Macromolecules **2000,** *33,* 7675−7678

Communications to the Editor

Mechanico-Optical Effects in a Polypropylene Oxide/Polybutadiene Bi-Soft Segment Urethane/Urea Elastomer

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Received May 2, 2000
Revised Manuscript Received August 14, 2000

Segmented polyurethanes consisting of sequences of soft segments and hard segments[1] that are thermodynamically incompatible may present, due to their chemical linkage, a phase separation that is not complete and may display segregation in microdomains.[2] The development by Zhao and Pinho[3] of cross-linked urethane/urea polymers with two soft segments, polypropylene oxide and polybutadiene, opened wide horizons on the tailoring of polymer films that display different degrees of phase separation and, associated with that, very different optical and mechanical properties. In fact, the variation of the proportion of the two soft segments gave evidence at the macroscopic level that one could produce very clear films of polypropylene oxide-based prepolymers with three isocyanate terminal groups (PU) and that with incorporation of the more hydrophobic soft-segment, polybutadiene, the films became slightly translucent, indicating microphase separation to some degree. However, with increasing polybutadiene content to above 50%, the membrane transparency became clearer again, suggesting an improvement of the phase mixing degree.[3] The characterization of these films by infrared spectroscopy (IR) and dynamic mechanical thermal analysis (DMTA) confirms that the type and relative amount of the two soft segments introduces different hydrogen bonding environments and different degrees of segregation.

Although the IR spectra are of very complex nature, Zhao and Pinho[3] propose that the increase of polybutadiene content on the bi-soft segment urethane/urea polymers yields the weakening of the hydrogen bonding between urethane/urea groups favoring their freedom and their mixing with polypropylene oxide.

Also the dynamic mechanical thermal properties of the bi-soft segment urethane/urea polymers show a strong stechiometry dependence. Then again, when the polybutadiene content in the films is less than 50%, two peaks appeared in the DMTA spectra, corresponding to the glass transitions of polybutadiene and polypropylene oxide segments, respectively. The two transitions got closer to each other with increasing polybutadiene content, and only one glass transition was observed when this content was equal or higher than 60%. The high dispersion of the two soft segments results even in a molecularly mixed phase for the films with 60% polybutadiene.[3] Associated with these characteristics, these elastomeric films present very specific mechanico-optical effects that are related to liquid crystalline properties and are the subject of this work.

The synthesis of the first elastomers with liquid crystalline properties dates from 1981,[4] and they are obtained by converting a liquid crystalline polymer to a three-dimensional network by a cross-linking reaction. If the cross-linking density is not too high, the anisotropic arrangement of the mesogenic groups is still possible and these materials can combine the rubber elasticity with liquid crystalline properties.[5] The deformation of a liquid crystalline elastomer (LCE) causes reorientation processes of the director of the liquid crystalline phase analogous to the electric or magnetic field effects on low molar mass liquid crystals. In the LCE films referred to in the literature, by action of a mechanical stress a translucent polydomain sample can be converted to an optical transparent one.[6]

The present work reports mechanico-optical effects observed in elastomeric thin films (~60 μm thick) of a bi-soft segment urethane/urea polymer with a polybutadiene content of 60 wt %.

It was found that a mechanical stress induces two states in the elastomeric material, a transparent (on) and a translucent (off) one. The intense scattering exhibited by the sample in the off state condition is due to a periodic pattern (bands) that develops with the wave vector parallel to the axis of the initial uniaxial applied stress. The process of band formation is completely reversible in cycles of increasing and decreasing strain ratios and the recovery time of the elastomer is less than 2 s.

The periodic pattern was investigated by means of optical microscopy and light transmission and scattering.

The PU prepolymer was supplied by Portuguese Hochest, S.A. 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-isomers, and 50−60 wt % *trans*-1,4 isomers. The dibutyltin dilauryate (DBTDL) supplied by Aldrich was

