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

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Received 7 December 1997; accepted 7 June 1998

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 in a chemically bonded form and the effects of the composition (polyurethane–acrylate) of the block copolymer were studied. In general, it was observed that the photoresponse for the spiropyranes and especially the bis-spiropyranes obey the combination of several factors, mainly 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: 259–266, 1999

Key words: photoresponsive polymers; photo-optical effects; photochromism; polyurethane–acrylate block copolymers; photochromic spiropyranes; bis-spiropyranes

INTRODUCTION

A large number of organic and inorganic materials that exhibit photochromism have been know for many years;¹ such materials have been applied in many areas of the technology, including as dosimeter materials, light control filters, recording films in photography, and decoration paint.

Now the optical technology has raised interest in these photoresponsive materials, application in three-dimensional optical storage memory and lasers devices^{2,3} or infrared sensitive spiropyranes,⁴ are now the focus of the investigation in this field.

Photochromism is the phenomenon whereby the absortion spectrum of a molecule or crystal changes reversibly when the sample is irradiated by light of a certain wavelength. A colorless compound A changes its structure to a quasi-stable colored structure B when irradiated by ultraviolet (UV) light; B can be returned to the colorless compound A by exposure to visible light or heating (see Fig. 1).

When such photoisomerization reaction is carried out in a polymer matrix instead of in solution, a strong decrease in the reaction rate (coloration = decoloration) is observed.⁵ The polymeric effects are more strongly pronounced when the photochrome is chemically bonded to the polymer matrix; such an effect has been attributed to the reduction of chain segment mobility.^{6,7}

The following two general types of measurements have been carried out on the fading of spiropyranes: One, called long-time scale (from tenths of seconds to hours) kinetic behavior, has been performed on slightly viscous solutions at

Correspondence to: E. A. Gonzalez-de los Santos. Journal of Applied Polymer Science, Vol. 71, 259–266 (1999)

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$$A \xrightarrow{hv} B$$

Figure 1 Schematic representation of photochromic phenomenon.

room temperature; the second one has been performed in highly viscous media at low temperature and during time intervals less than 1 s. Such experiments show the kinetic behavior on a shorttime scale. However, the long-time studies take into account the structure of the molecules and correspond to the potential applications of photochromism. These long-time fading rates are in aggrement with a first-order kinetic law.⁸

The present report describes the observation and measurement of the photo-optical 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 chemically bonded. The interesting photomechanical behavior observed in these systems will be analyzed and discussed in the second part of this series.

EXPERIMENTAL PROCEDURE

Synthesis of Photochromic Compounds

In a recent report,^{9,10} we described the novel synthesis of spiropyranes and bis-spiropyranes compounds employing ultrasound as the energy source to promote the condensation reaction between the indoline or the bis-indoline and the desired salicylaldehyde, as well as the potentiality of the method, which offers advantages over the conventional method.

Because the synthesis of spiropyrane compounds is difficult, the reaction rates are slow, and the purification of the products is tedious, the new method of synthesis described using sonochemistry provides an excellent route for the synthesis of such compounds at reasonable rates of reaction and in good yields; hence, the process offer a profitable alternative compared with others synthetic methods.

As already was mentioned, the photochromic compounds employed in this study were synthesized using the novel ultrasound method and are shown in Figure 2.



bis-p-xylene spiropyrane

Figure 2 Photochromatic compounds employed in this study.



POLYURETHANE-ACRYLATE (A-B-A) BLOCK COPOLYMER

Figure 3 Chemical reactions for the synthesis of polyurethane–acrylate (A-B-A) block copolymers.

Synthesis of Polyurethane–Acrylate Block Copolymers

The synthetic methodology followed to obtain polyurethane–acrylate block copolymers that are optically transparent is described in Figure 3. The synthesis consists of the preparation of an urethane prepolymer terminated with acrylate active groups, followed by a copolymerization reaction employing an acrylate monomer, which gave the desired polyurethane–acrylate block copolymer. All the chemicals were supplied by Aldrich Chemical Co. (Milwaukee, WI).

