polymer reports

Photocontractile effects in nylon-6,6 films containing β-carotene, and 4-nitro-4'-hydroxy-α-cyanostilbene

Hal S. Blair and Tak-Kau Law
Department of Industrial Chemistry, The Queen's University of Belfast, 21 *Chlorine Gardens, Belfast, BT*9 5*DL, UK*

(*Received* 8 *August* 1980)

INTRODUCTION

Several systems exhibiting photomechanical effects have been described. Lovrien[1] prepared and investigated systems showing photoviscosity effects; van der Veen and Prins[2] described photoresponsive gels consisting of poly(hydroxyethyl methacrylate) containing Chrysophenine G, from which swollen membranes were prepared which possessed reversible photocontractile properties. A number of photomechanical effects in the solid state have also been reported[3].

More recently the photoresponsive properties of poly(methyl methacrylate)/spiropyran and polystyrene/spiropyran systems in the form of monolayers[4], and the photoviscosity and photomechanical properties of some azopolyamides[5] have been described.

The present paper describes the photoresponsive effects observed with polyamide/β-carotene and polyamide/cyanostilbene systems.

EXPERIMENTAL

Materials

Nylon-6,6 film was supplied by ICI Ltd and had a thickness of 24 μm. The *trans-β*-carotene was obtained from Sigma Chemicals Ltd and was stored under dark cool conditions. 4-Nitro-4'-hydroxy-α-cyanostilbene was prepared by condensing equimolar quantities of 4-nitrobenzylcyanide with 4-hydroxy-benzaldehyde using the method of Merck[6].

All solvents used were of spectroscopic grade.

Irradiation was by a Phillips HPW 125 high pressure mercury lamp. Spectra were recorded on Pye–Unicam SP800 spectrophotometer.

Preparation of the polymer–photochrome films

Nylon-66/β-carotene film. Nylon film was immersed for 4 h in a dispersion of β-carotene in distilled water at 80°C in the dark. The carotene exhausted on to the film as a disperse dye. The dyed film was rinsed and dried at < 50°C and then conditioned in a Perspex cabinet for 48 h before irradiation. To ensure that the carotene had not decomposed in the bath, the residue was extracted with cyclohexane and its absorption spectrum determined.

Nylon-6,6/cyanostilbene film. This film was prepared in the same way as the nylon–carotene film but dyeing was carried out at 100°C for 1 h.

Measurement of photomechanical effect

The sample of polymer film of length 10 cm was placed in a Perspex cabinet under a load of 24 g and allowed to condition in the dark for 12 h. The change in length of the film during irradiation or during recovery in the dark was measured using a cathetometer.

DISCUSSION

Nylon-β-carotene film

In solution *trans-β*-carotene is isomerized on irradiation to a *cis* compound with a loss of colour intensity and with the formation of a new absorption maximum at lower wavelength — the *cis*-peak[7]. The irradiated solution on standing in the dark only partly recovers to the *trans* form. *Figure* 1 shows the effect of irradiation on *trans-β*-carotene in nylon-6,6 film. The *trans* peak at

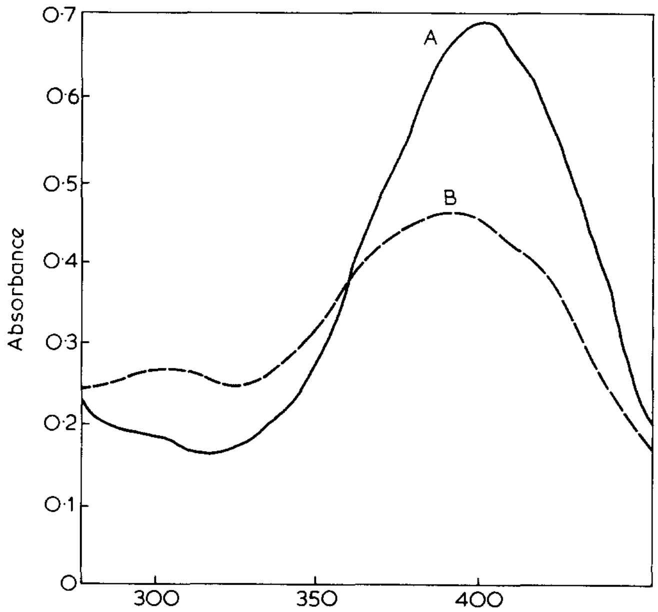

Figure 1 Absorption spectrum of *trans-β*-carotene in nylon film: A, before irradiation and B, after 15 min irradiation

