Investigation of photoresponsive effects in polymer monolayers

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The photomechanical properties of a polymer system containing 6-nitro-1,3′,3′-trimethyl-spiro-(2H-1-benzopyran-2,2′-indoline) as a photosensitive additive, were investigated. Mixed monolayers containing various proportions of this spirobenzopyran and polymethyl methacrylate were examined – using a Langmuir trough, and π *versus* area curves were obtained for the various compositions in both dark and u.v. conditions. The results show a reduction in apparent area of the spiran molecule under u.v. light. This is attributed to the conversion of the compound from its bulky spiro form into a planar merocyanine type structure. This reduction in area is controlled by other factors such as miscibility of the components, the spreading nature of the mixed monolayer, the non-ideal nature of the polymer component and the ionic nature of the merocyanine structure.

INTRODUCTION

Many compounds such as stilbene and azo derivatives undergo photoisomerization which is usually accompanied by a change in the overall shape of the molecule. If a film is made of a polymer containing such a derivative as part of the polymer backbone, or as a side chain, or having the compound embedded in the polymer matrix, the photoisomerization may result in a change in the linear dimensions of the polymer film. The earliest published example of a polymer showing a photocontractile effect is probably that of Husy, Merian and Schetty[1]. Samples of acetate ribbon were dyed using the yellow disperse dye (I), and also with the yellow disperse dyes (II) and (III).

The dyed materials, together with undyed acetate ribbon were exposed to sunlight. The authors observed that the ribbon dyed with dye (I), contracted by 1.2 mm, and at the same time a pronounced shade change occurred; on storage in the dark it regained its original length and shade. The effect was reproducible several times. Under the same conditions the undyed ribbon, and those dyed with dyes (II) and (III) were unaffected. The authors attributed this photocontractile effect to a rearrangement of the azo dye (I), and also to the fact that it is monomolecularly dispersed in the cellulose acetate. Since the original observation, a number of other workers have reported similar effects. Agolini and Gay[2] observed photo- and thermo-contractile effects with several aromatic polyimides which contained an azo linkage. They state, however, that the rates of contraction or dilation are not controlled by the rates of isomerization of the azo compound, but probably by viscoelastic characteristics of the polymer.

Van der Veen and Prins[3] prepared poly(hydroxyethyl methacrylate) membranes 0.1 mm thick and containing 0.6% of the stilbene azo dye Chrysophenine G, and on irradiation observed a reversible contraction of about 1.2%. This change is attributed to the conversion of the dye to the *cis* form, causing macroscopic contraction of the polymer membrane. The effect was not observed when the membrane was irradiated in the absence of the dye. Similar effects were reported with PMA and Chrysophenine G[4]. The opposite effect (i.e. photodilation) occurred with PMA in the presence of the cationic dye (IV).

Smets and De Blauwe[6] observed a reversible photocontractile effect with a methacrylate spirobenzopyran–ethacrylate copolymer. On irradiation a thread of the polymer stretches with a relative elongation of about 2%, and contracts reversibly in the dark, after a few minutes. Smets also reported the converse effect, i.e. the application of a very large pressure causes the formation of colour[7].

The present paper describes an investigation of photoresponsive effects in monolayers of poly(methyl methacrylate)–photochrome (V) mixtures using a Langmuir–Adam film balance.

EXPERIMENTAL

Materials

6-Nitro-1′,3′,3′,-trimethyl-spiro-(2H-1-benzopyran-2,2′-indoline) (V) was prepared as described by Koelsch and Workman[8]. Melting point 178°C (literature m.p. 179°C).

The poly(methyl methacrylate) used was a commercial sample which was purified by precipitation from toluene and then vacuum dried. All solvents used were of spectroscopic grade and the subphase used in the Langmuir film balance was deionised water which had been distilled twice.

Apparatus

The mixed monolayers were investigated using a Langmuir type film balance. The balance had a sensitivity of 1.01 dynes/cm/degree of rotation. A 0.5 mW He–Ne laser system was used to monitor deflections of the barrier. This was necessitated by the need to work in complete darkness in order to obtain results for the closed ring spiropyran.

A Philips MBW/U125W Blacklight was used as an ultraviolet source. This was mounted above the air–water interface in a position which allowed irradiation of the entire film area at all times.

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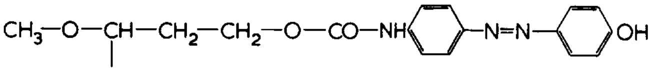
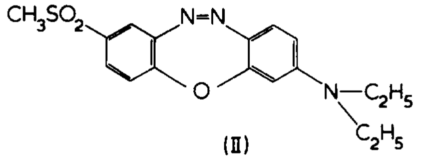


(I)



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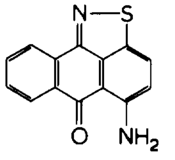

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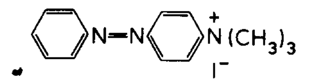

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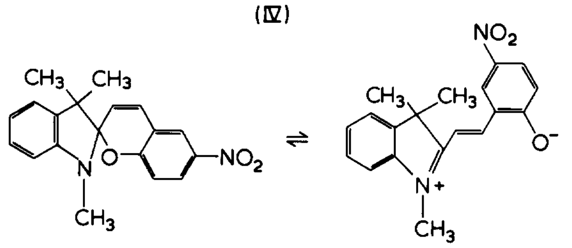

