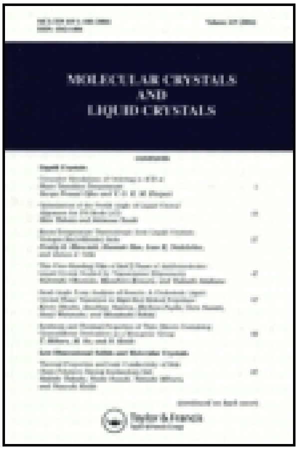

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Effects of UV Radiation on Optical Birefringence of a Polyurethane Elastomer

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Structural changes were induced in a polyurethane elastomer by irradiating the film with UV light and the effects were monitored through birefringence measurements, thermal analysis and infrared spectroscopy. UV irradiation induces two competing effects: i) weakening and breaking of hydrogen bonding between the urethane groups, which improve the mobility of the hard segments and cause the glass transition temperature to decrease; ii) reticulation in the polymer network, causing the glass transition temperature to increase. For short periods of irradiation, up to four hours, breaking of H-bonds predominates and the birefringence increases. Upon further, prolonged irradiation, the effect from reticulation takes over and the birefringence decreases.

Keywords: birefringence; elastomer; hydrogen bonding; polymer

1. INTRODUCTION

Segmented polyurethane have been widely investigated because of their versatility to cover a wide range of mechanical properties. They are composed of soft and hard segments that can be phase separated or

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totally mixed, depending on factors such as the composition, preparation procedure and thermal history. The phase separation is due to the incompatibility of the two types of structural units and is characterized by domains rich in hard segments dispersed in a soft-segment matrix [1–3]. Hydrogen bonding has a stabilizing role in the domains rich in hard segments, and indeed structural changes in these polymers can be directly correlated to weakening or dissociation of hydrogen bonding [1–3]. With infrared spectroscopy it has been shown that the weakening in H-bonding between hard groups in polyurethane polymers improves their freedom and mixing of hard and soft segments.

Different degrees of phase separation have been reported by Zhao and Pinho [1] on urethane/urea elastomer, prepared from polypropylene oxide based isocyanate terminated triol prepolymer (PU) and polybutadiene diol (PBDO). It was noted that the polymer presents two glass transition temperatures, that become only one with increasing content of polybutadiene, for a certain composition. Mechanico-optical effects were also reported for this material [4], consisting of the development of a band texture under a uniaxial mechanical stress accompanied by a change from a translucent to a transparent optical state, denoting an anisotropic character of the polymer. Further experiments have confirmed shear-induced order effects on this urethane/urea elastomer, strongly dependent on the ratio urethane/urea in the polymer [5,6]. A theoretical approach has been recently proposed to explain the non-homogeneous deformation observed in these elastomers [7].

This work is aimed at investigating the anisotropic nature on this urethena/urea elastomer and the relationship between the microscopic structure and the orientational order. The elastomers may suffer structural changes while absorbing UV, particularly in the presence of oxygen, via the so-called photooxidative processes. In general, unsaturated polymers such as rubbers are highly amenable to photo oxidation mediated by free radicals. Here we study the effects from irradiating the elastomer with UV light, and the changes caused in H-bonding between urethane groups are monitored with IR spectroscopy. The effects from UV irradiation on the orientational order were determined by measuring the birefringence induced by a mechanical stress, as a function of the irradiation time. Structural changes were also followed with thermal analysis techniques, by determining the energy absorption ($\tan\delta$) as a function of irradiation time.

2. MATERIAL AND METHODS

The Samples

The polyurethane elastomer is prepared from a prepolymer based on polypropylene oxide with a triol isocyanate terminated (PU and polybutadiene diol PBDO, respectively). The synthesis of the elastomer was performed according to the procedure described in reference [4], using PBDO and PU with average molecular weights of 3500 and 2800, with the relative concentration of 60% in weight of PBDO, The PU was obtained from Hoechst Portuguese and the PBDO is composed of 20–30% of vinil, 10–25% *cis* and 50–60% *trans* 1–4, from Aldrich. For the above composition only urethane groups are present in the final product, as is shown in the schematic representation of the polymer in Figure 1. The samples are self-standing films with thickness varying from 150 to 400 μm with a translucent appearance. However, the films become transparent and optically anisotropic if submitted to a mechanical stress. The absorption spectra of the elastomers were obtained using a UV-vis-IR spectrometer (Cary 500-Scan, Varian) for wavelengths ranging from 190 to 3300 nm. Both, non stressed and stressed films are transparent in the visible with some absorption bands in the UV and IR region.

