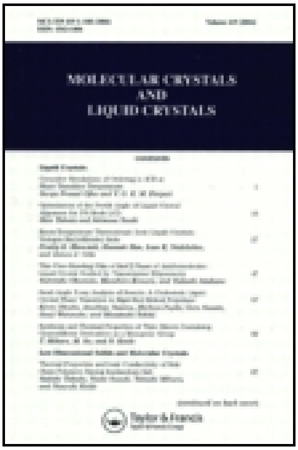

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Shear-Induced Order Effects in Bi-Soft Segment Urethane/Urea Elastomers

M. H. Godinho [a] , J. L. Figueirinhas [b d] , C.-T. Zhao [c e] & M. N. De Pinho [c]

[a] Dept. Ciĕncia dos Materiais and CENIMAT, Faculdade de Ciĕncias e Tecnologia, Universidade Nova de Lisboa, 2825-114, Monte da Caparica, Portugal

[b] Dept. de Física, ICEMS, Instituto Superior Técnico, 1049-001, Lisboa, Portugal

[c] Dept. de Engenharia Química, ICEMS, Instituto Superior Técnico, 1049-001, Lisboa, Portugal

[d] Centro de Física da Matéria Condensada, Universidade de Lisboa, Avenida Professor Gama Pinto 2, 1649-003, Lisboa, Portugal

[e] IRC in Polymer Science and Technology, School of Chemistry, University of Leeds, LS2 9JT, Leeds, West Yorkshire, UK

Version of record first published: 27 Oct 2006

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 447-457

To link to this article: http://dx.doi.org/10.1080/10587250108025324

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 447-457
Reprints available directly from the publisher
Photocopying permitted by license only

Shear-Induced Order Effects in Bi-Soft Segment Urethane/Urea Elastomers

M.H. GODINHO[a*], J.L. FIGUEIRINHAS[bd], C.-T. ZHAO[c†] and M. N. DE PINHO[c]

[a]*Dept. Ciência dos Materiais and CENIMAT, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2825–114 Monte da Caparica, Portugal,* [b]*Dept. de Física and* [c]*Dept. de Engenharia Química, ICEMS, Instituto Superior Técnico, 1049–001 Lisboa, Portugal and* [d]*Centro de Física da Matéria Condensada, Universidade de Lisboa, Avenida Professor Gama Pinto 2, 1649–003 Lisboa, Portugal*

In this work we study shear-induced order effects, observed on thin films (~20–60 μm) of urethane/urea elastomers prepared from a polypropylene oxide based isocyanate terminated triol prepolymer (PU) and polybutadiene diol (PBDO) in the amount of 25% (PU/25PBDO), 50% (PU/50PBDO), 60% (PU/60PBDO) and 75% (PU/75PBDO) by weight of polybutadiene. Optical microscopy and light scattering as a function of temperature were used in this study. The initial isotropic elastomers, PU/60PBDO and PU/75PBDO, after cessation of a uniaxial mechanical deformation relax to a band texture, consisting of equidistant bright and black lines perpendicular to the shear direction. If the uniaxial mechanical stress is applied again perpendicular to the band structure in PU/60PBDO, a new periodicity with wave vector perpendicular to the axis of the field develops, while for PU/75PBDO two new periodicities can be observed, one with wave vector perpendicular to the axis of the field and the other transverse. The process of band formation is completely reversible in cycles of increasing and decreasing strain ratios. In samples PU/25PBDO and PU/50PBDO this kind of effect is not observed. The bands periodicity is temperature independent. The temperature dependence of the scattered intensity produced by the bands is different for bands perpendicular and transverse to the axis of the stress field. We show evidence that the urethane linkage is responsible for the relaxation instabilities observed, in this kind of material.

Keywords: urethane/urea elastomers; shear effects; band textures; bisoft segment; light scattering; optical microscopy

* Author for correspondence: tel.00351212948584; fax.00351212957810; e-mail mhg@mail.fct.unl.pt

† Current address: IRC in Polymer Science and Technology, School of Chemistry, University of Leeds, LS2 9JT, Leeds, West Yorkshire, UK.

INTRODUCTION

It is well known that a translucent polydomain of a liquid crystalline elastomer (LCE) can be converted to an optical transparent monodomain, by action of a mechanical field [1]. This macroscopic behaviour was found recently in a new kind of cross-linked class of urethane/urea polymers prepared with two soft segments – polypropylene oxide and polybutadiene [2].

Usually a uniaxial mechanical deformation of a liquid crystalline elastomer can cause a macroscopically uniform alignment of the director over the whole sample dimensions. By removing afterwards the external mechanical field the liquid crystalline elastomer relaxes to a polydomain structure with an isotropic director orientation [3]. From previous studies it was also found that a common feature to many liquid crystalline polymers and LCEs is the appearance of the so-called band texture upon cessation of flow (see for example ref. [4]).