Synthesis of Urethane-Acrylate Prepolymers

Hexamethylene diisocyanate (HDI, 28.8 mL, 30 g, 0.178 mol, 2 eq wt) was placed in a

QUICKFIT wide-neck reaction vessel, then 2-hydroxyethyl-acrylate (HEA, 20.1 mL, 20.4 g, 0.178 mol, 1 eq wt) was added dropwise under a nitrogen atmosphere with mechanical stirring. The reaction temperature was kept at 45°C for 30 min to avoid thermal polymerization through the vinyl groups. After such time, a noticeable peak at 1526 cm^{-1} assigned to the absortion of urethane groups remains constant, indicating that the reaction was ended. When the temperature of the reaction mixture started to drop, a stoichometric quantity of dry polypropylene glycol (PPG), MW 725, hydroxyl number 147 mg of KOH/g (67.4 mL, 67.8 g, 1 eq wt) was added along with dibutyl-tin-dilaurate catalyst (0.674 mL, 0.678 g, 1% wt). The mixture was heated to 70°C and stirred for 2 h to complete

Sample ID	Acrylate Content ^a	Prepolymer ^b	MMA ^c	$\operatorname{AIBN^d}$	Photochromic ^e Agent
Control:					
E77	72	4.46	3.41	0.0957	_
E76	50	6.38	3.41	0.0957	_
E65	37	8.68	3.41	0.0957	_
Methvl:					
E68	72	4.46	3.41	0.0957	0.0796
E69	50	6.38	3.41	0.0957	0.0957
E66	37	8.68	3.41	0.0957	0.120
Bis-benzyl:					
E70	72	4.46	3.41	0.0957	0.0796
E71	50	6.38	3.41	0.0957	0.0957
E72	37	8.68	3.41	0.0957	0.120
Bis-decvl:					
E73	72	4.46	3.41	0.0957	0.0796
E74	50	6.38	3.41	0.0957	0.0957
E75	37	8.68	3.41	0.0957	0.120

 Table I
 Formulations Employed in the Synthesis of Polyurethane–Acrylate (A-B-A) Block

 Copolymer, Where the Photochromic Material Was Incorporated as a Solid Solution

 $^{\mathrm{a}}$ The acrylate monomer content (MMA) is in wt % with respect to prepolymer.

^b The prepolymer content is in grams.

^c The MMA monomer is in milliliters.

 $^{\rm d}$ The AIBN content is in grams, 3% wt with respect to MMA.

^e The content of photochromic material is in grams; 1% wt with respect to whole sample.

the reaction. A white wax-like material was formed with a T_{σ} at -47°C and a T_m at 40°C.

Synthesis of Polyurethane–Acrylate (A-B-A) Block Copolymers

The thermal curable liquid mixture were formulated from the above prepolymer (melted at 45°C) by adding (under nitrogen atmosphere) the required amount of methyl methacrylate (MMA) and azo-bis-isobutyronitrile (AIBN) catalyst (see Table I). The solution was stirred for 1 min and immediately after injection into the mold, which was preheated at 80°C. The mixture was cured for 15 min into the mold. The mold cavity has the dimensions of $100 \times 100 \times 0.5$ mm, which gave plaques of conventional size for the subsequent material analysis. Release agent [chemical identity: "Super Release S" (E.C.L. Chemicals L.T.D.)] was used to facilitate demolding of the plaques.

The photochromic materials were dissolved and added along with the MMA. The technique to incorporate the photochromic material into the

Table IIFormulations Employed in the Synthesis of Polyurethane-Acrylate (A-B-A) BlockCopolymer, Where the Photochromic Material Was Incorporated as Side Group

Sample ID	Acrylate Content ^a	$\mathrm{HDI}^{\mathrm{b}}$	HEA ^c	PPG	$\mathrm{DBTDL}^\mathrm{d}$	MMA ^e	$\operatorname{AIBN^{f}}$	Photochromic ^g Agent
E80	72	1.51	1.03	1.89	0.0179	3.41	0.0957	0.0796
E79 E78	$50 \\ 37$	$\begin{array}{c} 2.17\\ 2.88 \end{array}$	$\begin{array}{c} 1.49 \\ 2.06 \end{array}$	$2.73 \\ 3.78$	$0.0259 \\ 0.0358$	$\begin{array}{c} 3.41\\ 3.41\end{array}$	$0.0957 \\ 0.0957$	$0.0957 \\ 0.120$

^a The acrylate monomer content (MMA) is in wt % with respect to the prepolymer formed.

