Photoresponsive Polyurethane–Acrylate Block Copolymers. II. Photomechanical Effects in Copolymers Containing 6'-Nitro Spiropyranes and 6'-Nitro-bis-Spiropyranes

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ABSTRACT: The photochromic effect of polyurethane–acrylate block copolymers containing 6'-nitro spiropyranes and 6'nitro-bis-spiropyranes has been investigated. The influence of incorporation of the photochromic agent into the polymeric matrix as a simple solid solution or via a chemically bonded form and the effect of the composition rate (polyurethane–acrylate) of the block copolymer were studied. In general, it was observed that the photoresponse (photomechanical effect) for the spiropyranes and, especially, the bis-spiropyranes is influenced by a combination of several factors, primarily, the spatial and electronic differences between the two forms (Sp.–Mer.) in the photoisomerization of these compounds. Such factors are discussed here. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 267–272, 1999

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INTRODUCTION

In light-sensitive polymers containing photochromic compounds, proper irradiation leads to a photoisomerization of the photochrome and, under certain conditions, also leads to conformational changes of the matrix that contains the photochrome. In solution, this effect is reflected in a change of the viscosity properties after the irradiation.[1,2] In solid samples, a change in the macroscopic dimensions and mechanical characteristics of the sample[3–8] is observed.

In the first part of this work, we described the photo-optical response of these materials, where the influence of the electronic and structural properties of the photochrome has an important role, mainly with the bis-spiropyranes, in determining the photo-optical response.

The present report describes the observation and measurement of the photomechanical responses on polyurethane–acrylate block copolymers in which a photochrome (spiropyrane or bis-spiropyrane) has been incorporated in the form of a simple solid solution or in chemically bonded form.

EXPERIMENTAL PROCEDURE

Sample Preparation

The synthetic methodology followed to obtain polyurethane–acrylate block copolymers optically

N-methyl spiropyrane

N-ethanol spiropyrane

bis-decyl spiropyrane

bis-p-xylene spiropyrane

Figure 1 Photochromatic compounds employed in this study.

transparent was described separately in the first part of this series.[9] The synthesis consists of the preparation of a reactive urethane prepolymer terminated with acrylate active groups, followed by a copolymerization reaction, employing an acrylate monomer, which gives the desired polyurethane–acrylate block copolymer.

The photochromic compounds employed in this study are shown in Figure 1 and were synthesized using a novel sonochemistry method, which we already report.[10–12]

Measurement of Photomechanical Response

A tensile tester (Instron Model 5564, 1 KNw load capacity frame) was used to carry out measurements of the photomechanical response at a constant length. Rectangular tensile samples (50 × 10 × 0.5 mm) were cut from the films obtained as described in the previous work of this series, which were stored in the dark for 48 h in order to allow any color to decay. The samples were mounted in the jaws of the Instron, leaving 30 mm of free sample for irradiation purposes. The specimen was loaded with a constant stress load (80 g), allowing 10 min for relaxation.

The sample was irradiated for 5 min with a UV lamp (325 nm) (Model P66100/9 Philip Harris) placed 30 cm away from the sample. In order to remove any heat radiation from the lamp, a heat-absorbing filter was used (Model HG3 Melles Griot, Schott KG glass). Additionally, a thermocouple was placed close to the sample, and the temperature was monitored through the experiment and kept constant at 20 ± 0.08°C. After 5 min of irradiation, the lamp was switched off, and the specimen was left in the dark for another 5 min. Stress changes with time were recorded for each light–dark cycle.

RESULTS AND DISCUSSION

The measurement of photomechanical response was carried out at a constant length on strips of polyurethane–acylate copolymer containing different concentrations of acrylate (72, 50, and 37%) and 1% w/w of physically or chemically blended photochromatic dye in all cases.

A typical response of these polymers systems in a light–dark cycle is shown in Figure 2. On irra-

Figure 2 Typical response for a photoresponsive polymer in a light–dark cycle (sample E73, 72%; bis-decyl spiropyrane).

diation, the initial stress applied to the sample decreases, indicating an expansion of the sample; while in the dark, length recovery takes place by a subsequent contraction, indicated by an increase in stress; the process can be repeated many times.

A rapid response was observed within a few seconds after the UV light was irradiated. The recovery of the sample was similarly rapid. Table I shows the final stress changes (expansion) for all the samples tested; as can be seen, the highest photomechanical response is observed in the sample containing bis-decyl spiropyrane.

A graphical representation for these values is shown in the Figure 3. It can be seen that the larger the acrylate content, the larger the photomechanical response, and the trend for the photochromatic dyes observed was bis-decyl > etha-nol spiropyrane > bis-p-xylene > n-methyl, inducing photomechanical response.

The dependence of acrylate content and the photoresponse observed can be explained in terms of the properties of the homopolymers synthesized in the work. The acrylate is a rigid homopolymer so it can transmit the work more easy than the polyurethane (soft material), which can absorb the work applied by the photochromic transformation.

As a control, polyurethane–acrylate copolymers containing no photochromic agents were subjected to the same photomechanical test. No significant photomechanical response was observed with composition. Figure 4 shows the dependence of stress change versus time for these samples. Only sample E65, 72% shows relaxation behavior with time.

Table I   Stress Change Values of Photomechanical Response (Expansion) for the Samples Tested

Acrylate %	n-Methyl Sample		bis-Xylene Sample		Ethanol Sp. Sample		bis-Decyl Sample	
37	E66	1.34	E72	2.17	E78	2.86	E75	3.1
50	E69	2.13	E71	2.64	E79	3.41	E74	5.34
72	E68	2.36	E70	2.78	E80	4.73	E73	7.54

The numbers are in grams and represent stress changes before and after irradiation.

