

Home Search Collections Journals About Contact us My IOPscience

Cross-link-induced autophobicity in polymer melts: A re-entrant wetting transition

This content has been downloaded from IOPscience. Please scroll down to see the full text. 1997 Europhys. Lett. 38 207 (http://iopscience.iop.org/0295-5075/38/3/207)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 132.72.9.170 This content was downloaded on 25/11/2014 at 09:28

Please note that terms and conditions apply.

## Cross-link-induced autophobicity in polymer melts: A re-entrant wetting transition

T. KERLE, R. YERUSHALMI-ROZEN and J. KLEIN

Department of Materials and Interfaces, Weizmann Institute of Science 76100 Rehovot, Israel

(received 22 July 1996; accepted in final form 21 February 1997)

PACS. 68.45Gd – Wetting. PACS. 68.15+e – Liquid thin films. PACS. 61.25Hq – Macromolecular and polymer solutions; polymer melts; swelling.

**Abstract.** – We have investigated the wetting behaviour of a polymer melt on top of a cross-linked network of itself. For substrate films that were not cross-linked at all (or at very low cross-link densities) the melt completely wets the underlying layer. At intermediate cross-linking densities we observe dewetting, which we suggest is due to the brush-like surface of the network. At higher cross-linking densities the melt again completely wets the network, due, we believe, to increased roughening of the surface of the cross-linked substrate.

Polymer networks are important in technological applications ranging from microelectronics to membrane filtration to controlled drug release. One of the methods which may be used for creating a polymer network is based on cross-linking the polymer by exposing it to ionbeam irradiation; the effect of this on bulk properties such as diffusion coefficient, cross-link density, solubility and rheological behaviour has been thoroughly investigated [1]-[5]. Much less is known about the effect of cross-linking on interfacial properties. Related problems of a polymer liquid in contact with a substrate covered by a densely grafted brush or diblock copolymer lamellae of identical chemical structure were recently studied theoretically [6], [7] and experimentally [8]-[10]. An interesting theoretical prediction is that a melt of "infinitely" long chains which is forced to spread into a thin film on top of a surface-attached polymer brush will dewet to form droplets of finite contact angle. This phenomenon termed "autophobicity" was observed experimentally for diblock copolymer subphases [9]. Here we report the wetting behaviour of a polymer melt on a cross-linked network of itself. We find autophobicity to be a sensitive function of the crosslink density —the melt wets the substrate for both low and high cross-link densities, but dewets at intermediate densities. Further we are able to study independently the extent of free-chain/cross-linked matrix interdiffusion, which shows that even in the regime of dewetting at the interface linear chains may diffuse into the matrix.

The polymers studied were statistical random copolymers of ethyl-ethylene (EE) and ethylene (E) monomers, with mean microstructure

$$\begin{bmatrix} (C_4H_8)_{0.14}(C_2H_3)_{0.86} \\ | \\ (C_2H_5) \end{bmatrix}_N .$$
(1)

The chains were synthesized via anionic polymerization of the precursor, unsaturated polybutadiene (PBD) chains, of polydispersities below 1.08. The precursor samples were divided © Les Editions de Physique and each half was subjected to hydrogenation or deuteration (to provide <sup>2</sup>H labeling where required) to the saturated state [11]. In this way the samples within the saturated pair had identical degrees of polymerization. The degree of polymerization was N = 1520, molecular weight  $M_{\rm W} = 8.5 \times 10^4$  and degree of deuteration  $f_{\rm D} = 40\%$  (for the case of the deuterated batch). Samples were kindly donated by Dr. Lewis Fetters.