^b The HDI content is in milliliters, plus the equimolar amount of photochromic material.

^c The HEA content is in milliliters.

^d The DBTDL content is in milliliters, 1% wt with respect to the polyol content.

^e The MMA monomer is in milliliters.

^f The AIBN content is in grams, 3% wt with respect to MMA.

^g The content of photochromic material is in grams, 1% wt with respect to the whole sample.

Table III	Maximum	Wavel	length	Absorb	ance
for Each	Photochron	nic Co	mpoun	ds	

Compound	λ Max
<i>N</i> -Methyl spiropyrane	561.4
<i>N</i> -Ethanol spiropyrane	565.3
bis-Decyl spiropyrane	568.5
bis- <i>p</i> -Xylene spiropyrane	572.8

The numbers represent nanometers.

polymer matrix as a chemically bonded side group was the same as described above with some modifications. The prepolymer was synthesized *in situ* in a one-shot process. The photochromic material was added to the reaction mixture immediately after the HEA was added, using the appropriate extra amount of HDI to compensate the additional hydroxyl groups existing in the photochromic material. The amount of each component used in each reaction is listed in Table II.

Measurement of Photochromic Response

The photochromic response is a function of the absortion characteristics of the photochrome. The maximum wavelength absorbance were measured in all photochromic pigments (see Table III). Samples of $50 \times 10 \times 0.5$ mm were cut from the plaques with a sharp die and irradiated with



Figure 4 The UV-vis spectrum obtained before and after irradiation for each photochromic compound into the polyurethane-acrylate matrix at 37% of acrylate content.

a specific UV wavelength of 325 nm for 30 s, which activate the photochromic compound in the polymer matrix. The material developed a characteristic color on irradiation; immediately after irradiation, the samples were scanned from 380 to 900 nm at 20°C. The visible spectrum was recorded using a ultraviolet–visible (UV–vis) spectrophotometer (Philips Scientific PU8730).

The decoloration rate at the maximum absortion wavelength were also measured, and fresh specimens were activated using the procedure described above. The specimens were monitored at the appropriate wavelength, and the decoloration rate was measured for 100 min at 20°C. The decoloration rate constants (k) were determinated assuming that the fading is a first-order reaction. Plots of $\ln k$ versus acrylic content for each photochromic compound were constructed.

RESULTS AND DISCUSSION

Determination of the Maximum Wavelength

In Figure 4, the visible spectrum obtained before and after irradiation for each photochromic compound employed in the study is shown. The polyurethane-acrylate matrix had a 37% acrylate content. Notice that even when the sample has not been irradiated, some absorbance was observed, despite the fact that precautions were taken to avoid activation of the photochrome before measurement. This effect can be attributed to the solvato-chromism phenomenon.¹¹ The solvato-chromism phenomenon is connected with the weak equilibrium between the spiropyrane (colorless) and the merocyanine (colored). This balance can be modified by solvent effect, polar solvents (that is, ethanol, water) displace the equilibrium to the merocyanine, which is associ-



Figure 5 The maximum absorbance observed for each individual formulation, obtained at its maximum wavelength of absorbance.

ated with the development of some color. In the same way, it is possible that the polymer matrix polarity modifies the weak equilibrium between the two forms, having a small absorbance even when the sample has not yet been irradiated.

The maximum absorbance for each individual formulation after 30 s of irradiation is given in Figure 5. The general trend observed is that the lower the acrylate content, the bigger the absorbance. The lower the acrylate content, the softer the material (see Fig. 6). Consequently, the photochrome has less steric restriction in the surroundings, which makes the photoisomerization easier. Also, the bis-decyl spiropyrane series has slightly higher absorbance, within the 30 s of irradiation, compared with the rest of the series. Notice that the bis-*p*-xylene spiropyrane series has the lower absorbance, even when this has twice the number of active centers than *N*-methyl spiropyrane or *N*-ethanol spiropyrane.