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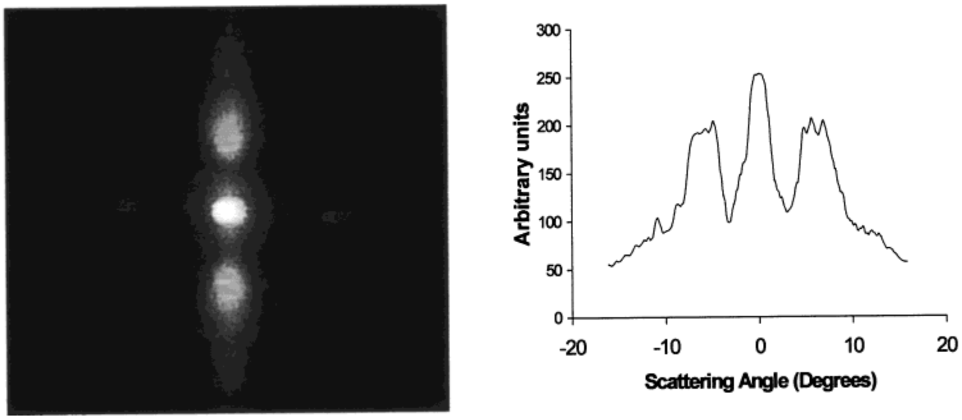
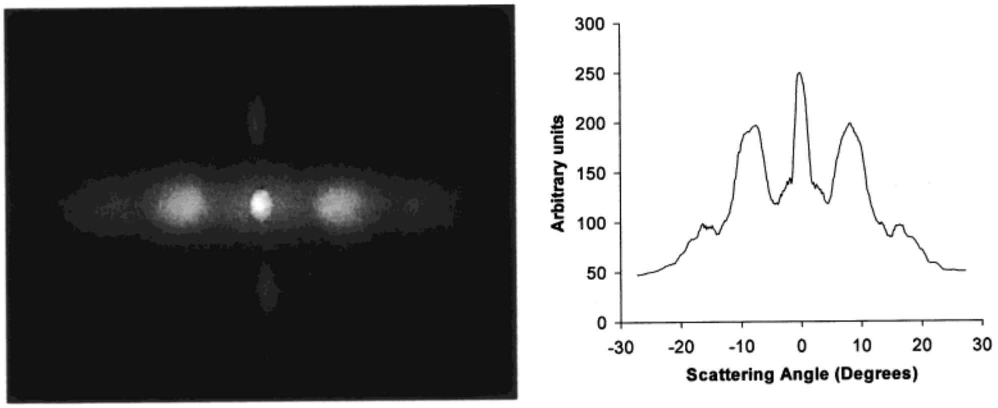
10.1021/ma000755q CCC: $19.00



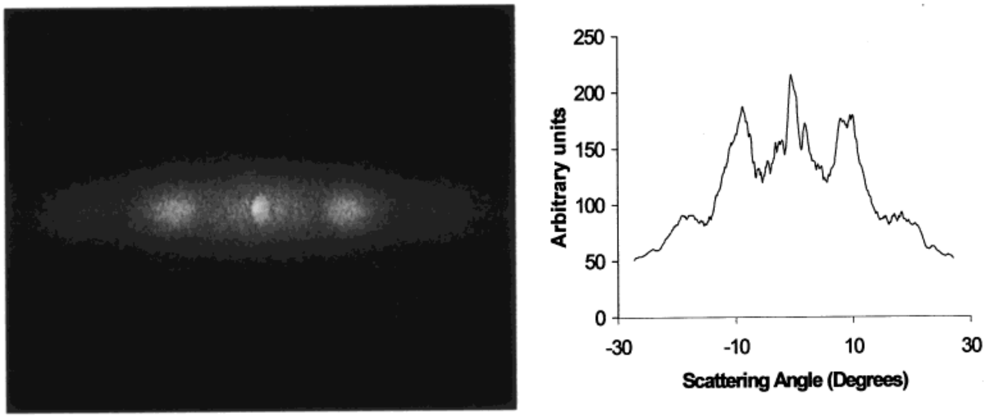
I (a) L/L_o=1.23

II(a)



I(b) L/L_o=1.11

II(b)



I(c) L/Lo=1

II(c)

Figure 1. Light scattering patterns (I) and intensity profiles (II) for the bi-soft segment urethane/urea elastomer with 60 wt % of polybutadiene, for different elongation values: (a) $L/L_o = 1.23$; (b) $L/L_o = 1.11$; (c) $L/L_o = 1$.

used as a catalyst. The proanalysis toluene supplied by Merck was used as a solvent.

Prepolymers PU and PBDO, in a weight ratio of 40:60, respectively, were co-dissolved in toluene, and 1−2 drops of DBTDL were added. The solid film was prepared according to the procedure described previously[3] (an idealized structure of the elastomer appears in this reference).

Optical microphotographs were taken using an Olympus transmission and reflection polarizing microscope equipped with a camera.

The measurements of the mechanical (tensile) properties were carried out on a Rheometric Scientific (Minimat-Firmware Vsn 3.1) testing machine at room temperature. A film sample was cut into pieces with sizes of 5 × 2 cm. Five successful determinations were used to obtain average values.