Polymer layers were prepared by spin casting the polymer from toluene solution (40 mg polymer per ml toluene) onto polished silicon wafers. The resulting thickness was controlled by the spin-casting rotation frequency and was in the range of 200–600 nm. After thorough drying these layers were cross-linked by exposing them to a uniform flux of high-energy (1.2 MeV) alpha particles (<sup>4</sup>He) from a Van de Graaff accelerator [12]. The overall ion fluence was controlled by varying the exposure time t. Films appeared optically smooth before and after irradiation. AFM scans of the surfaces, however, indicate clearly that over smaller scales the cross-linking induces a roughness whose extent increases at higher cross-linking times [13]. Two sets of experiments were carried out: A set of diffusion experiments designed to characterize the properties of the cross-linked matrix, and a set of experiments designed to characterize the wetting properties of the cross-linked matrix/melt interface.

In the diffusion experiments 250 nm thick films of the hydrogenated polymer (h86) were spin-cast on the silicon wafer and then cross-linked by exposing them to the beam for different time intervals t = 8 s, 16 s and 1 min, equivalent to fluences of  $1.9 \times 10^{13}$ ,  $3.8 \times 10^{13}$  and  $1.5 \times 10^{14}$  ions/cm<sup>2</sup>, respectively. A second layer of deuterated polymer (d86) was similarly spin-cast on a piece of freshly cleaved mica, floated off in water and then mounted upon the first cross-linked film to cover it and form a bilayer. The thickness of this second overlay film was 120 nm. The bilayers were annealed under vacuum  $(p = 5 \times 10^{-3} \text{ Pa})$  for 12 h at T = 80 °C. To monitor the diffusion of d86 into the h86 matrix, d86 concentration vs. depth profiles were measured using  $D({}^{3}\text{He}, p){}^{4}\text{He}$  nuclear-reaction analysis (NRA), as described in detail elsewhere [14], [15]. Figure 1 shows typical d86 composition-depth profiles. A non-cross-linked control sample (fig. 1a) shows complete interdiffusion of the d86 and h86 polymers [16], [17]. Cross-linking times as short as 8 s (equivalent to  $1.9 \times 10^{13}$  ions/cm<sup>2</sup>) suppress significantly the interdiffusion of the free chains into the matrix. The modification of the interdiffusion rate between free and cross-linked polymer was already reported by other authors [2], [4], [5]. As the degree of cross-linking is increased, the matrix becomes progressively less penetrable for the deuterated marker chains. The transition from penetrable to non-penetrable matrix has already occurred by the time the matrix was cross-linked for 1 minute (equivalent to  $1.5 \times 10^{14}$ ions/cm<sup>2</sup> of exposure to the ion beam). Control measurements carried out at elevated annealing temperatures and times indicate that the interdiffusion of free chains into the cross-linked matrix is suppressed for radiation dosages above 1 min. Calcagno et al. [2], who observed a similar effect in a different polymer system, relate this remarkable drop in interpenetration to a change of solubility of the cross-linked material. In the limit of low cross-link densities non-cross-linked chains of the matrix polymer can diffuse out of the matrix, enabling chains from the overlay film to diffuse counter-current into the matrix. For higher radiation dosages, such that each chain has at least one cross-link, nearly no chains diffuse out of the matrix —so, non-diffusing chains have to swell the matrix, which causes a large entropy loss, opposing the diffusion [18].

For the characterization of the wetting properties of the cross-linked matrix/melt interface a double-layer configuration was again chosen. On 500 nm thick layers of cross-linked d86, 300 nm thick layers of non-cross-linked d86 were floated. The bilayers were then annealed under vacuum  $(5 \times 10^{-3} \text{ Pa})$  for 12 h at an elevated temperature of T = 120 °C [19]. Visual inspection of the samples exposed to different cross-linking times reveals that samples where the underlying layer of d86 was cross-linked for times in the range 4–32 s the polymer melt dewets on top of the cross-linked film. Samples which were cross-linked for 1 min or longer



Fig. 1. – Volume fraction vs. depth profiles for d86 melt on cross-linked h86 layers after annealing under vacuum  $(5 \times 10^{-3} \text{ Pa})$  for 12 h at T = 80 °C, as recorded by NRA. a) shows the case of a non–cross-linked control sample. The two layers interdiffused completely, resulting in a homogenous distribution of d86 over the whole sample. In the other cases the layer was cross-linked for b) 8 s, c) 16 s and d) 1 min.