The films were irradiated with a Hg(Xe) lamp located 1 m apart from the films. During irradiation, the temperature of the samples was kept at 27°C by a water bath controlling system, under atmospheric conditions. At the plane of the films the beam is homogeneous, with a diameter of about 12 cm and incident power of 1.5 mW. With the superimposition of the lamp emission and the film absorption spectra one expects strong absorption by the film in the UV, from 200 to 300 nm.

IR Spectroscopy

The vibration spectra of the elastomer in the infrared region were obtained with a spectrometer (Bomem DA3) coupled to a photoacoustic cell (MTEC-200), with spectral resolution of $4\,\mathrm{cm}^{-1}$. The purging gas was He and a rubber/charcoal composite was used as reference. To characterize hydrogen bonding between the urethane groups belonging to different chains, the analysis of the vibrational spectra is focused in the N–H and C=O stretching vibrations [5]. The measurements were performed at room temperature (~24°C).

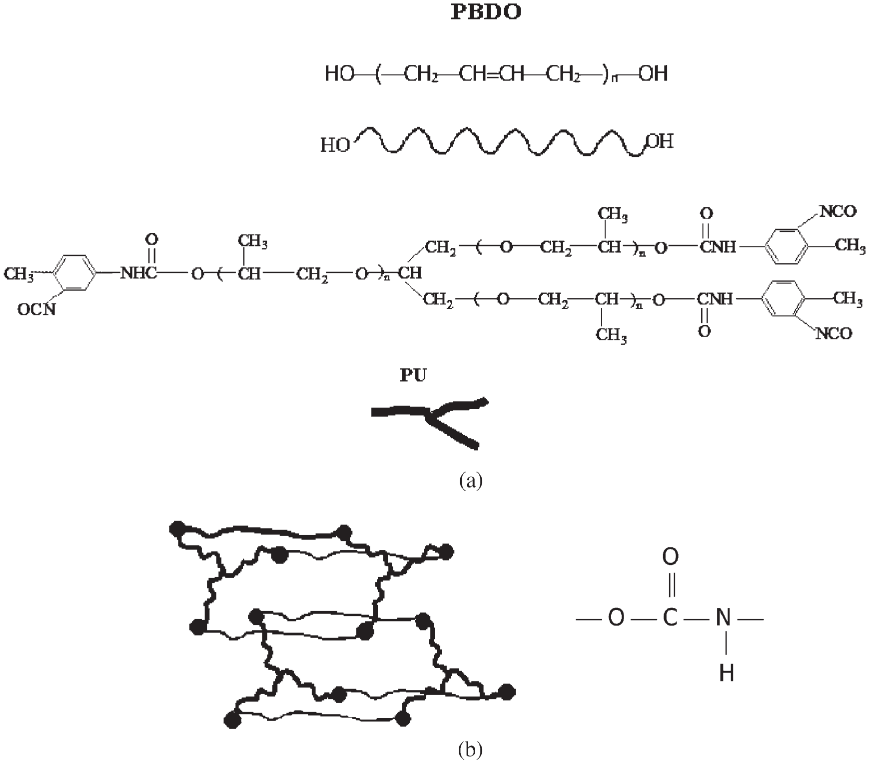


FIGURE 1 Schematic representation of the PU and PBDO segments (a) and of the copolymer PU/PBDO (b).

Thermal Analysis

Thermal analysis techniques were employed to investigate the effects of UV irradiation on the glass transition temperature, degradation temperature and mechanical properties of the elastomers. The degradation process was investigated using thermal gravimetry analysis (TGA). For this experiment platinum pans were used containing ~15 mg of the elastomer in air dynamic atmosphere, with flux of 50 mL min^{-1} and heating rate of 10°C min^{-1}.

The elasticity of the PU/PBDO elastomer was investigated by determining the energy absorption (tan δ) using dynamic mechanical analysis (DMA). The instrument used was a *Netzsch-DMA242*, with a nitrogen cooling system. The experiments were carried out in the temperature range of -80°C up to 55°C, with a heating and cooling rate of 2°C min^{-1}. For these experiments thin films about 8 mm in diameter were superimposed forming a pile about 1 mm thick that was placed in a stage for compression essays, at a frequency of 1 Hz and measurement amplitude of 120 μm.

