Photoresponsive effects in azo polymers

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Photoresponsive effects associated with two photochromic polyamides [poly(3,3'-azo dibenzoyl-*trans*-2,5-dimethylpiperazene) (I) and poly(4,4'-azo dibenzoyl-*trans*-dimethylpiperazene) (II)] are reported. (i) Langmuir film balance measurements show a reduction in area/monomer unit on changing from dark to light conditions and this is interpreted as being the result of *trans*→*cis* isomerization. From detailed consideration of pressure–area curves for I and II, it is postulated that I exists as a helical structure whereas the structure of II is linear. (ii) I and II are also shown to exhibit a photoviscosity effect where the viscosity is reduced upon irradiation. This effect is discussed in terms of the postulated structures. (iii) The polymers also exhibit photomechanical properties. The photocontractile effect observed on switching off the radiation is attributed to incomplete isomerization of a fraction of the azo residues in locations within the polymer matrix.

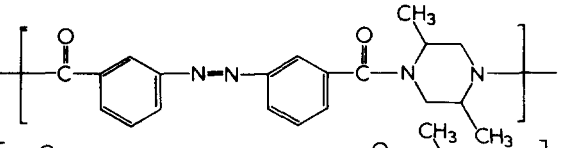
INTRODUCTION

In a recent paper the authors reported the photoresponsive effects of mono-layers of a spiropyran/polymethyl-methacrylate mixture as demonstrated using a Langmuir film-balance[1]. Several examples of photoresponsive effects in polymers containing azo-dyes[2] and stilbene-azo-dyes[3] and in polymers containing an azo linkage[4] have also been reported. The present paper describes an investigation of the photoresponsive properties associated with the photochromic azo-polyamides, I and II, and is in three parts:

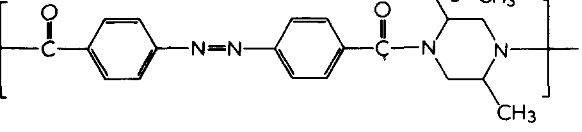
(i) an assessment of the change in molecular dimensions and conformation brought about by isomerization,

(ii) the detection of a photoviscosity effect,

(iii) the detection and measurement of the photomechanical properties in the solid state.



I



II

EXPERIMENTAL

Materials

The polyamides, poly(3,3'-azodibenzoyl-*trans*-2,5-dimethylpiperazine) I (the *meta* polymer), and poly(4,4'-azodibenzoyl-*trans*-2,5-dimethylpiperazine) II (the *para*-polymer) were prepared[5]. All solvents used were of spectroscopic grade and the subphase used in the Langmuir trough was deionized water, which had been twice distilled. Pressure area curves were determined at 25°C[1].

Viscosity measurements were made in a modified Ubbelohde viscometer in chloroform solution at 25°C ±0.1°C, and illumination was by a Phillips BMW/U125w black light suspended in close proximity to the viscometer. The photomechanical properties were detected and measured using an Instron Tensile Tester suitably modified by screening to ensure that the effects observed were not of thermal origin. The experiments were carried out at constant length and the change in stress with time was monitored during both irradiation of the surface and its recovery in the dark.

RESULTS AND DISCUSSION

Film balance measurements

Figures 1 and 2 show the pressure–area curves for compounds I and II respectively, under dark conditions and under irradiation; both polymers appeared to form stable monolayers as the isotherms obtained were reproducible. With each of the polymers there is a significant reduction in area/monomer unit on changing from dark to light conditions and this is interpreted as being the result of *trans–cis* isomerization; the more extended conformation of the *trans*-isomer giving a larger apparent molecular area as indicated by the film balance. This, however, is only part of the explanation as consideration of the shapes of the pressure/area isotherms for the *para*-azo-polymer and the *meta*-azo polymer shows. The isotherms for the *meta*-polymer are essentially linear, at higher pressures, whereas those of the *para*- polymer show

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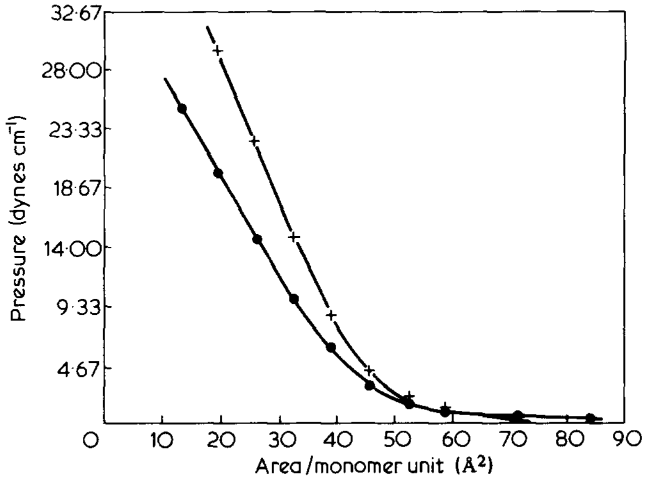