show no signs of rupture or dewetting. In fig. 2 we present bilayers where the matrix was not cross-linked (a), cross-linked for t = 8 s (b) and t = 1 min (c). Figure 2d) shows a phase contrast micrograph of the ruptured area of the sample presented in fig. 2b). While the films on top of the non-cross-linked sample (fig. 2a) and the 1 min cross-linked sample (fig. 2c) are flat and homogeneous, macroscopic holes are clearly visible in the film on top of the matrix which was cross-linked for only 8 seconds (fig. 2b), d). In the case of the non-cross-linked sample one expects complete interdiffusion of the two layers, similar to the case shown in fig. 1 a). Control experiments on the effects of longer cross-linking times up to several minutes of the matrix, elevated annealing temperatures and longer annealing periods up to 2 weeks at 120 °C always showed a stable polymer melt layer wetting the matrix. Use of different isotopic combinations made no difference to these observations. These results indicate clearly that the wetting properties of the polymer melt on top of a cross-linked matrix depend on the degree of cross-linking. A re-entrant wetting transition is observed: No cross-linking (or very slight cross-linking) results in complete wetting and interdiffusion, intermediate degrees of cross-linking lead to dewetting of the melt, while a high degree of cross-linking again induces complete wetting.

Our experimental findings may be related to a recent theoretical treatment of wetting of a polymer brush melt by a melt of the same polymer [6]. The model describes the spreading of a *P*-mer on a surface covered by a brush of densely grafted *N*-mers with identical monomers (*i.e.* athermal conditions). The basic assumptions of the model are that the density  $\Sigma^{-1}$  of

 $\mathbf{209}$ 





Fig. 2. – Images of bilayers where the matrix was a) not cross-linked, b) cross-linked for 8 s and c) cross-linked for 1 min after annealing under vacuum  $(5 \times 10^{-3} \text{ Pa})$  for 12 h at  $T = 120 \,^{\circ}\text{C}$ . d) shows a phase contrast micrograph of the ruptured area of the sample presented in b). While the films on top of the non–cross-linked sample a) and the 1 min crosslinked sample c) are flat and homogeneous (characteristic of complete wetting), macroscopic holes are visible in the film on top of the matrix which was cross-linked for 8 seconds (b), d)).

the grafted layer ( $\Sigma$  = area per brush chain) is high enough to form a stretched brush even in the absence of a solvent. In order to determine if the equilibrium state is wetting or partial wetting the theory compares the gain of melt translational entropy which favours the swelling with the loss of conformational entropy due to the stretching of the grafted chains. Enthalpic interactions are neglected by the model. Qualitatively, one expects that for short *P*-mers and long *N*-mers the brush will be solvated and complete wetting is favoured. The other extreme favours partial wetting only. In terms of the effective spreading parameter *S* complete wetting is expected for S > 0 (*S* may be viewed as the change in free energy due to a unit change in the area of the wetting film). The model gives the spreading parameter as

$$S = -\gamma_{\rm AM} + \gamma_{\rm AB} - \gamma_{\rm BM} - k_{\rm B}T \left[\frac{A}{\lambda a} - \frac{B\lambda}{Pa^3}\right],\tag{2}$$

where  $\gamma_{AM}$ ,  $\gamma_{AB}$  and  $\gamma_{BM}$  are the surface tensions, respectively, at the air/melt, air/brush and brush/melt interfaces. The terms in the square brackets account for the loss of conformational entropy of the brush and the gain of translational entropy of the melt, where *a* is the Kuhn length of the polymer, *A* and *B* are constants of order unity, and  $\lambda = (12/\pi^4)^{1/3} (Na\Sigma)^{1/3}$ . The model indicates that a crossover between complete and partial wetting will occur for melt chain lengths  $P \ll P^*$ , where

$$P^* = (N\Sigma/a^2)^{2/3}.$$
 (3)

Complete wetting is expected for  $P \ll P^*$ , and partial wetting for  $P > P^*$ .