Birefringence Measurements

The measurements were performed in a polarized optical microscope with a Berek compensator which allows the determination of the optical path difference (Λ) introduced between the ordinary and the extraordinary rays by the elastomers. The birefringence is $\Delta n = \Lambda e$, where e is the film thickness. For these experiments, the films of elastomer were cut with dimensions $5 \times 11\,\mathrm{cm}^2$ and fixed to a sample holder, connected to a micrometer system to stretch the film.

The uncertainty in the calculated birefringence arises from the uncertainty in the film thickness, the positioning of the interference fringe and non-homogeneity of the films. In the birefringence measurements, the films are stretched and become thinner, however it is not possible to directly measure the new thickness simultaneously. Therefore, the thickness depends on the deformation ($\Delta L/L_0$), where L_0 is the natural length of the film and ΔL is the change in length induced by the mechanical stress. The film thickness dependence on the deformation was determined with a micrometer after the birefringence measurements and these values were used to calculate the birefringence.

The interference fringes seen under polarizing microscope equipped with the compensator are very uniform, indicating that a macroscopic domain is induced by the mechanical stress. However, the fringes are thick, pointing to a dispersion in the orientation of the domains rich in hard segments around the direction of the mechanical stress. Together with the uncertainty in the measurement of film thickness, one expects a 5% uncertainty for the estimation of birefringence. Nevertheless, the most important source of uncertainty is the non-homogeneity of the films, which are prepared by shearing the solution containing the copolymer. By measuring the birefringence of non-irradiated films obtained from different pieces of the same batch of material, the total uncertainty in the birefringence was estimated to be around 15%.

3. EXPERIMENTAL RESULTS

IR Spectroscopy

For comparison purposes the photoacoustic IR spectra obtained for non irradiated and irradiated films are shown in Figure 2. The analysis of absorption spectra for irradiated thin films of PU/PBDO elastomers is

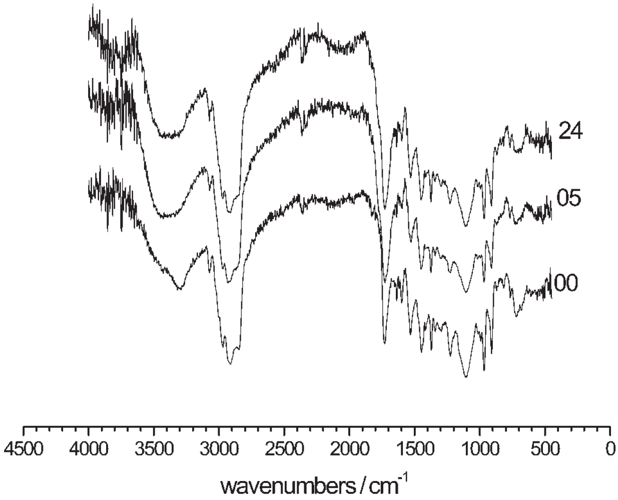


FIGURE 2 Photoacoustic IR spectra of films non irradiated (00), irradiated by 5 h (05) and 24 h (24) by UV light. The spectra are shifted for purpose comparisons.

focused in the changes of hydrogen bonding between the urethane groups. The formation of hydrogen bonds alters the electronic distribution associated with N–H bonds and for the C=O group. Therefore, we are particularly interested in the vibration stretching of N–H and C=O groups, because the hydrogen bonding improve the pairing of the urethane groups reducing their mobility. The stretching vibrations of the N–H groups free from hydrogen bonding appear at 3450 cm^{-1}, while the groups involved in hydrogen bonding have a lower wave number, ranging from 3300 to 3200 cm^{-1} depending on the strength of hydrogen bonding [2,3]. The relatively localized vibrations with the largest potential energy from C=O stretching are usually referred to as Amide I vibrations, which are very sensitive to hydrogen bonding. The vibration stretching band associated with the carbonyl groups have contributions both from free and hydrogen bonded groups and typically the weakening or dissociation of hydrogen bonding shifts the absorption frequency to higher frequencies.