The mechanico-optical data were obtained with an optical bench equipped with a green (λ = 543.5 nm) helium neon laser and an electronically controlled stretching apparatus. The axis of the applied stress was perpendicular to the laser beam and parallel to the light

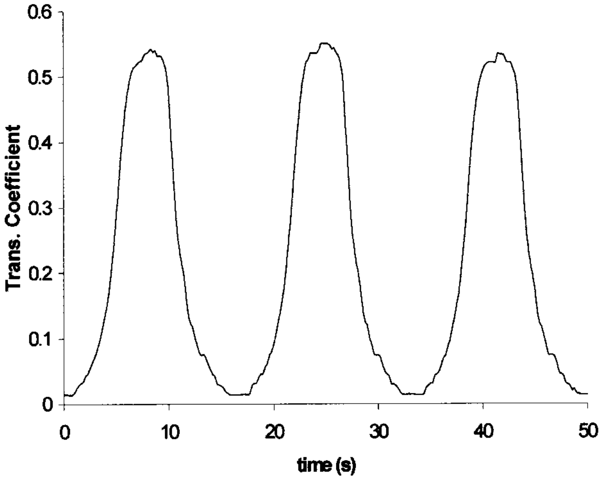


Figure 2. Transmission coefficient vs time, after 100 cycles, for the bi-soft segment urethane/urea elastomer with 60 wt % of polybutadiene. The minimum and maximum transmissions correspond to values of $L/L_0 = 1$ and $L/L_0 = 1.23$, respectively.

polarizing axis. The small-angle light-scattering (SALS) patterns were recorded with the help of a video camera using parallel polarized light. Perpendicular polarized light was also used and identical patterns were obtained. The SALS patterns (Figure 1) and the light transmission curve presented in Figure 2 were recorded while the sample was being submitted to a periodic rate of extension with a value of $+0.0286$ s^{-1} in half of the cycle and -0.0286 s^{-1} in the other half, reaching a maximum elongation of 1.23. The data were recorded after the sample had experienced at least 100 stretching cycles.

Prior to the application of any mechanical uniaxial stress the elastomeric film is isotropic and slightly translucent. If a mechanical stress is applied, at a rate of extension equal to 0.0286 s^{-1}, the extended elastomer, with $L/L_0 = 1.23$ ($(L/L_0)_{\text{fracture}} = 1.6$) and $\sigma = 0.45$ N/mm^2, becomes transparent with a transmittance around 55%.

The transparent stretched film was observed by transmission optical microscopy and it is found to be strongly birefringent with stripes parallel to the stretching axis. To complement the optical microscopy observations, the SALS technique was used to follow changes occurring during the deformation of the film. In the stretched state, a typical light scattering pattern and the intensity profile can be observed in Figure 1, parts I(a) and II(a), respectively. The two-lobe pattern observed, perpendicular to the axis of the uniaxial applied stress, indicates that a periodicity develops, in the film, with the wave vector perpendicular to the direction of the applied stress.

When the mechanical stress is removed the elastomer, as expected, returns to its undeformed dimensions. For $L/L_0 = 1$, between parallel polars, a band structure is observed. This texture consists of long, black, parallel, fine equidistant lines (Figure 3), perpendicular to the direction of the axis of the previous applied mechanical stress. If the film is observed between cross polars there is almost total extinction of light. If the film in this unstretched state is seen under reflection optical microscopy (Figure 4), between parallel polars, colored bands are observed, parallel to the axis of the applied stress. This is due to selective reflection of certain colors by ordered regions acting as a Bragg diffractor.

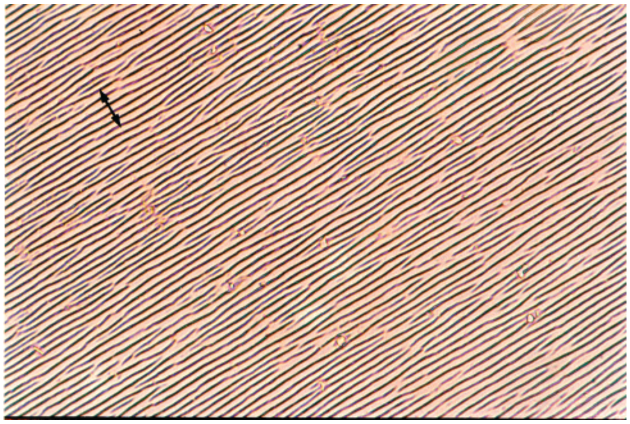


Figure 3. Periodic pattern observed in the bi-soft segment urethane/urea elastomer with 60 wt % of polybutadiene, at rest, after being submitted to one deformation cycle. Transmission light, between parallel polars. Arrow indicates the direction of the axis of the previous applied mechanical field; its length indicates 20 μm.