Figure 3 shows sketches of the interfacial area between the two layers. In the non-cross-linked case (fig. 3a) chains can interdiffuse freely between the two layers. Cross-linking pins the chains in the layer (fig. 3b), c). Chain ends and loops can stick out of the matrix, but



 $\mathbf{211}$ 

Fig. 3. – Schematic representation of the interfacial area between the two layers. In the non-crosslinked case a) chains can diffuse freely from the lower into the upper layer. Cross-linking pins the chains in the layer (b), c)). Chain ends and loops are pinned by the cross-links within the matrix, forming a brush-like surface. Higher degrees of cross-linking reduce both the effective length N of the brush "hairs", and the mean area per "hair"  $\Sigma$ .

are anchored at the cross-link points, forming in this way a surface reminiscent of a brush melt (with cross-linked loops acting as pseudo-"hairs" on the brush). By varying the degree of cross-linking we decrease the effective chain length between two cross-link points, and so also the length of the "hairs" and the area  $\Sigma$  per "hair". Using now expression (3) from the Leibler model, this implies that  $P^*$  decreases with increasing cross-link density. A change from complete wetting (when no cross-linking or when very slight cross-linking occurs, so that the cross-linked chain moieties are not overlapping) to partial wetting, is predicted as the cross-link density increases, as is indeed observed.

The second crossover back to complete wetting cannot be described by the model. We suggest that, as indicated by our AFM data, this second crossover occurs because the surface of the matrix gets rougher as the cross-linking density gets higher. This leads to an increased surface area of the cross-linked polymer (our "brush"), by a factor  $\alpha$  say. Thus when the melt on top of the cross-linked polymer spreads, so that the smooth air/melt interface changes its area by A say, the cross-linked-polymer/melt and cross-linked-polymer/air interfaces (which are rough) change by an area  $\alpha A$ . The influence of this on the spreading parameter is such as to make it

$$S = -\gamma_{\rm AM} + \alpha(\gamma_{\rm AB} - \gamma_{\rm BM}) - k_{\rm B}T \Big[\frac{A}{\lambda a} - \frac{B\lambda}{Pa^3}\Big].$$
(4)

The first term  $\gamma_{AM}$  is unaffected by the roughening, since it is due to the air/melt interface which remains smooth. The second term corresponds to the energy changes resulting from the increased surface area  $\alpha$  (> 1) of both the air/brush ( $\gamma_{AB}$ ) and the brush/melt ( $\gamma_{MB}$ ) interfaces. The final square brackets is the Leibler term. It should be mentioned that with increasing cross-linking density also N and  $\Sigma$  decrease and so the last (negative) terms of eq. (4) increases; but we expect this change to be small compared with the increase of other roughness-related term (see below). We also expect the increase in roughness to change the magnitude of the two terms in the square brackets (in rather a complicated fashion), but once again the magnitude of these changes is expected to be small and has not been included explicitly.

The essential point concerns the magnitude of the different terms in (4):  $\gamma_{AM}$  and  $\gamma_{AB}$  are very similar to each other, and are easily the dominant terms in S. In comparison to them, both  $\gamma_{MB}$  and the Leibler term (in the square brackets) are negligible, with or without the roughness factor  $\alpha$ . For the case where there is no roughness, as in eq. (2) ( $\alpha = 1$ ),  $\gamma_{AM}$  and  $\gamma_{AB}$  largely cancel each other and then the smaller terms (in particular the Leibler term) are important (and can lead to dewetting). But where  $\alpha > 1$ , the dominant part of eq. (4) is the difference  $(\alpha \gamma_{AB} - \gamma_{AM})$ , which is positive and which for large enough  $\alpha$  swamps all the other terms. Hence S > 0 and the polymer melt spreads. This simple picture of the effect of higher cross-linking via the associated effect of roughness accounts for the second crossover from dewetting (S < 0) to wetting (S > 0).

