Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Temperature Dependent AFM on Ultrathin Oriented Films of FLC Elastomers

H. M. Brodowsky [a] , F. Kremer [a] , E. Gebhard [b] & R. Zentel [b]

[a] Physik anisotroper Fluide, Universität Leipzig, Linnestr.5, D 04103, Leipzig

[b] Fachbereich Chemie, BUGH Wuppertal, Gauss Str. 20, D-42097, Wuppertal

Version of record first published: 24 Sep 2006

To cite this article: H. M. Brodowsky, F. Kremer, E. Gebhard & R. Zentel (1999): Temperature Dependent AFM on Ultrathin Oriented Films of FLC Elastomers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 328:1, 429-436

To link to this article: http://dx.doi.org/10.1080/10587259908026086

Mol. Cryst. Liq. Cryst., 1999, Vol. 328, pp. 429-436
Reprints available directly from the publisher
Photocopying permitted by license only

Temperature Dependent AFM on Ultrathin Oriented Films of FLC Elastomers

H.M. BRODOWSKY[a], F. KREMER[a], E. GEBHARD[b] and R. ZENTEL[b]

[a]*Physik anisotroper Fluide, Universität Leipzig, Linnestr.5, D 04103 Leipzig and*
[b]*Fachbereich Chemie, BUGH Wuppertal, Gauss Str. 20, D-42097 Wuppertal*

Crosslinked ferroelectric liquid crystalline polymers are studied by atomic force microscopy. Polysiloxane copolymers have been synthesized with mesogenic and photo-crosslinkable side groups, the latter connected either directly to the backbone via a short spacer, or as terminal group on a part of the mesogens. These elastomers are prepared as thin freely suspended films in homeotropic orientation. The topography consists of plateaus separated by steps of characteristic height, corresponding to the surfaces and edges of smectic layers. From the temperature behavior as well as from the reaction to mechanical deformation, a model for the network architectures is proposed: In the first case ("intra-layer crosslinking"), a predominantly two dimensional network is formed within the backbone layers separating the smectic layers, in the second case ("inter-layer crosslinking") a primarily three dimensional network is established which is dependent on the mesophase of crosslinking.

Keywords: ferroelectric liquid crystalline elastomers; crosslinking; atomic force microscopy; mechanical deformation

INTRODUCTION

In ferroelectric liquid crystalline (LC) elastomers , the inherent anisotropy leads to an unusual mechanical behavior. In this study, three different FLC-polymers are discussed (fig. 1). The substances have either no crosslinkable group (Pol I), a crosslinkable group attached to the polymer backbone

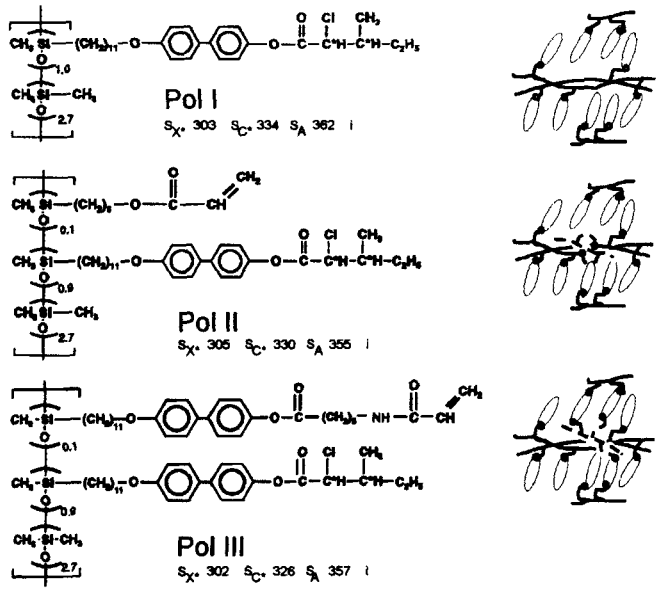

FIGURE 1 Structures of three FLC polymers along with cartoons of the polymers after crosslinking, (acrylate chain dashed).

via a short spacer (Pol II), or a terminal crosslinkable group replacing the chiral endgroup in 10% of the mesogens (Pol III). But for this crosslinkable group, they are identical. The synthesis is described in [1-3] and further characterisations in [4-6]