Figure 1 Pressure/area isotherms for Polymer I. +, Dark conditions; ●, under u.v. irradiation

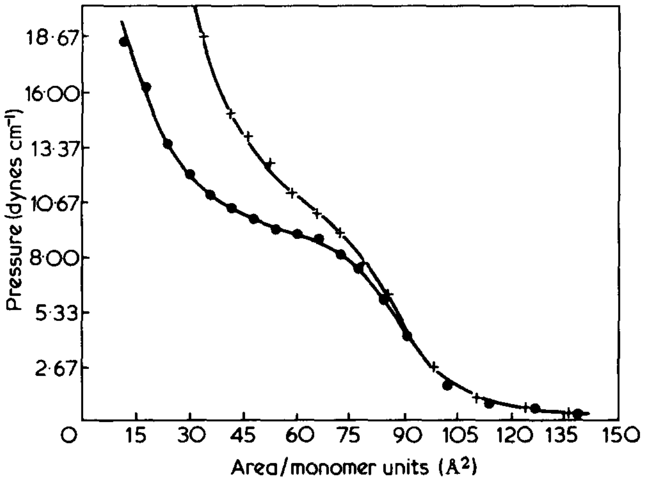

Figure 2 Pressure/area isotherms for Polymer II. Symbols as for *Figure 1*

a transition or step at pressures between 8 and 10 dynes cm^{-1}. Also, the apparent area/monomer unit of the *meta*-polymer is smaller at any surface pressure than that of the *para*-polymer at the same pressure. To explain these differences it is suggested that the *meta*-azo polymer chain may have a helical structure while the *para*-azo polymer has a linear structure. The helical structure of the *meta*-polymer would result in fewer of the monomer units residing in the interface and thus the measured area per unit would be smaller. The apparent reduction in unit area on irradiation may be attributed to either a change of pitch, or a change in the diameter of the helix due to isomerization. The linear structure of the *para*-azo polymer will result in more of the monomer units residing in the interface, hence giving a larger measured area. The effect of isomerization in this case is merely to produce a shorter but broader monomer unit (*Figure* 3).

To explain the difference between the pressure-area characteristics of the *meta*- and *para*-azo polymers the effect of increasing surface pressure on the proposed structures must be examined. Considering first the *meta*-azo polymer which it is suggested has a helical structure. As the surface area (A) decreases, the molecules will pack together and the surface pressure will increase. Since the helix is symmetrical, the molecule in a state of compression, will have no preferred orientation and as the area is decreased still further, the compressibility will remain constant, as suggested by the linear portion of the pressure–area curves. The *para*-azo polymer however can adopt two distinct orientations whether in the *cis* or *trans* form, i.e. that in which the benzene rings are perpendicular to the subphase surface. *Figures* 2*a* and *c*) and that in which the molecule is rotated through 90° as in *Figures* 3(*b*) and (*d*).

It is suggested that at larger surface areas the predominant orientation is that illustrated in the projection in *Figures* 3(*a*) and (*c*). As the pressure increases the molecular orientation will change to that of the more easily 'packable' form as in *Figures* 3(*b*) and (*d*). The change to this orientation will result in an increased compressibility at this point in the pressure/area curve. The curves obtained suggest that this change takes place at a pressure between 8 and 10 dynes cm^{-1} and as might be expected there is apparently a larger reduction in the surface area in the case of the *cis*-isomer.

Tables 1 and 2 show the calculated and extrapolated projected surface areas for the projection shown in *Figure* 3. The apparently large discrepancy in the molecular areas at low pressures is attributed to the lack of close packing at such pressures. However, at higher pressures reasonable agreement is achieved, with both sets of results confirming that the *cis*-isomer gives a smaller projected area than the *trans*-isomer.