The results obtained from this analysis are shown in Figures 3a and 3b for the N–H and C=O stretching region of the spectra, respectively, as a function of the irradiation time. The UV irradiation shifts the stretching vibration of the N–H groups to higher wavenumbers, as the irradiation time increases. The effect is more pronounced for short irradiation times; up to 4 h, after which a saturation is observed and

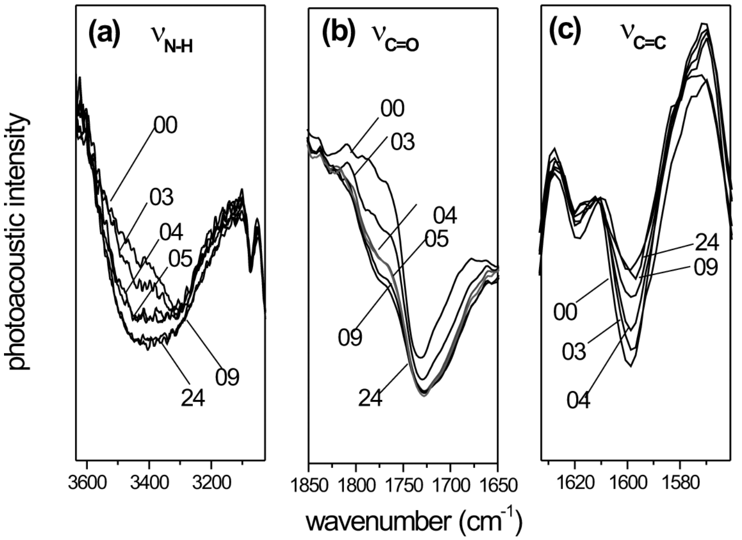


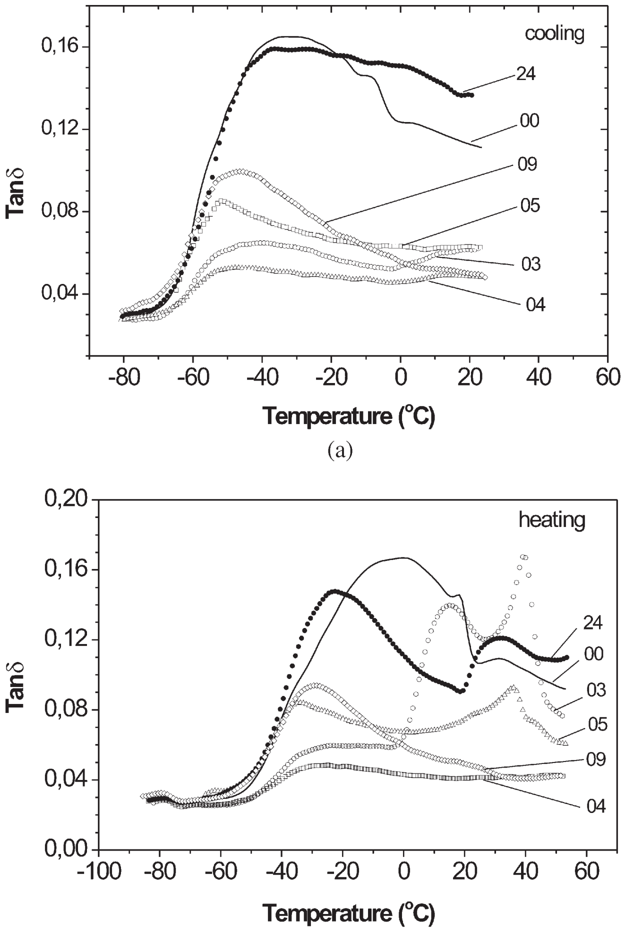
FIGURE 3 Photoacoustic IR spectroscopy results for (a) N−H stretching vibration, (b) C=O stretching vibration and (c) C=C stretching vibration for PU/PBDO elastomer films with different exposures to UV light. The numbers 00, 03, 04, 05, 09 and 24 denote the irradiation time in hours.

no further changes are seen with continued irradiation. The same behavior is observed for the absorption band of the carbonyl groups, where a shoulder appears at higher frequencies when the irradiation time is increased. Again, the effect from irradiation is more pronounced in the beginning of irradiation, in the first 4 h. These results indicate that when the films are exposed to UV light, there is a weakening or breaking of the hydrogen bonding in the urethane groups, which improves the mixing of hard and soft segments domains and the elasticity of the polymer.