EXPERIMENTAL

The preparation as freestanding films (fig. 2, steps 1,2, crosslinking temperature 348 K) leads to a homeotropically ordered film typically 200nm thick. It is transferred onto a glass substrate [7] (cf. fig.2), placed on a custom built hot stage [8] and imaged with a commercial AFM (Digital Instruments). For the deformation experiments, the crosslinked film was

either (method A) stretched directly in the drawing aparatus (fig. 2, steps 1-5 affinity controlled by reflection microscopy [9]) and then transferred onto a glass substrate for imaging (as it may not be removed undamaged, a new film must be prepared for every stretching ratio λ) or (method B) transferred over a piezo adjustable gap (fig. 2, steps 3,4B). In this setup, the same area of a film may be imaged for several λ. However, at λ < 10%, the AFM images of the sub-μm suspended films are too blurred to determine any details. For λ< 30%, preparation A is used, the results of methods A and B coincide for λ of 10%-30%. By method B, λ>100% may be studied.

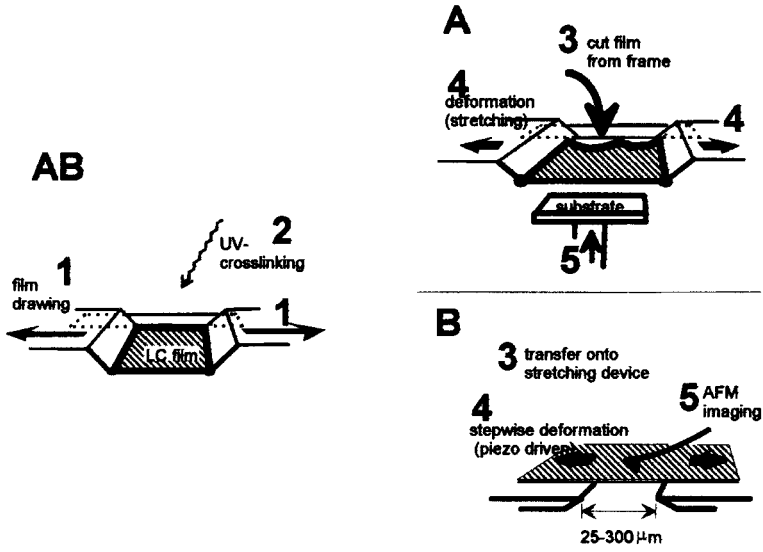

FIGURE 2 Scheme of the sample preparation procedure: 1 Drawing of films[7] 2. UV crosslinking. For mechanical deformation, either (method A) the film is 3 cut loose from the frame edges, 4 stretched via blades and 5 transfered to a substrate for AFM imaging. Alternative preparation B:3 transfer the elastomer film onto a 50 μm gap that may be widened by piezos and 4 image the freely suspended film at various stretching ratios.

RESULTS AND DISCUSSION

Figure 3 shows a typical image of the surface of a transferred freestanding film of Pol I at 295 K. Plateaus with a root mean square roughness (R_{rms}) of 0.5 nm are seperated by steps of multiples of 4.1 nm height. These are interpreted as the surfaces and edges of smectic layers[8]. Above 300 K, they are too soft to be imaged. However, crosslinked films of Pol II and Pol III are mechanically stable enough to be imaged up to 370 K.

In Pol II, the surface is again made up of plateaus (R_{rms}: 0.5 nm) separated by steps (Fig.3 b). If the same area of a film of Pol II is imaged for several temperatures (corresponding to S_C*, S_A, i in uncrosslinked film), no change in the surface topography (roughness or steps) is found. Only the height changes in accordance with the tilt angle. Apparently, an „intra-layer" network stabilises the film without hindering the mesogens[8].

In Pol III, the crosslinkable unit replaces the chiral group in 10% of the mesogens. Here, the step heights show no clear dependence on the mesophase, but rather on the thermal history of the sample: Annealing reduces the layer thicknesses. This indicates that the crosslinked mesogens disturb the formation of the mesophase. The surface topography shows "lumpy" structures about 1.5 nm high (fig. 3), superposed to an otherwise similar surface pattern. This surface morphology specific of the temperature of crosslinking does not disappear during annealing. It is explained by microphase separation effects[8].

The difference in the behavior may be explained by a model of the network architectures [8]: For Pol II, the crosslinking reaction primarily takes place within the (microphase separated) backbone layers („intra-layer cross-linking"). Hence it results in undisturbed phases and a smooth surface morphology. In Pol III, adjacent backbone layers are connected („inter-layer" crosslinking), so network irregularities cause vertical distortions.