Figure 3 Graphical representation for the photomechanical response.

With 72% acrylate content, the sample shows a plastic behavior with a relaxation tendency along time, and a plastic material can transmit the work applied on it by deforming. However, the materials containing 50 and 37% acrylate show an elastic behavior. Therefore, the work done (photomechanical effect) by the photochromic agent on the polymer matrix would induce more deformation in plastic material than an elastomers, as observed in Figure 3.

Smets and De Blauwe,[13] tested polymers crosslinked with bifunctional photochromic compounds observing photocontraction behavior, which was attributed to the entropy increase of the system, due to the higher flexibility of the merocyanine (open ring) compared to the stiffness of the sp3 spiro carbons in the spiropyrane form (closed ring).

In contrast, Blair and Pogue[14] reported a photoexpansion in samples with photochromic mate-

Figure 4 Photomechanical response for polyurethane–acrylate (control) at different concentrations of acrylate (the light was switched on at 10 min).

Table II Maximum Values of Volume Obtained by Computer-Based Modeling for Spiropyranes and Merocyanines

Compound	Spiropyrane	Merocyanine	Difference
N-Methyl	431.43	280.56	150.87
N-Ethanol	440.67	275.69	164.98
bis-*p*-Xylene	1087.30	734.66	352.64
bis-Decyl	1462.13	1199.89	262.24

The numbers represent $Å^3$.

rial just incorporated in the form of a simple solid solution. Using the Smets theory, they consider the transformation of the photochromic species involved in the photomechanical process to induce a decrease of entropy. They conclude that "the spiropyrane molecule has a comparatively bulky structure when compared with the planarity of the merocyanine molecule. The disturbance resulting from the presence of a spiro molecule will be greater than that resulting from a planar merocyanine molecule. Hence, a conversion from the spiro structure to the planar merocyanine will result in an overall decrease in entropy of the system since the polymer molecules will be allowed to pack close together."

In our experiments and from the volume calculations (Table II) obtained by computer-modelling,[15] it was assumed that the bis-*p*-xylene would induce more spatial disruption in the polymer matrix, as the transformation from spiropyrane to merocyanine reflect more spatial changes (352 $Å^3$); therefore it could be reasoned that it would induce the greatest photomechanical effect. However, Figure 3 shows that the greatest photomechanical response (expansion) is observed for bis-decyl spiropyrane. The spatial disruption is not the main driving force for the photomechanical effect in this case.

There are two postulated mechanisms for photomechanical response, which, put together, can explain the photochromic effect seen in this work. The first, postulated by Lovrien,[16] suggests that if a polymer interacts with some photochromic chromophore, it may undergo a conformational change when irradiated because the interactions between the polymer and the chromophore change.

The second, which was postulated by Matejka et al.[17] and Irie and Suzuki,[18] suggest that some photochromic molecules have a big dipolar moment; hence, they tend to orient parallel each others, so-compact coil conformations are preferred. Hence, some reduction in the entropy of the system will bring about an expansion in the sample.

From the theoretical energy calculation, the bis-decyl showed the biggest dipolar moment (45.4 Debyes) compared with bis-*p*-xylene (27.9 Debyes). The charge–charge interaction shows the same trend, as follows: -88.1 Kcal for bis-decyl and -79.8 Kcal in the bis-*p*-xylene case.

Taking this into account, it is possible that bis-decyl having less spatial disruptance (262.24 $Å^3$) compared with bis-*p*-xylene (352.64 $Å^3$) has given the greatest photomechanical response, according to the two postulated mechanisms mentioned above.

The ethanol spiropyrane showed a bigger response than the bis-*p*-xylene and *n*-methyl spiropyrane. Irie et al.[19] reported that polymers having pendant groups of spiropyrane shrinks. Using the second postulated mechanisms (formation of strong dipoles), Irie et al. suggest that the intramolecular attractions between the pendant merocyanine in the polymer chain overcomes compact conformation coils.

However, according to the theory of Smets,[13] a compact conformation arrangement of the polymer chains would reflect a diminished entropy of the system, so an expansion of the sample would be expected. If, by some reason, the sample suffers an increase in temperature, the entropy would increase, and a shrinkage of the sample would be observed.

According to the second mechanism mentioned above[17,18] and the theory of Smets, the ethanol spiropyrane sample should show an expansion on irradiation because of the decrease in the entropy of the system. However, the response is no greater than that shown by bis-decyl spiropyrane, so it seems that there is a compromise between the dipolar formation, spatial disruptance, and the effect obtained by attaching the photochromic material to the backbone.

CONCLUSION

The general observations that (1) the higher the acrylate content into the copolymer, the higher

the photomechanical response, and that (2) rigid homopolymers can transmit more easily the work than soft materials have been established. Also, it was demonstrated that the spatial disruption generated by the phototransformation of the photochrome is not the main driving force for the photomechanical effect observed here. It is important to take into account the stereoelectronic interactions between the polymer matrix and the photochrome, especially in the merocyanine form.

From this study, it was concluded that an ideal photochromic spiropyrane for inducing a large photomechanical effect would be such that it exhibits big spatial disruptance and high formation of dipoles in the merocyanine form and will preferably be bonded to the polymer backbone.

This can be done readily by computer modelling in order to establish the properties of the molecule in both forms (spiro and merocyanine), helping to understand, predict, and even anticipate the photomechanical behavior of such compounds into a determinated polymer matrix.

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