Another region of the IR absorption spectra that exhibits significant changes when the polymer is irradiated is shown in Figure 3c and corresponds to the stretching of C=C bonds, with wavenumber in the range 1700–1500 cm^{-1}. Increasing the irradiation time reduces the intensity of the absorption band, at 1600 cm^{-1}, pointing to photo-degradation processes that may increase the reticulation of the network and the oxidation of the polymer. These photo-oxidation processes cause the elasticity and mobility of the segments in the polymeric network to decrease, due to crosslinking. In fact, a visual examination of the films shows that the irradiated films become yellowish and more rigid and brittle.

Thermal Analysis

TGA experiments indicated that the degradation process starts at 253°C for non-irradiated films and at 236°C for a film irradiated for 24 h. The dynamic mechanical thermal analysis curves of the films exposed to UV irradiation are shown in Figure 4 for a cooling cycle from room temperature (Fig. 4a) down to –80°C followed by heating cycle shown on Figure 4b. All curves are shifted toward higher temperatures in the heating cycle due to the reorganization of the polymeric chains in the cooling,



(a)

(b)

FIGURE 4 Dynamic thermal analysis; tan δ (a) for a cooling and (b) heating cycles. The numbers 00, 03, 04, 05, 09 and 24 denote the irradiation time in hours.

which allows for a good packing of both hard and soft segments, thus decreasing their mobility. However, the shift is not accompanied by any significant change in the maximum of the curves at low temperatures, corresponding to the glass transition temperature (T_g). The non-irradiated sample and the sample irradiated for 24 h have similar spectra and absorb more energy than the others in a large range of temperatures, denoting a distribution of chain lengths (or molecular weight). For irradiation times up to 9 h the glass transition temperature is shifted towards lower temperatures and starts to increase again by further exposing the film to UV irradiation. The shift (up to 9 h of irradiation) is accompanied. The weakening and breaking of hydrogen bonding would improve the mobility of the hard segments, favoring their ordering. The breaking of this order could be related to the appearance of the secondary peaks at higher temperatures, which are particularly evident in the heating cycle.

Birefringence

The birefringence of the elastomer PU/PBDO is induced by mechanical stress, which tends to align domains rich in hard segments. The interference fringes in the microscope are thicker than for well-oriented liquid crystals, but they are homogeneous indicating that the mechanical stress induces a macroscopic domain. The measurements were initially performed for a film that was not exposed to UV light, as a function of the deformation ratio, $\Delta L/L_0$. Figure 5 shows

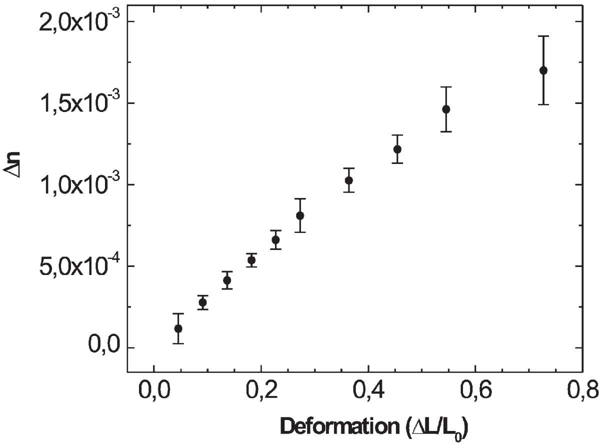


FIGURE 5 Birefringence of a non-irradiated film, as a function of the deformation induced by a mechanical unidirectional stress.

that for small $\Delta L/L_0$, up to 0.3, the birefringence increases linearly, but then the slope of increase is smaller for larger deformations. The birefringence measured, of the order of $\sim 10^{-3}$, is comparable to other elastomers. For the irradiated films, the measured birefringence shown in Figure 6 for various deformation ratios, in spite of the