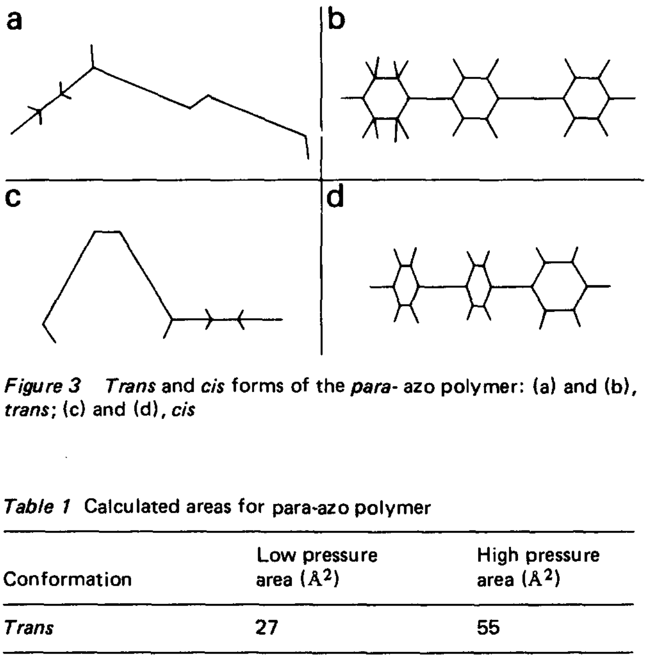

Figure 3 *Trans* and *cis* forms of the *para*- azo polymer: (a) and (b), *trans*; (c) and (d), *cis*

Table 1 Calculated areas for para-azo polymer

Conformation	Low pressure area (Å²)	High pressure area (Å²)
Trans	27	55
Cis	27	45

Table 2 Extrapolated areas for para-azo polymer

Conformation	Low pressure area (Å²)	High pressure area (Å²)
Trans	107	65
Cis	107	53

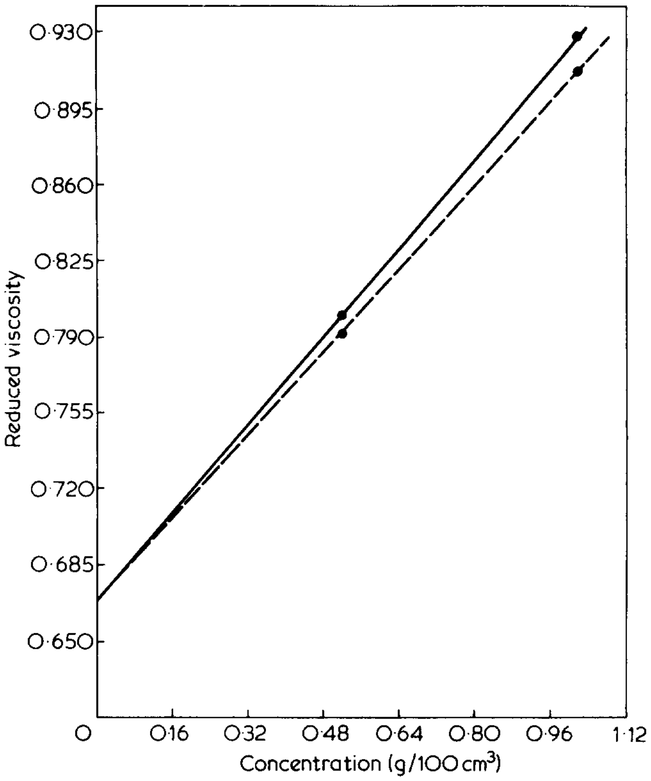

Figure 4 Photoviscosity effect with Polymer I. (——), Dark conditions; (— — — —) under irradiation

Viscosity measurement

Lovrien has reported examples of reversible changes in viscosity of solutions of polymers containing a photochromic group[6]. The polymers examined were polyelectrolytes and of two types–(a)those containing a photochromic azo group as a side chain in the polymer, and (b) those in which a charged azo dye was associated with the polymer in solution. The compounds of type (a) examined were copolymers of acrylic acid or methacyrlic acid with 4-acrylamido azo benzene or one of its derivatives. The net charge on the polyelectrolyte tends to extend the polymer due to electrostatic forces and the *trans* form of the side chains generate non-polar interaction forces which tend to contract the polymers. On irradiation in the *cis*-isomer of the photochromic group is formed, the hydrophobic forces are lessened and the polymer coils can then expand, bringing about an increase in viscosity. Lovrien found this to be the case and solutions of such polymers showed an increase in viscosity on irradiation.

In the case of polymer–photochromic system (b), solutions of polymethacrylic acid or polyvinylpyrrolidone mixed with Chrysophenine G or a related compound were examined. The *trans* form of the dye being strongly bound to the polymer chain tends to keep the chains extended. On irradiation the molecules of the *cis* form of the the dye are not so strongly bound and tend to leave the polymer, so allowing the polymer chains to relax to a more coiled form. This should cause a reduction in viscosity and this was observed.

In the case of the azo polyamides I and II being considered, photoviscosity effects would also be expected. *Figures* 4 and 5 show plots of reduced viscosity of chloroform solutions, against concentration for the *meta*- and *para*-polymers I and II, in the dark, and during illumination. In each case there is a reduction in viscosity on irradiation, the change being more marked in the case of the *para*-polymer. This, however, is to be expected if the *para*-polymer has the linear structure and the *meta*-polymer has the helical structure postulated earlier. Isomerization of the linear polymer molecules will cause larger changes in molecular dimension giving less extended and hence more compact molecules with a consequently larger fall in viscosity when compared with the *meta*-polymer in which the change in molecular dimensions will be considerably less.

