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PATTERN FORMATION IN A BI-SOFT SEGMENT URETHANE ELASTOMER

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In the present work we study pattern formation in a bi-soft segment urethane/urea elastomer. The material under study is a film prepared from a polypropylene oxide based isocyanate terminated triol prepolymer (PU) and polybutadiene diol (PBDO) with 60% by weight of PBDO. Small angle light scattering (SALS) patterns were recorded as a function of elongation for different rates of extension. It was found that the process of band and stripe formation is dependent upon the sample elongation and rate of extension with a strong increase of band and stripe amplitude with increasing elongation. The SALS data also reveals that the bands' periodicity is independent of the rate of extension within the range studied.

Keywords: liquid crystalline elastomers; pattern formation; urethane/urea elastomers

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INTRODUCTION

It has been discovered recently [1] that, under appropriate conditions of synthesis, bi-soft segment urethane elastomers can exhibit pattern formation when subjected to a deforming mechanical stress. Two states can be induced in the elastomeric material by the action of a mechanical field [2]. Initially the elastomeric film seems to be isotropic and slightly translucent, but once an external force is applied it becomes transparent (the on-state), further removal of the applied force produces a optically scattering state (the off-state). In the off-state a set of banded textures composed of a periodic pattern (bands) that develops with wave-vector **q** parallel to the axis of the initial uniaxial applied field **F** are observed under a polarising microscope between parallel polars. In the on-state, a periodic pattern (stripes) with the wave-vector perpendicular to **F** can also be observed. The process of band texture formation is completely reversible in cycles. Furthermore, the recovery time of the elastomeric material is less than two seconds. A remarkable aspect of this cyclic process concerns the behaviour and the form of these textures when the mechanical field is switched on and off, with the simultaneous presence of bands and stripes for intermediate sample elongations.

These functional elastomers offer new perspectives of application for preparing mechanico-optical devices because they combine several optical properties that can respond to external conditions.

Here we report the effect of the rate of extension and maximum elongation on the process of band and stripe formation in a solid urethane/urea elastomer film.

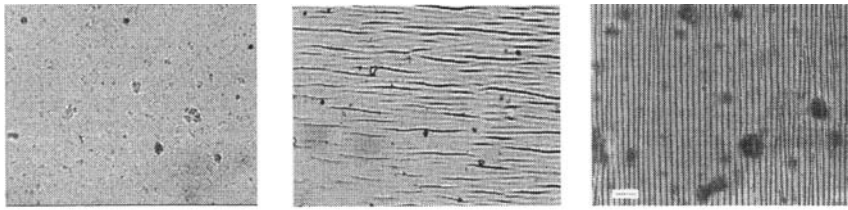

FIGURE 1 Optical microphotographs between parallel polars, for the 40PU/60PBDO film: (a) without application of a mechanical field; (b) for elongation equal to 1.10 and (c) after the application of a mechanical field (the elongation direction is along the white bar that corresponds to 20 μm).

EXPERIMENTAL

The sample was a 100 μm thick film prepared from polypropylene oxide based isocyanate terminated triol prepolymer (PU) supplied by Portuguese Hoechst Co. ($M_w = 3500$) and polybutadiene diol (PBDO) supplied by Aldrich ($M_w = 2800$) containing 20–30 wt% vinyl, 10–25 wt% cis-1,4 and 50–60 wt% trans-1,4 isomers, with 60% by weight of PBDO. The synthesis of this block copolymer membrane was described in literature [3] and additional details are described elsewhere [4].

We report results obtained from optical microscopy and also mechanico-optical data. The optical microphotographs were taken using an Olympus