To conclude, we find that wetting of a cross-linked network by a melt of similar chains depends on the degree of cross-linking. When cross-linking is absent or very low the chains interdiffuse and no dewetting occurs. At higher cross-linking times we observe dewetting, which we suggest is due to the brush-like surface of the network. At the highest cross-linking time the melt again wets the network, due to increased roughening of the surface of the cross-linked material.

\*\*\*

We thank L. J. FETTERS for kindly providing the polymer samples used in this study, and thank P.-G. DE GENNES and F. BROCHARD for a fruitul discussion. We thank the German-Israel Foundation, the Israel Science Foundation, the European Commission, the Ministry of Sciences and Arts (Israel) and the Minerva Foundation for financial support of this work.

## REFERENCES

- [1] CALCAGNO L., FOTI G., LICCIARDELLO A. and PUGLISI O., Appl. Phys. Lett., 53 (1988) 1495.
- [2] CALCAGNO L. and FOTI G., J. Appl. Phys., 71 (1992) 3216.
- [3] CALCAGNO L., COMPAGNINI G. and FOTI G., Phys. Rev. B, 46 (1992) 46.
- [4] CALCAGNO L., PERCOLLA R., MASCIARELLI D. and FOTI G., J. Appl. Phys., 74 (1993) 7572.
- [5] ZHENG X., RAFAILOVICH M. H., SOKOLOV J., ZHAO X., BRIBER R. M. and SCHWARZ S. A., Macromolecules, 26 (1993) 6431.
- [6] LEIBLER L., AJDARI A., MOURRAN A., COULON G. and CHATENAY D., in: OUMS Conference on Ordering in Macromolecular Systems, Osaka, 1994 (Springer-Verlag, Berlin, Heidelberg).
- [7] SHULL K. R., Faraday Discussions, 98 (1994).
- [8] HENN G., BUCKNALL D. G., STAMM M., VANHOORNE P. and JEROME R., Macromolecules, 29 (1995) 4305.
- [9] LIU Y., RAFAILOVICH M. H., SCHWARZ S. A., ZHONG X., EISENBERG A., KRAMER E. J. and SAUER B. B., Phys. Rev. Lett., 73 (1994) 440.
- [10] YERUSHALMI-ROZEN R., KLEIN J. and FETTERS L. J., Science, 263 (1994) 793; YERUSHALMI-ROZEN R. and KLEIN J., Langmuir, 11 (1995) 2806.
- [11] BALSARA N. P., FETTERS L. J., HADJICHRISTIDIS N., LOHSE D. J., HAHN C. C., GRAESSLEY W. W. and KRISHNAMOORTI R., *Macromolecules*, **25** (1992) 6137.
- [12] The cross-linking was done in the scattering chamber of the NRA setup. The beam was defocused to a beamspot with radius 1 cm in order to give a homogeneous beam over the whole sample.
- [13] KERLE T., YERUSHALMI-ROZEN R. and KLEIN J., to be published (1996).
- [14] CHATURVEDI U. K., STEINER U., ZAK O., KRAUSCH G., SCHATZ G. and KLEIN J., J. Appl. Phys. Lett., 56 (1990) 1228.
- [15] KERLE T., LOSCH A., SCHEFFOLD F., SALAMANOVIC R., STEINER U., SCHATZ G. and KLEIN J., to be published (1996).
- [16] This is consistent with the work of Losch *et al.* [17], who measured for T = 23.5 °C a self-diffusion coefficient of  $D = 2.3 \times 10^{15} \text{ cm}^2/\text{s}$  for this kind of polyolefin.
- [17] LOSCH A., SALOMONOVIC R., STEINER U., FETTERS L. J. and KLEIN J., J. Polymer Sci., 33 (1995).
- [18] DE GENNES P. G., Macromolecules, 19 (1986) 1245.
- [19] At low temperatures the dewetting process is much slower than the diffusion process. But for long enough annealing times also at T = 80 °C dewetting could be observed.