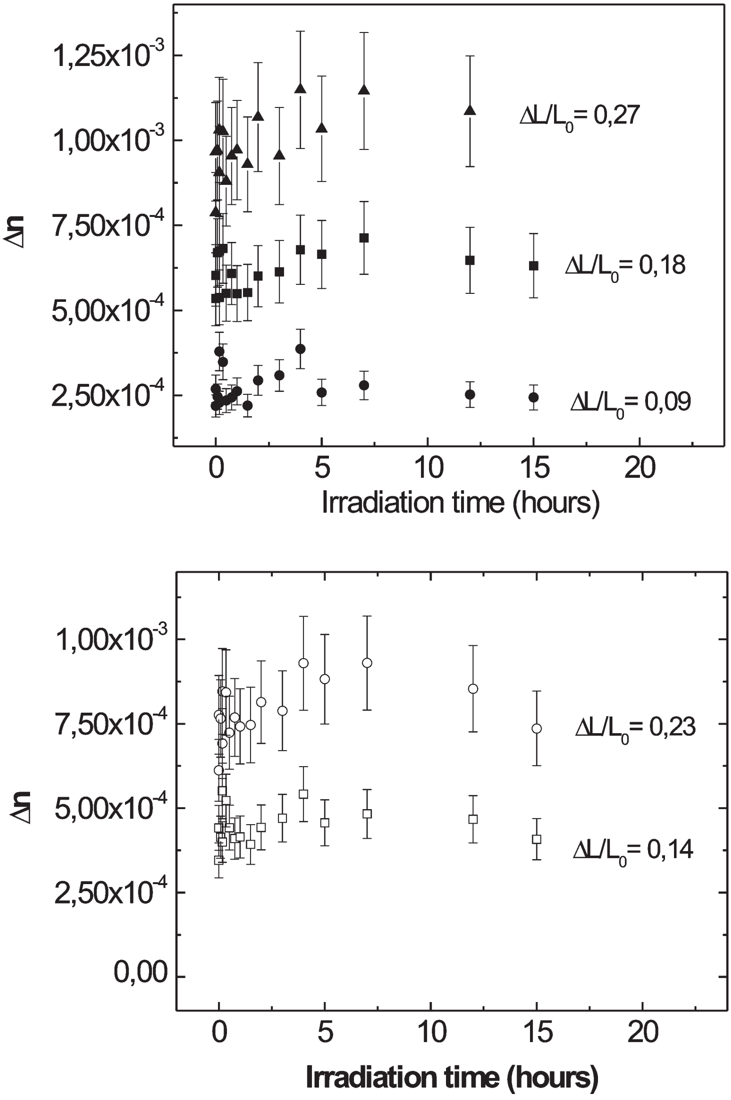


FIGURE 6 Birefringence of irradiated film, for different deformations.

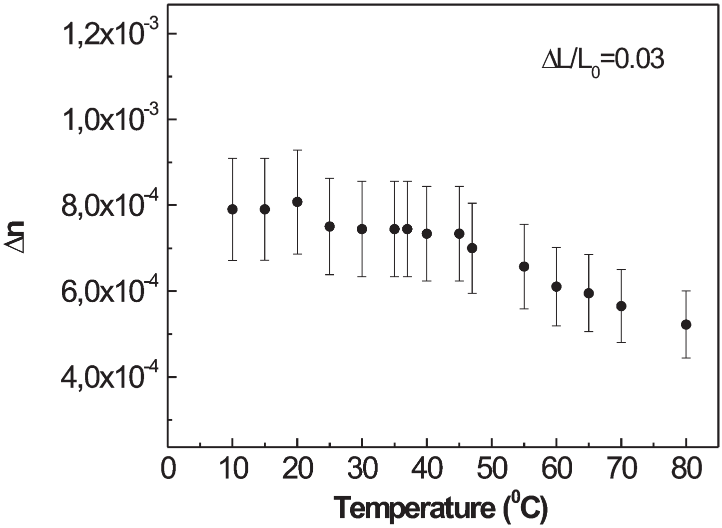


FIGURE 7 Effect of the temperature on the birefringence of a non irradiated film.

fluctuations, tends to increase a little for irradiation times up to 4 h. For longer irradiation times, the birefringence starts to decrease again, returning approximately to the same level of the beginning of the experiment (before irradiation).

The effect of the temperature on the birefringence was also investigated for temperatures ranging from 10 to 80°C. Due to experimental limitations it was not possible to perform these experiments for temperatures close to T_g. The measurements were performed for two values of deformation ratios, $\Delta L/L_0 = 0.05$ and $\Delta L/L_0 = 0.30$. The results for $\Delta L/L_0 = 0.30$ are presented in Figure 7, for a non-irradiated film and a film irradiated for 5 h. Within the uncertainty in the values, the birefringence is approximately constant for temperatures between 10°C and 40°C and then decreases. This decrease in orientational order may be due to disordering of the hard segments, when the sample is heated.