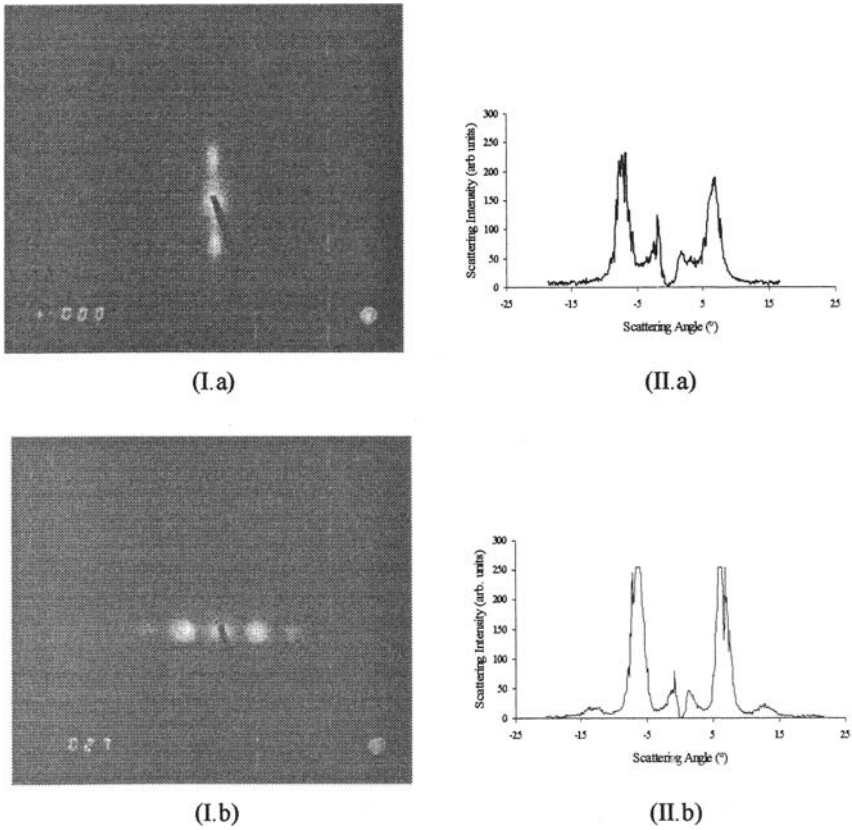

FIGURE 2 Light scattering patterns (I) and intensity profiles (II), from the 40PU/60PBDO film for a rate of extension of $\pm 1.34 \times 10^{-3}\,s^{-1}$: (a) scattering from stripes for the maximum elongation ($l/l_o = 1.20$) and (b) scattering from bands at $l/l_o = 1.01$, when the maximum elongation reached is 1.25.

transmission polarising microscope equipped with a camera. The mechanico-optical data was obtained with a green ($\lambda = 543.5\,\text{nm}$) helium neon laser equipped optical bench and a dynamical stretching apparatus. The axis of the applied stress field was perpendicular to the laser beam. The small angle light scattering (SALS) patterns were recorded with the help of a CCD video camera. The SALS patterns presented here were recorded during and after the sample was being submitted to an extension-relaxation cycle with a rate of extension of $\pm 5.40 \times 10^{-3}\,\text{s}^{-1}$, $\pm 2.70 \times 10^{-3}\,\text{s}^{-1}$ and $\pm 1.34 \times 10^{-3}\,\text{s}^{-1}$, reaching different maximum values of elongation $l/l_o = 1.05$, 1.10, 1.15, 1.20 and 1.25.

RESULTS AND DISCUSSION

Photomicrophotographs of the elastomeric film are presented in Figure 1. Before the application of any mechanical stress field, the elastomeric film appears with no typicall texture associated and is slightly translucent see Figure 1a. When the film is submitted to a stress field ($l/l_o = 1.10$) stripes can be observed see Figure 1b. At rest, after deformation, the 40PU/60PBDO sample shows a banded texture, Figure 1c, consisting of long and black thin lines, perpendicular to the direction of the axis of the previously applied mechanical field.