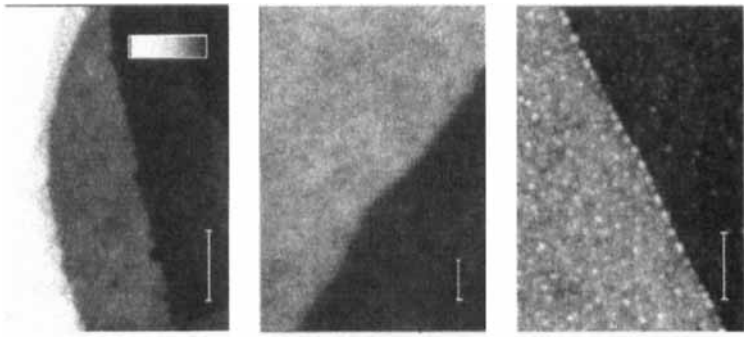

FIGURE 3 Comparison of the surface topography of films transferred onto a solid substrate: a) Pol I, b) Pol II crosslinked at 343K, c) Pol III crosslinked at 353K
(See color plate XXIII at the back of this issue)

For a better understanding of the network architecture, the crosslinked films are stretched [9] (Fig. 2, steps 1-5 A or B). In Pol II, for $\lambda \geq (100 \pm 4)\%$, the aspect of the film is not changed, cf. Fig. 4, the surface remains even (R_{rms} 0.5nm). As the crosslinking takes place predominantly within the backbone layers to form a 2d network with relatively few knots connecting the layers, vertical forces, which would lead to a roughening of the surface, are negligible.

In Pol III, stretching the 3d network leads to a characteristic roughening of the surface (fig. 5). In an undeformed film of Pol III crosslinked at 318 K, the surface is even as for Pol II, and remains so for small λ. However, around λ=12% the onset of a depression pattern is observed: On the same film, an isotropic irregular pattern on a 2 μm length scale is seen as well as areas of unchanged topology, fig 5, b,c. The pattern is not influenced by the edges but passes over them, indicating that it is not an effect of a single layer but of the film bulk. At λ=30%, patterns are seen on all length scales.

For a quantitative image analysis of these topography changes, the surface R_{rms} is determined as a function of the image size: In this way, the

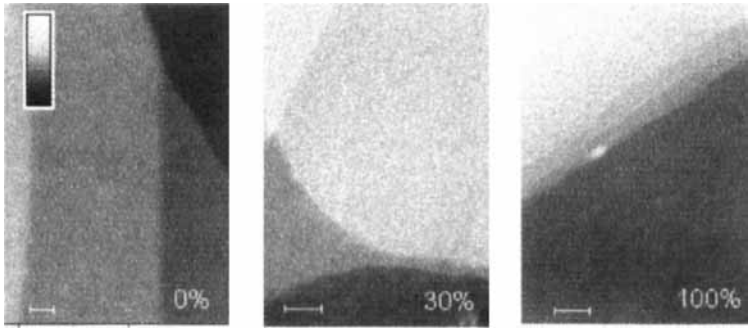

FIGURE 4 Surface topography of stretched (0%, 30%, 100%) films of Pol II. Scale bars 1μm, height scale 25nm valid for all three images. The surface of the film remains even in spite of the mechanical deformation.
(See color plate XXIV at the back of this issue)

length scale on which a roughness occurs can be quantitatively calculated (fig.20). For undeformed films, this R_{rms} is 0.5 nm for images larger than $1\mu m^2$ and diminishes as the size of the image approaches that of the structural details In Pol II, the surface pattern, and therefore the R_{rms} is not changed by the deformation process on any length scale. In contrast, in Pol III, the stretching leads to a change in topology: For λ=12%, there is an additional pattern on a 3μm scale, while on a smaller scale the surface remains unchanged: the R_{rms} calculated on small areas is unchanged but jumps to a significantly higher value for a $5*5\mu m^2$ surface. For λ=30%, the surface is uneven compared to an untreated film on all length scales.