In this paper we report a new kind of material [2] that macroscopically resembles the behaviour of liquid crystalline elastomers and relaxes showing band textures.

We report results of optical microscopy and light scattering, as a function of temperature for elastomers prepared from a polypropylene oxide based isocyanate terminated triol prepolymer (PU) (M_w=3500) with four different amounts of polybutadiene diol (PBDO) (M_w=2800). The intense scattering exhibited by two of the samples in the relaxed state after stress removal is due to a band texture that develops, with the wave vector parallel to the axis of the initial uniaxial stress field applied. We found that the evolution of the band texture, upon application of a stress field, can show up to 3 superimposed periodicities with wave vectors respectively parallel, perpendicular and oblique, to the axis of the field, depending on the strain and the films' content of PBDO.

The process of band formation, is completely reversible in cycles of increasing and decreasing strain ratios and the recovery time of the elastomers is less than 2 seconds. Observations on the influence of temperature on the band texture are also reported.

EXPERIMENTAL

The polypropylene oxide-based prepolymer, with three isocyanate terminal groups, is designated as PU. It was supplied by Portuguese Hochest, S.A. (an idealised structure is in ref. [5]). The molecular weight is approximately 3500. The polybutadiene diol (PBDO) supplied by Aldrich has a number average molecular weight of 2800 and contains 20-30 wt% vinyl, 10-25 wt.% cis-1,4 and 50-60 wt.% trans-1,4 isomers. The dibutyltin dilauryate (DBTDL) supplied by Aldrich was used as a catalyst. The proanalysis toluene supplied by Merck was used as a solvent.

Prepolymers PU and PBDO, in a weight ratio of 75:25, 50:50, 40:60 and 25:75, respectively, were co-dissolved in toluene, and 1-2 drops of

DBTDL were added. The solid films were prepared according to the procedure described previously [5].

Optical microphotographs were taken using an Olympus transmission polarising microscope equipped with a camera. The mechanico-optical data as a function of temperature was obtained with a green (λ=543.5 nm) helium neon laser equipped optical bench and a stretching apparatus.

The axis of the applied stress field was perpendicular to the laser beam and parallel to the light polarising axis. The small angle light scattering (SALS) patterns were recorded with the help of a CCD video camera. The SALS patterns presented were recorded after the samples had been submitted to a periodic rate of extension with a value of 0.015 s^{-1} in half of the cycle and -0.015 s^{-1} in the other half, reaching a maximum elongation of 1.2. The data was recorded after the samples had experienced at least 30 stretching cycles.

RESULTS AND DISCUSSION

The mechanico-optical characterisation, of the films with a polybutadiene content of 25% (PU/PBDO), 50% (PU/50PBDO), 60% (PU/60PBDO) and 75% wt (PU/75PBDO), was performed using optical microscopy and small-angle light scattering (SALS). These studies were performed as function of temperature for samples exhibiting a band structure respectively PU/60PBDO and PU/75PBDO.

The elastomeric films were all isotropic and slightly translucent prior to the application of any mechanical stress shear field. The PU/25PBDO and PU/50PBDO samples did not show a shear induced orientation after cessation of the shear.

Typical light scattering patterns, for samples PU/60PBDO and PU/75PBDO, can be observed in figure 1, I(a) and I(b), respectively with the samples submitted to elongations of 1.07 and 1.12 respectively. The two-lobe patterns observed, parallel and perpendicular to the axis of the uniaxial stress applied, indicate that two periodicities developed in the films, with wave vector parallel and perpendicular to the direction of the stress field. At low elongations the perpendicular lobes and corresponding periodicity are not present.

The two-lobe pattern, oblique to the direction of the stress field applied, indicates that a third periodicity can also be observed for sample PU/75PBDO. The corresponding textures observed under the optical microscope are shown in figure 1 (II (a) and II (b)).