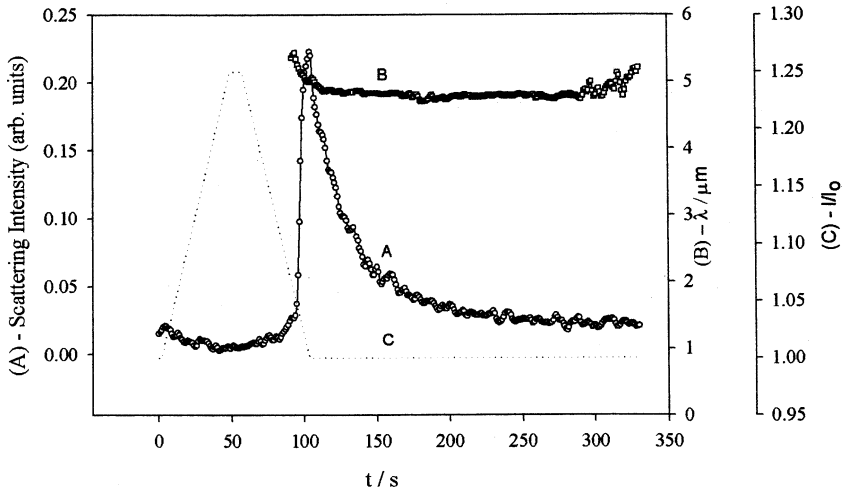

FIGURE 3 Time evolution of scattering intensity (A) and wavelength (B) of bands and sample elongation (C) during and after a deformation cycle for 40PU/60PBDO film. The rate of extension is $\pm 5.40 \times 10^{-3}\,\text{s}^{-1}$ and the maximum elongation reached is $l/l_o = 1.25$.

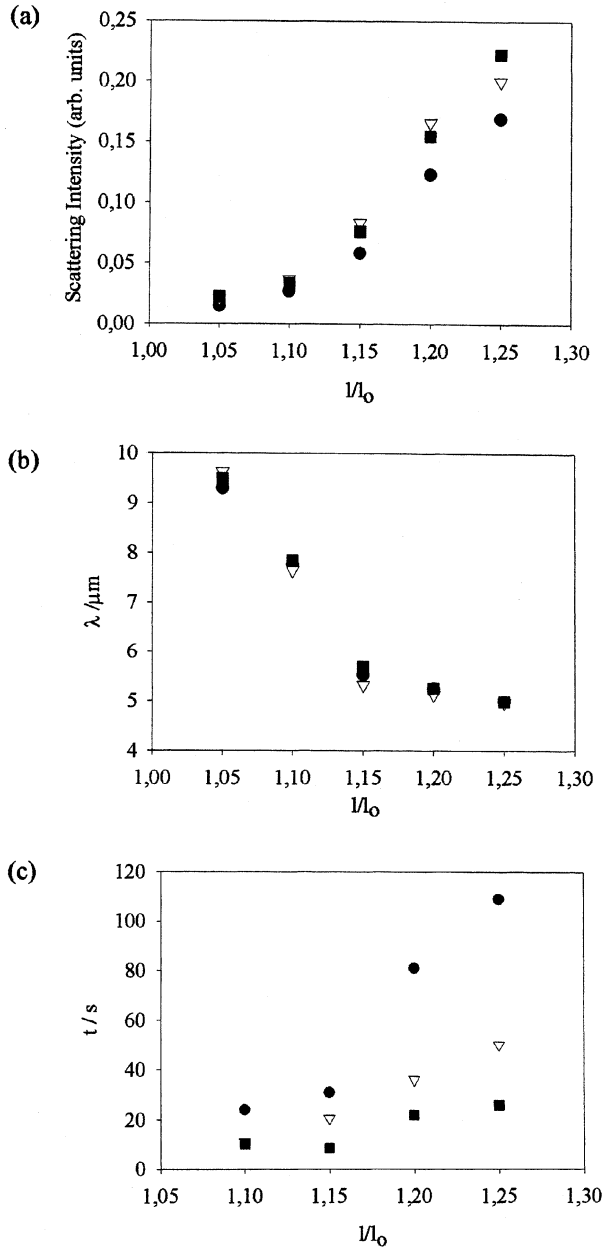

FIGURE 4 Light scattering data obtained for the 40PU/60PBDO film bands versus elongation for three different rates of extension (■ $5.40 \times 10^{-3}\,s^{-1}$, ▽ $2.70 \times 10^{-3}\,s^{-1}$, and ● $1.34 \times 10^{-3}\,s^{-1}$): (a) maximum scattering intensity; (b) wavelength at the maximum band scattering intensity and (c) band relaxation time.