Detection and measurement of the photomechanical properties

An idealized photomechanical response for a photresponsive azo polymer is shown in *Figure* 6 and actual curves for the *para*-isomer are shown in *Figure* 7. The response curves for the *meta*-isomer are similar.

When irradiation commences the stress increases indicating a contraction of the sample length. The stress continues to increase until a photstationary state is

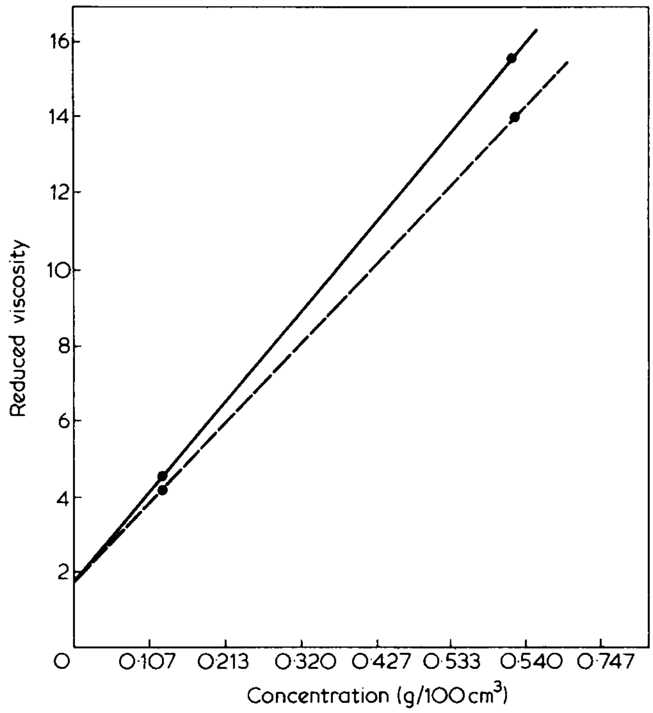

Figure 5 Photoviscosity effect with Polymer II. (——), Dark conditions; (— — — —) under irradiation

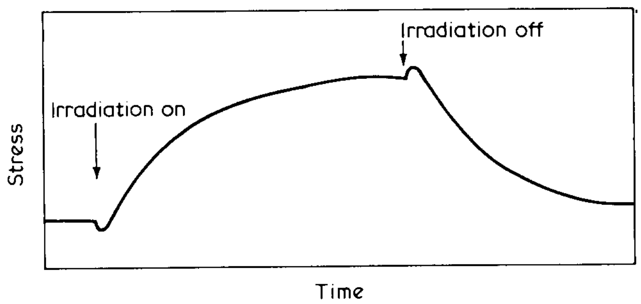

Figure 6 Idealized photomechanical response curve

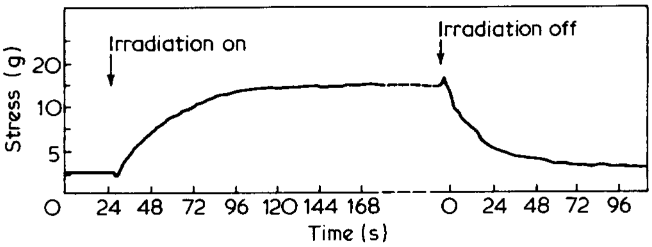

Figure 7 Photomechanical response curve for para-isomer (Polymer II)

reached (about three minutes in the case of the two polymers investigated) and the stress remains constant until the irradiation ceases, after which the stress decreases indicating a relaxation of the sample. The process is reversible and may be cycled many times. The maximum change in stress observed with a sample measuring 6.0 cm × 1.5 cm × 33 μm was 8.65 g. This represents a change in stress of 500 tonnes m^{-3}.

The effect observed is in agreement with the observations of Agolini and Gay[4] and Smets and De Blauwe[7] using systems in which the photoresponsive unit is incorporated in the back bone of the polymer. The rate of contraction is similar to that observed by Smets and De Blauwe although the size of the effect is much smaller than might be expected from a polymer containing an isomerizable group in every monomer unit. This suggests that only a small number of the photresponsive units are contributing to the photomechanical effect.

The rate of relaxation in the dark is much more rapid than the normal thermal reversion of *cis* to *trans* in solution. This may be due to an incomplete isomerization of the photoresponsive units due to their being held in a strained state by the irradiation process. That this is so is supported by the observations of Paik and Morawetz[8] of anomalously fast reaction rates for the isomerization of azo groups in the solid state and who suggested that the speed of reaction was due to the isomerisation taking place within confined locations.

It is concluded therefore, that the photocontractile effect observed is a result of partial isomerization of a fraction of the azo residues in confined locations in the polymer matrix.

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