at large t .

Conclusions

To summarize, the wetting behavior of a polymer melt on top of a substrate consisting of a polymer network

of chemically identical chains depends on the cross-linking density of the network. When the substrate is either not cross-linked or highly cross-linked, a thin film of the melt forms a stable wetting layer. For intermediate cross-linking densities the films rupture and dewet into droplets. The contact angle measured for these samples is a function of the cross-linking density and goes through a maximum. As measurements of the bare surface energy do not indicate a dependence on the extent of cross-linking, the observed effects must be the result of physical (entropy-related) changes rather than changes in surface chemistry of the cross-linked substrate.

We relate the first cross-over from complete to partial wetting to autophobicity induced by interactions of entropic origin at the interface between the melt and the cross-linked substrate. The second crossover back to complete wetting is due to the progressive increase of surface roughness of the substrate at higher cross-link densities, as seen directly by AFM measurements.

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