4. CONCLUSIONS

From photoacoustic IR spectroscopy experiments presented above we can conclude that the changes in the vibration stretching frequencies of N–H and C=O groups due to the irradiation of the films with UV light can be related to weakening and breaking of hydrogen bonding in the urethane groups. This is expected to improve the mobility of the hard segments and the mixing of hard and soft segments, thus increasing the material elasticity. These effects are more pronounced for short irradiation times, up to 4 h. On the other hand, the decreasing intensity of the absorption band related to the C=C stretching vibration indicates photo-oxidation processes leading to an increase in crosslinking and rigidity of the polymer. Therefore, there are two competing processes: i) weakening and breaking of hydrogen bonding, which increase the mobility of the segments; ii) photo-oxidation that decreases the freedom of polymeric chains. This is schematically represented in Figure 8, as the mobility of the segments versus irradiation time, where (HB) stands for the breaking of hydrogen bonding and (PO) for the photo-oxidation processes. The superposition of the two processes would initially improve the mobility and then reduce it upon prolonged irradiation.

The DMA analysis indicated that when the sample starts to be irradiated the energy absorption is decreased, denoting that the polymer network becomes more rigid. However, this is accompanied by a tendency of decreasing the glass transition temperature. It is important to note the appearance of secondary peaks for higher temperatures,

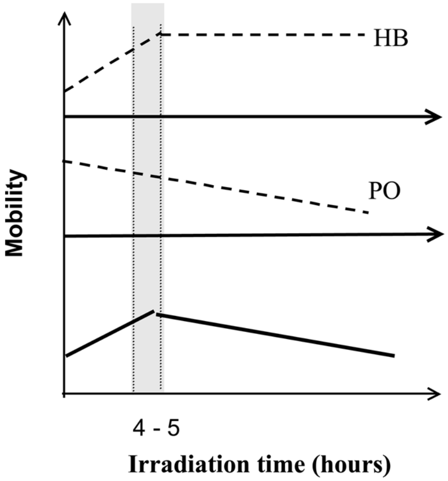


FIGURE 8 Schematic representation of the mobility of the segments in the polymer due to breaking of hydrogen bonding (HB) and photo-oxidation process (PO). The continuous line represents the superposition of the two processes.

clearly observed in the heating cycle, for irradiated samples. These peaks could be related to the disordering of urethane groups favored by the weakening of hydrogen bonding.

Therefore, for short irradiation times, there is a weakening or breaking of hydrogen bonding that increases the mobility of the hard segments, which can be oriented due to the mechanical stress. This would explain the initial increase in birefringence and the lowering of the glass transition temperature, in comparison with the non-irradiated film. However, upon prolonged irradiation, crosslinking hinders the orientation of these segments and the birefringence decreases. Then, the glass transition temperature increases again, and the polymer absorbs more energy than in the less irradiated samples. Experiments of atomic force microscopy (AFM) and electronic microscopy were done to investigate changes in the morphology due to UV irradiation, but they were not conclusive.

In DMA experiments, the fact that the energy absorption and the birefringence of the non-irradiated sample and the sample irradiated for 24 h are very similar, would lead us to say that they are similar. In fact, we think that in the two cases there are interactions that reduces the mobility of the chains, however in non irradiated film, this is due to the hydrogen bonding between the urethane segments that can, eventually, be broken, while in the irradiated film the network reticulation blocks the mobility of the chains. Therefore, the orientational order is a result of the balance between hydrogen bonding and the network reticulation.

REFERENCES

[1] Zhao, C.-T. & Pinho, M. N. (1999). *Polymers*, *40*, 6089.
[2] Lee, H. S., Wang, Y. K., & Hsu, S. L. (1987). *Macromolecules*, *20*, 2089.
[3] Ning, L., De-Ning, W., & Sheng-Kang, Y. (1997). *Macromolecules*, *30*, 4405.
[4] Godinho, M. H., Figueirinhas, J. L., Zhao, C.-T., & Pinho, M. N. (2000). *Macromolecules*, *33*, 7675.
[5] Godinho, M. H., Figueirinhas, J. L., Zhao, C. C.-T., & Pinho, M. N. (2001). *Mol. Cryst. Liq. Cryst.*, *365*, 1403.
[6] Godinho, M. H., Figueirinhas, J. L., Zhao, C.-T., & Pinho, M. N. (2001). *Liq. Cryst.*, *365*, 447.
[7] Trindade, A. C., Godinho, M. H., & Figueirinhas, J. L. *Mol. Cryst. Liq. Cryst.* (in press).
[8] Simões, M. & de Campos, A. (2004). *Phys. Rev. E, 69*, 061704.