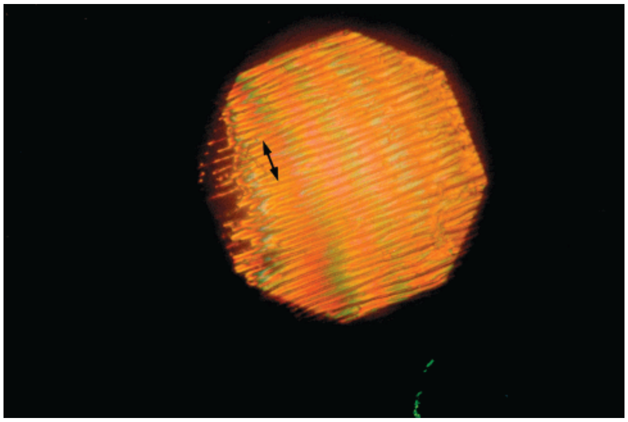


Figure 4. Periodic pattern and colored bands observed in the bi-soft segment urethane/urea elastomer with 60 wt % polybutadiene, at rest, after being submitted to one deformation cycle. Reflection light, between parallel polars. Arrow indicates the direction of the axis of the previous applied mechanical field; its length indicates 20 μm.

The SALS pattern and intensity profile, for $L/L_0 = 1$, are represented in Figure 1, parts I(c) and II(c), respectively. The main contribution is a two-lobe pattern observed in the same direction of the axis of the uniaxial applied stress, indicating a periodicity in the sample with the wave vector parallel to the direction of the previously applied stress. In this state, the sample strongly scatters light with a transmittance equal to 1.4%.

The bands' periodicity is determined, by SALS, to be $\sim$4 μm, in agreement with the value obtained by counting the number of bands, in a microscope photo, within a fixed distance.

If the sample is submitted to a periodic stretching rate of $+0.0286$ s^{-1} in half of the cycle and -0.0286 s^{-1} in the other half, the process of band/strip formation is completely reversible and the sample can be converted from a translucent to a transparent state continuously in time, as can be seen in Figure 2. If the period of the straining cycles is shortened down to 2 s with a maximum deformation of 1.3, the elastomer still follows the driving mechanism during the entire cycle, indicating that the proper recovery time of the elastomer is well bellow that value.

For $L/L_o = 1.11$ the SALS results are presented in Figure 1, parts I(b) and II(b), the four-lobe pattern that can still be seen in this figure corresponds to the transition between bands for $L/L_o = 1$ and stripes for $L/L_o = 1.23$. Under optical microscopy, stripes differ from bands in their orientation, their length, and their width; they are shorter and wider than the bands and only appear in stretched states. Macroscopically, a sample with stripes is transparent while one with bands is translucent.

The macroscopic behavior found in this type of elastomers is the same that can be observed in LCEs: both become transparent upon stretching. At the microscopic level strong similarities are also found. Both show stress-induced stripes and banded structures which are a well-known and almost exclusive characteristic of the liquid crystalline systems.[7,8] The stress-induced stripes and banded structures found in the urethane/urea elastomer are then a strong indication that this elastomer shows liquid crystalline behavior after the initial deformation. The confirmation of this point has however to be obtained by other experimental techniques since the bands found in the urethane/urea elastomer do not behave optically exactly like those in liquid crystalline systems; between crossed polars, they become weakly observable. Such behavior could nevertheless be caused by a low value of the order parameter. This system is also unique since it is isotropic before the induced order sets in after an initial deformation. Preliminary studies, on urethane/urea elastomers with different amounts of polybutadiene, indicate that the effect described in this work is not a typical one for all the amounts of polybutadiene considered.

The observed mechanico-optical properties of this material may render it suitable to be used as a device based on the action of a mechanical stress. The sample can be switched from a translucent to a transparent state in a reproducible way, by application of a uniaxial stress. The characterization by X-ray scattering will be performed to corroborate and complement the SALS patterns obtained; systematic characterization studies are now underway in order to better understand the reported effect.

Acknowledgment. The authors gratefully acknowledge Prof. C. Carfagna for helpful discussions. This work was supported in part by PRAXIS XXI Project No. 3/3.1/CEG/2620/95. C.-T.Z. gratefully acknowledges the financial support of the Institute of Science and Engineering of Materials and Surfaces (ICEMS)-Instituto Superior Técnico.

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