0032-3861/80/1475-02$02.00

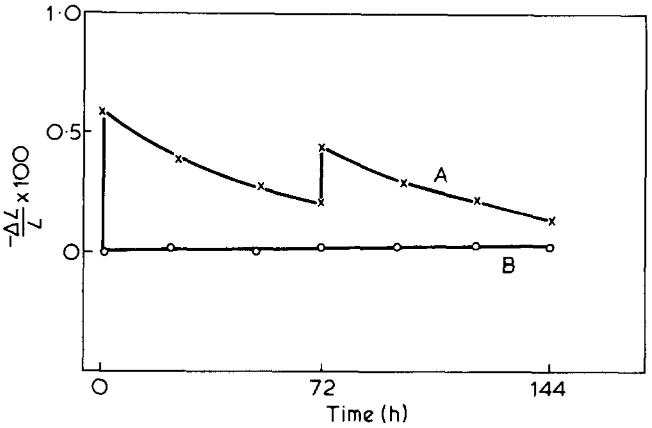

Figure 2 Photocontractile effect with nylon/*trans*-β-carotene film (two cycles)

about 400 nm is reduced considerably and a new *cis*-peak at about 305 nm is beginning to form. The recovery (i.e. the thermal stereomutation) of the carotene is also shown and is found to be very slow (about 50% after 72 h). *Figure* 2 curve A illustrates the photomechanical response of this system. During 15 min irradiation there is a contraction in length of the film of 0.6%. After 72 h in the dark at room temperature the film makes about a 70% recovery. A second 15 min period of irradiation causes a contraction of about 0.5% (based on the original length of the film which after a further 72 h in the dark makes about 68% recovery. This slow and not completely reversible photocontractile effect parallels the change in absorption spectrum behaviour of *trans*-β-carotene adsorbed on nylon-6,6 film and in solution. *Figure* 2 curve B shows nylon-6,6 film without carotene present and in this case no photomechanical effect occurs.

Nylon-6,6/cyanostilbene film

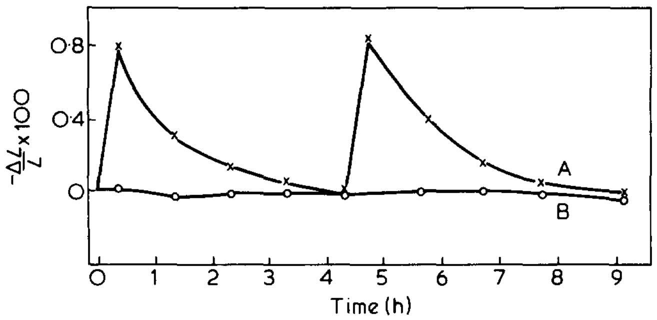

Figure 3 Photocontractile effect with nylon/cyanostilbene film (A) compared with untreated nylon (B) (two cycles)

The photoisomerization of *trans*-4-nitro-4′-hydroxy-α-cyanostilbene in nylon-6,6 film has already been reported[8]. Photoisomerization to the photostationary state takes about 30 min while thermal isomerization in the dark (the dark reaction) is much slower and takes about 4 h for its completion. The photocontractile effect and recovery in the dark of nylon-6,6/cyanostilbene films parallels this as shown by *Figure* 3.

Figure 3 curve A shows the contraction and recovery of nylon-6,6/cyanostilbene film over two light–dark cycles. *Figure* 3 curve B shows a sample of nylon-6,6 without cyanostilbene under the same conditions and in this case the photomechanical effect is absent.

CONCLUSION

The photoresponsive effects of nylon-6,6 films containing *trans*-β-carotene or 4-nitro-4′-hydroxy-*trans*-α-cyanostilbene appear to be due to the effects of isomerization of the chromophore in each case.

REFERENCES

1 Lovrien, R. 'Light Control of Viscosity of Reversible Macromolecular Photoresponses.' 148th *Am. Chem. Soc. Meeting*, 1964, Abstract
2 Van der Veen, G. and Prins, W. *Nat. Phys. Sci.* 1971, **230**, 70
3 Husy, H., Merian, E. and Schetty, G. *Text. Res. J.* 1969, **39**, 94; Agolini, F. and Gay, F. P. *Macromolecules* 1970, **3**, 349; Smets, G. and De Blauwe, F. *Pure Appl. Chem.* 1973, **39**, 225
4 Blair, H. S. and Pogue, H. I. *Polymer*. 1979, **20**, 99
5 Blair, H. S., Pogue, H. I. and Riordan, J. E. *Polymer* 1980, **21**,
6 Merckx, R. *Bull. Soc. Chim. Belg.* 1949, **58**, 460
7 Zechmeister, L. *Chem. Revs.* 1944, **34**, 267
8 Blair, H. S. and Boyd, N. L. *JSDC* 1973, **89**, 245