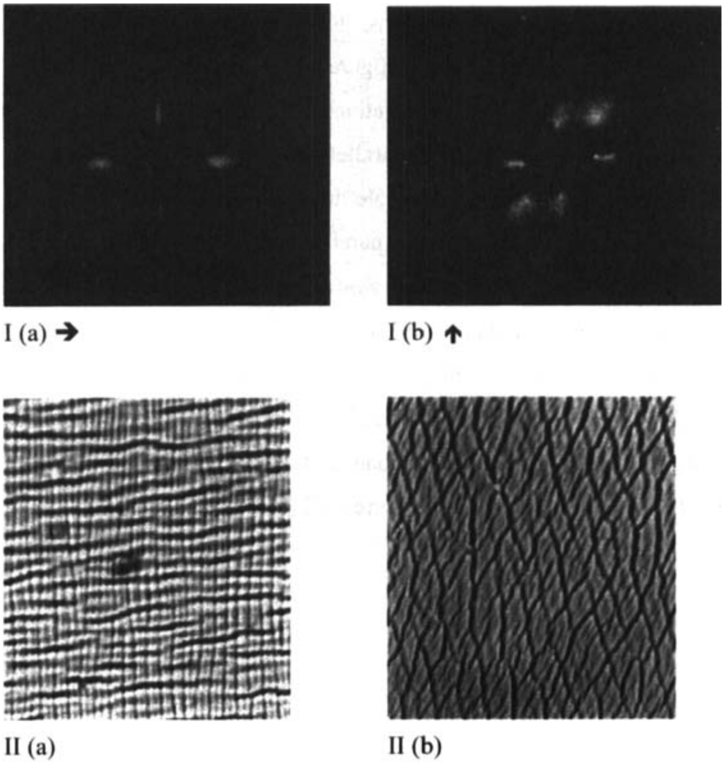

Figure 1 Light scattering patterns (I) developed for (a) PU/60PBDO and (b) PU/75PBDO for elongations equal to 1.07 (a) and 1.12 (b) and corresponding typical banded textures (II) (x 1000). Arrow indicates the shear direction. See Color Plate XXVIII at the back of this issue.

The texture observed for PU/60PBDO consists of long, black, parallel, fine equidistant lines (figure 1 II (a)), perpendicular and parallel to the direction of the axis of the applied mechanical field is well characterised by the results obtained by SALS. For PU/75PBDO a transverse striated pattern can be observed (figure 1 II (b)).

The evolution of the light scattering patterns with temperature, for both samples can be observed in figures 2 and 3. The evolution of textures' associated wavelength and of the scattering intensities, as a function of temperature, is represented in figures 4 and 5, for PU/60PBDO and PU/75PBDO, respectively.

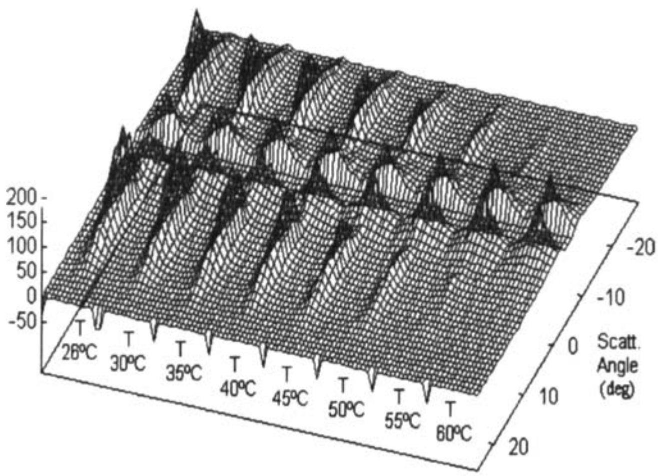

Figure 2 Evolution of light scattering patterns with temperature for (a) PU/60PBDO for elongation equal to 1.01. Data was recorded after the sample had experienced at least 30 stretching cycles.
See Color Plate XXIX at the back of this issue.

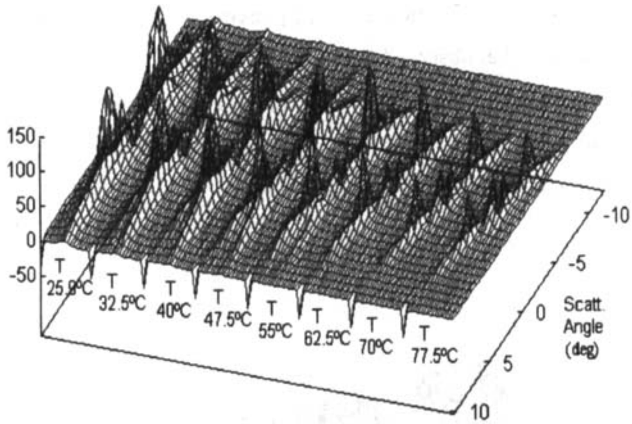

Figure 3 Evolution of light scattering patterns with temperature for PU/75PBDO for elongation equal to 1.05. Data was recorded after the sample had experienced at least 30 stretching cycles.
See Color Plate XXX at the back of this issue.