If it is assumed a priori that the larger the molecule, the larger the hindrance for the photochrome in the polymer matrix; then, the dimensions of the molecules (Table IV) do not agree with the results observed in the Figure 5. The theoretical maximum length for the spiropyranes and the merocyanines obtained by computer-based modelling calculation¹² using SPARTAN V4.11 are shown in the Table IV. The bis-p-xylene spiropyrane has the higher difference between the 2 forms (3.83 Å), and the bis-decyl spiropyrane has the lowest difference length (0.77 Å). In this case, is clear that the previous reasoning (the larger the molecule, the larger the hindrance in the polymer matrix) is incorrect, and a better hypothesis is that the larger the transformation of the photochrome (close to open form), the larger the hindrance in the polymer matrix. This agrees more closely with the experimental observation.

Determination of Decoloration Rate

The decoloration constants rate $(\ln k)$ estimated as a first-order reaction against the percentage of acrylate contents are shown in the Figure 7. In general, the lower the acrylate content, the faster the decoloration rate. The observed fading trend is as follows: *N*-methyl > bis-*p*-xylene > *N*-ethanol > bis-decyl spiropyrane. The *N*-methyl merocyanine has the faster decoloration rate, as expected; the *N*-ethanol merocyanine transformation presents a slowness in almost 0.7 units (at 37%) because it is chemically bonded as a side group. Out of trend is the noticeably high value of fading rate at 50% acylate content. During phase



Figure 6 Effect of the acrylate content in the reference sample (E77 72%, E76 50%, and E65 37%) observed on the storage modulus (E') and tan δ .

inversion (around 50/50) and when the two components are present as a cocontinuous phase, it is possible that important interactions observed for the photochrome chemically linked to the polyurethane backbone and the acrylate phase disappear, leaving the photochrome free to achieve the transformation (open to close form) without restrictions. Then at 76%, the fading rate becomes reasonable again in the trend.

For the bis-spiropyrane case, the bis-*p*-xylene merocyanine has the faster fading rate compared with the bis-decyl merocyanine. A *priori*, one would expect that the bis-decyl merocyanine would have a fast fading rate, taking into account that this molecule is larger (24.1 Å) than the bis-*p*-xylene merocyanine (20.4 Å); therefore it

will experience more stress into the polymer matrix so the recovery rate to the spiropyrane would be faster. An additional effect is obviously involved.

From the modeling calculations, it was observed that the bis-decyl merocyanine has a larger dipole moment (45.4 Debyes) than bis-*p*xylene merocyanine (27.9 Debyes). Since the merocyanine form develops a big dipolar moment several times larger than the spiropyrane form, it can be anticipated that this dipole interacts with the polar polymer matrix; hence, the larger the dipole, the larger the interaction. If this occurs, then the transformation from the merocyanine (colored form) to the spiropyrane (colorless form)

Table IVMaximum Values of Length Obtained by Computer-BasedModeling for Spiropyranes and Merocyanines

Compound	Spiropyrane	Merocvanine	Difference
	r ry		
N-Methyl	12.82	14.36	1.54
N-Ethanol	11.98	14.38	2.40
bis- <i>p</i> -Xylene	16.66	20.49	3.83
bis-Decyl	23.38	24.16	0.77

The numbers represent Å.



Figure 7 Decoloration constant rate $(\ln k)$ along the percentage of composition for all photochromic compounds.

will experience an important delay; consequently, this delay will decrease the fading rate.

Similar mechanisms have been postulated^{13,14} in order to explain the photomechanical response phemonena, which will be discussed in the second part of this series.

CONCLUSION

From this study, it was concluded that the lower the acrylate content into the copolymer, the faster the photoresponse of such compounds, and also that simple photochrome molecules linked to the polymer backbone are sensitive enough to observe the phase invertion in copolymer, as was the case of *N*-ethanol spiropyrane.

We have demonstrated that the reasoning that the larger the molecule, the higher the hindrance for the photochome into the polymer matrix does not apply for bis-spiropyrane. A better reasoning instead would be to focus on the transformation (close to open form) of the photochrome.

The fading rate in these systems is dictated by a combination of several factors which are as follows: the spatial difference between the spiropyrane and the merocyanine form, the electronic difference of both forms (that is, the dipole moment), and the softest of the polymer matrix. However, doing a little computer-based modeling in order to establish several properties of the molecules in both forms can help to understand, predict, and even anticipate the photoresponsive behavior of such compounds into a determined polymer matrix. The authors thank the IRC in Polymer Science and Technology for their generous support for this project. E. A. Gonzalez also thanks the National Research Council of Mexico (CONACYT) for the funding of his Ph.D. studies.

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