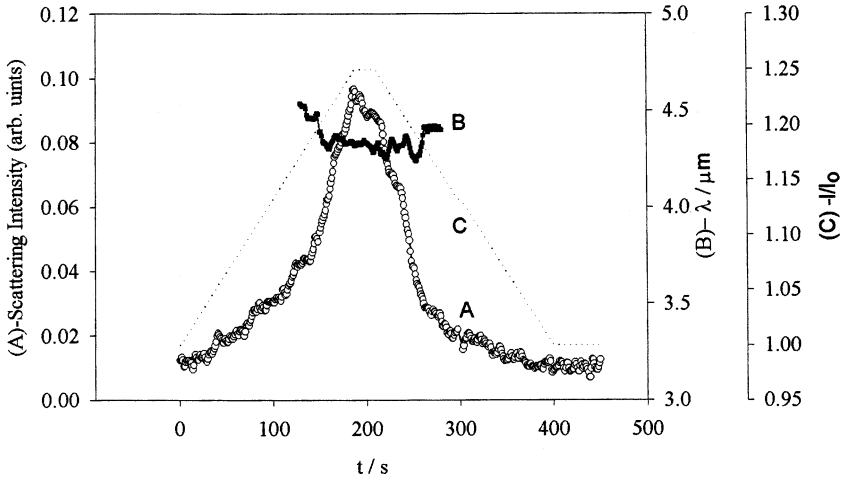

FIGURE 5 Time evolution of scattering intensity (A) and wavelength (B) of stripes and sample elongation (C) for 40PU/60PBDO film. The rate of extension is $\pm 1.34 \times 10^{-3}\,s^{-1}$ and the maximum elongation reached is 1.25.

The dynamical process of band/stripe formation was followed by the SALS technique. Typical light scattering patterns and intensity profiles can be observed in Figure 2. Figure 2a corresponds to the stripe scattering pattern and intensity profile obtained at an elongation of 1.20 in the deformation/relaxation cycle when the maximum elongation is 1.25 at a rate of extension of $1.34 \times 10^{-3}\,s^{-1}$. Figure 2b corresponds to the band scattering pattern and intensity profile at $l/l_o = 1.01$ for the same deformation/relaxation cycle as in Figure 2a. Scattering data from the bands obtained for the 40PU/60PBDO sample as a function of time during the elongation/relaxation process is presented in Figure 3, for a rate of extension of $\pm 5.40 \times 10^{-3}\,s^{-1}$ and a maximum elongation of 1.25. In this figure the evolution of the bands wavelength and scattering intensity during and after the application of the mechanical field can be also observed. Similar data was obtained when the sample was submitted to the rates of extension of $\pm 2.70 \times 10^{-3}\,s^{-1}$ and $\pm 1.34 \times 10^{-3}\,s^{-1}$ and reaching different maximum elongation values (l/l_o equal to 1.05, 1.10, 1.15 and 1.20). From these data we determined the elongation dependence of the maximum scattering intensity, the wavelength corresponding to the maximum band scattering intensity, the relaxation time of the bands and the results appear in Figure 4.

Similar analysis was performed for the stripes' scattering data, the evolution of the scattering intensity and wavelength during the deformation