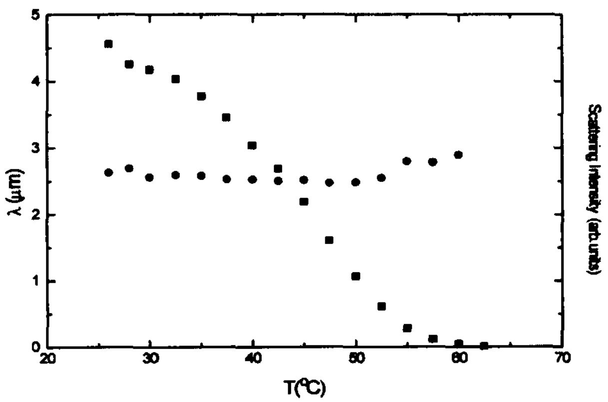

Figure 4 Variation of the scattering intensity (■) and band's periodicity (•), with temperature, for PU/60PBDO.

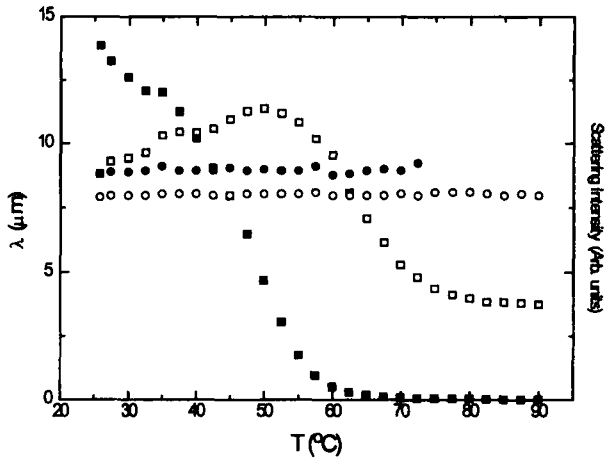

Figure 5 Variation of the scattering intensity (□, ∃) and band's periodicity(•, o), with temperature, in PU/75PBDO for the two periodicities present.

The data obtained for the two samples shows a quite distinct behaviour. The band's periodicity does not change significantly with temperature but the light scattering intensities, for parallel lobes, vanish as the temperature increases. The intensity of the tilted lobes reaches a maximum at 50°C but remains even after the disappearance of the parallel ones.

The band textures, in the relax state, if suppressed with the increase in temperature can be made to reappear at room temperature by submitting the samples to a periodic stretching for a short period of time (few minutes). This behaviour of the mechanical instability is a strong indication of the liquid crystalline nature of these systems.

CONCLUSION

The different results obtained with different amounts of polybutadiene indicate that the presence of urethane/urea is determinant in the developing of the liquid crystalline phase. When the polybutadiene is not enough to react with all the three sites of PU, ureas can form and the liquid crystalline behaviour disappears. When PBDO is in excess, ureas do not form, the liquid crystalline behaviour can be observed but the band texture presents transverse striated patterns. The development of a liquid crystalline structure induced by shear, for this kind of material, from an isotropic state is then strongly depending on the ratio urea/urethane. There seems to be a critical value of the PBDO weight percentage for the appearance of the induced liquid crystalline phase.

The presence of two periodicities in PU/75PBDO for low elongation values with very distinct temperature behaviours points for the existence of two subsystems in this sample where one of them is similar to the system of PU/60PBDO. The temperature dependence of the parallel lobes intensities is, in principle, explainable in terms of the temperature evolution of the viscoelastic parameters of a LCE. For LCE systems an increase in temperature decreases the anysotropies that favour the appearance of mechanical instabilities. The distinct temperature behaviour observed for the transverse lobes seems to indicate that they do not share the same origin as the parallel ones. X ray studies, that are under way, are expected to clarify these aspects.

The mechanico-optical properties observed in these materials may be interesting for use as a device based on a mechanical external applied field. The sample can be switched from a translucent to a transparent state in a reproducible way, by application of a uniaxial stress field.

Acknowledgments

This work was supported in part by PRAXIS XXI Project n° 3/3.1/CEG/2620/95.C.T. Zhao gratefully acknowledges the financial support of the Institute of Science and Engineering of Materials and Surfaces (ICEMS)-Instituto Superior Técnico

References

[1] W. Meier, H. Finkelmann, Condensed Matter News, **1(7),** 15 (1992).
[2] M.H. Godinho, J.L. Figueirinhas, C.-T. Zhao, M.N. de Pinho, "Mechanico-Optical Effects in a Polypropylene Oxide/Polybutadiene Bi-Soft Segment Urethane/Urea Elastomer", to be published.
[3] J. Kupfer, H. Finkelmann, Makromolecular Chem., Rapid Commun., **12,** 717 (1991).
[4] J. Vermont, P. Moldenaers, J. Mewis, S.J. Picken, J. of Rheology, **38(5),** 1571 (1994).
[5] C.-T. Zhao, M.N. de Pinho, Polymer, **40,** 6089 (1999).