CONCLUSION

To analyze the impact of the molecular structure on the network formation in ferroelectric liquid crystalline polymers, three copolymers are studied,

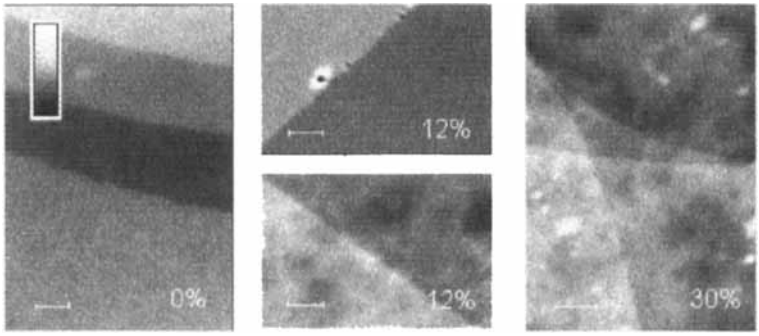

FIGURE 5 Surface topography of stretched (0%, 12%, 30%) films of Pol III. Scale bars 1μm, height scale 25nm valid for all images. The depression pattern caused by the mechanical deformation is evident. (See color plate XXV at the back of this issue)

which are identical but for the molecular position of the crosslinkable group: Pol I without crosslinkable group, Pol II with crosslinkable groups attached to the backbone via a short spacer and Pol III with the crosslinkable group in terminal position of a mesogenic side group. These molecular particuliarities result in distinct network structures: For Pol II, intra-layer crosslinking results in 2d networks in each backbone layer, separated by liquid-like FLC sidegroup layers. In Pol III a 3d network is formed.

When mechanical stress is imposed on thin films in homeotropic orientation by stretching, the two elastomers react differently to the deformation: In Polymer A each layer is stretched, but as there are no vertical connections in this intralayer network, no vertical distortions occur. In Polymer B the system reacts with mesogen and backbone reorientation, as well as, beyond 10% deformation, a distortion of the smectic layering.

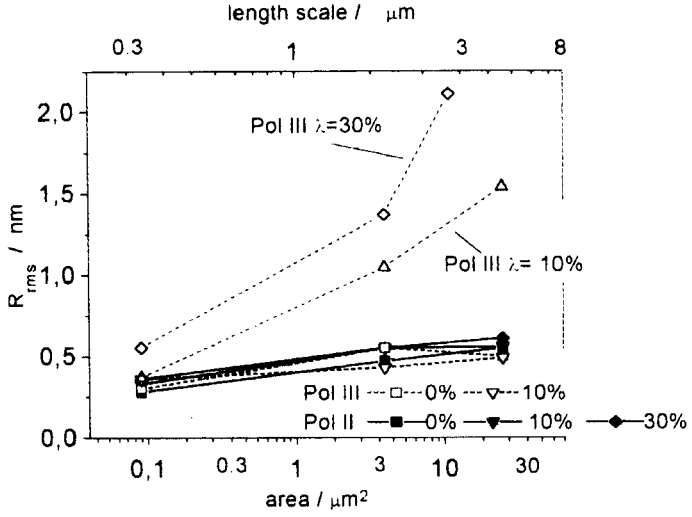

FIGURE 6 Root mean square roughness R_{rms} determined for images of different sizes to characterize the surface patterns resulting from the deformation.

References

[1] A. Kocot, R. Wrzalik, J.K. Vij, M. Brehmer, R. Zentel, *Phys. Rev. B*, 50, 16346, (1994).
[2] M. Brehmer, R Zentel, *Macromol. Rapid, Comm.*, 16, 659, (1995).
[3] M. Brehmer, R. Zentel, G. Wagenblast, K. Siemensmeyer, *Macromol. Chem. Phys.*, 195, 1891, (1994).
[4] M. Brehmer, R. Zentel, F. Gießelmann, R. Germer, P. Zugenmaier, *Liq. Cryst.*, 21, 589, (1996).
[5] S Shilov, H. Skupin, F. Kremer, E. Gebhard, R. Zentel, *Liq. Cryst.*,22, 203, (1997).
[6] S.V. Shilov, H. Skupin, F. Kremer, T. Wittig, R. Zentel, *Phys. Rev. Lett.*, 79, 1686, (1997).
[7] J Mclennan, G. Decher, U. Sohling, *Appl. Phys. Lett.*, 59, 917, (1991).
[8] H.M. Brodowsky, U.-C. Boehnke, F. Kremer, E. Gebhard, R. Zentel, *Langmuir*, 13, 5378, (1997).
[9] H.M. Brodowsky, U.-C. Boehnke F. Kremer, E. Gebhard, R. Zentel in press: *Langmuir* (1998).