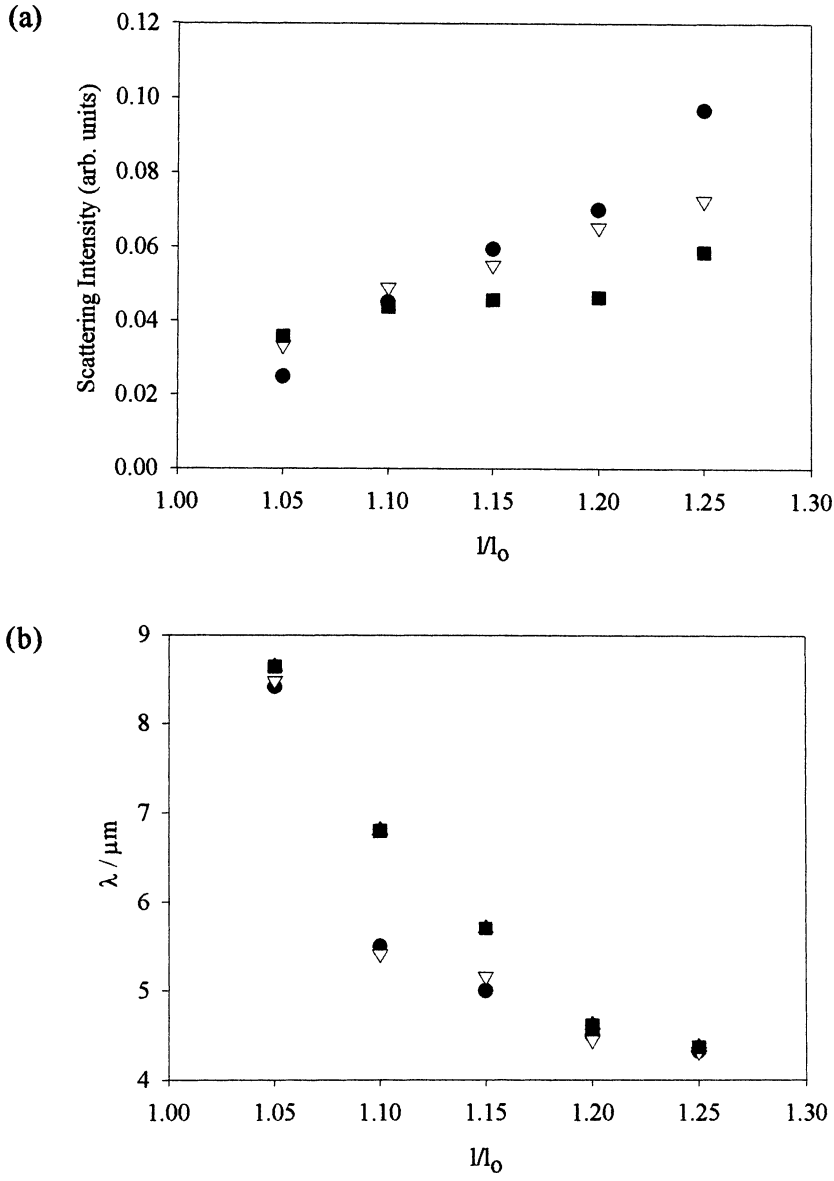

FIGURE 6 Light scattering data obtained for the 40PU/60PBDO film stripes versus elongation for three different rates of extension (■ $5.40 \times 10^{-3}\,s^{-1}$, ▽ $2.70 \times 10^{-3}\,s^{-1}$, and ● $1.34 \times 10^{-3}\,s^{-1}$): (a) maximum scattering intensity and (b) wavelength corresponding to the maximum stripe scattering intensity.

process for three different rates of extension namely $5.40 \times 10^{-3}\,s^{-1}$, $2.70 \times 10^{-3}\,s^{-1}$ and $1.34 \times 10^{-3}s^{-1}$, reaching maximum elongations of 1.05, 1.10, 1.15, 1.20 and 1.25 was recorded. In Figure 5 we present the time dependence of the stripes scattering intensity and wavelength obtained when the sample was deformed at a rate of extension of $\pm 1.34 \times 10^{-3}\,s^{-1}$ and for a maximum elongation of 1.25.

In Figure 6 the elongation dependence of the maximum scattering intensity of stripes and the wavelength corresponding to the maximum stripe scattering intensity is shown for different rates of extension.

The 40PU/60PBDO film optical behaviour is dependent upon both the maximum elongation and the rate of extension. Maximum elongation has a strong effect upon scattering intensity, patterns' periodicity and relaxation time. Regarding the band behaviour, increasing the elongation of the sample increases the scattering intensity and the band relaxation time and decreases the bands' periodicity. Increment of the rate of extension seems not to affect the band periodicity while slightly increasing the scattering intensity and decreasing the band relaxation time. The independence of the band periodicity on the rate of extension can be an indication that the anisotropic elastic properties of the medium are determining the bands periodicity and that dynamical related quantities, such as viscosities, do not significantly affect it [5]. A static model considering the anisotropic elastic properties of the medium may then be sufficient to describe the bands' periodicity. Regarding the scattering intensity and the band relaxation time, a full description of both their elongation dependence and their rate of extension dependence requires a dynamical model for these systems. For stripes the behaviour is similar to the one found for bands except that for the higher elongations the scattering intensity decreases with increasing rate of extension.

CONCLUSIONS

The dynamic behaviour described for the elastomeric film studied is not compatible with isotropic elastomers [5] and implies anisotropic viscoelastic properties. Moreover it also shows that these elastomers belong to the class of systems which, in response to external dynamical actions driving them out of equilibrium, develop transient periodic structures [6,7]. The known elastomers that belong to that class and also exhibit anisotropic viscoelastic properties are liquid crystalline elastomers [8]. The similarities between the dynamical behaviour reported here and that of liquid crystalline elastomers is a strong indication that the theoretical analysis of these results can be made using the models developed for nematic elastomers [9].

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