(V) (VI)

Procedure

All normal precautions were taken to ensure non-contamination of the monolayer. A small pump was used to aid cleaning of the interface. The film balance was operated in the normal manner using a null-point method, with 60 sec being allowed for equilibration before readings were taken. A dark room safelight was used to give enough illumination to apply the spreading solution to the surface. This was then switched off immediately and the experiment carried out in complete darkness. The spreading solutions used contained approximately 1 mg/ml of polymer and photochrome mixture. Solutions containing 10, 16, 28 and 40% (w/w) photochrome polymer were prepared under safelight conditions; 20 μl of each was applied to the surface to give a monolayer having a reproducible area upon compression.

RESULTS AND DISCUSSION

Due to the use of the laser monitoring system and also the need to avoid local temperature changes resulting from the ultra-violet source, it would have been impracticable to enclose the whole system within a dust-excluding housing. This, necessitated therefore, an estimation of airborne contaminants which would settle on the interface during the time allowed for the completion of a film compression. *Figure 1* shows, A, a typical pressure area (π *versus* A) curve obtained for airborne contaminants. Justification for an allowance for the airborne contamination was obtained from the very good correlation between a curve obtained for polymethyl methacrylate and that given in the literature[9]. Curves B and C show the increase in area afforded by the airborne contaminants.

Figure 2 shows the π *versus* A curves obtained for the mixed monolayer of polymethyl methacrylate and 16% (w/w) 6-nitro-1',3',3'-trimethyl-spiro-(2H-1-benzopyran-2, 2'-indoline) (V) under both dark conditions, A, and ultra-violet light, B. Both curves shown have been corrected for airborne contaminants.

Figures 3 to *6* show the π *versus* A curves for the single component system of (V), as calculated using the equation below, for 10, 16, 28 and 40% (w/w) in mixed monolayers with poly(methyl methacrylate). In each case curve A represents the system in the dark, whilst B represents that under ultra-violet radiaiton.

If it is assumed that in the monolayer the two components are completely immiscible and do not interact chemi-

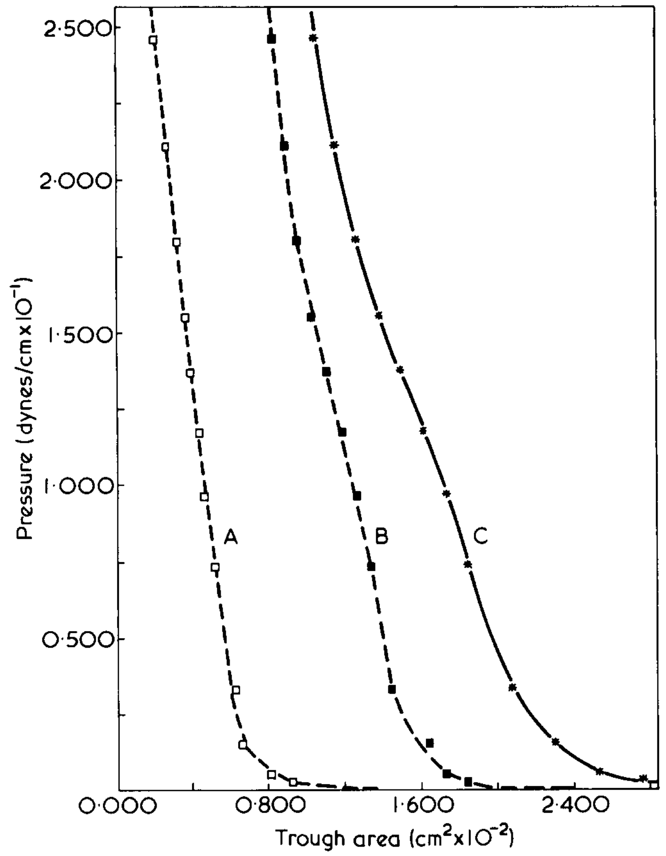

Figure 1 Pressure vs. trough area

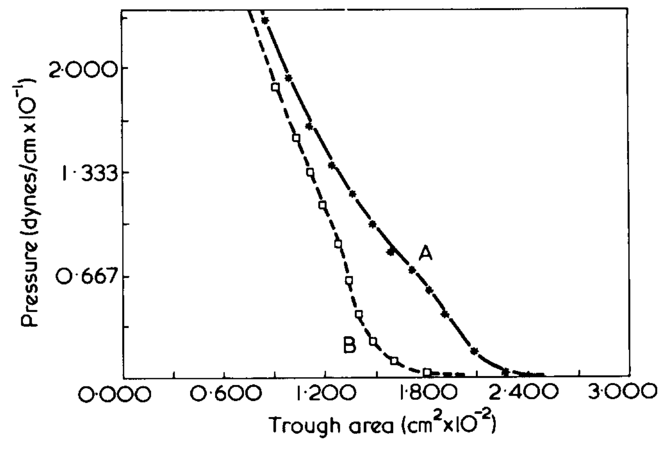

Figure 2 Pressure vs. trough area

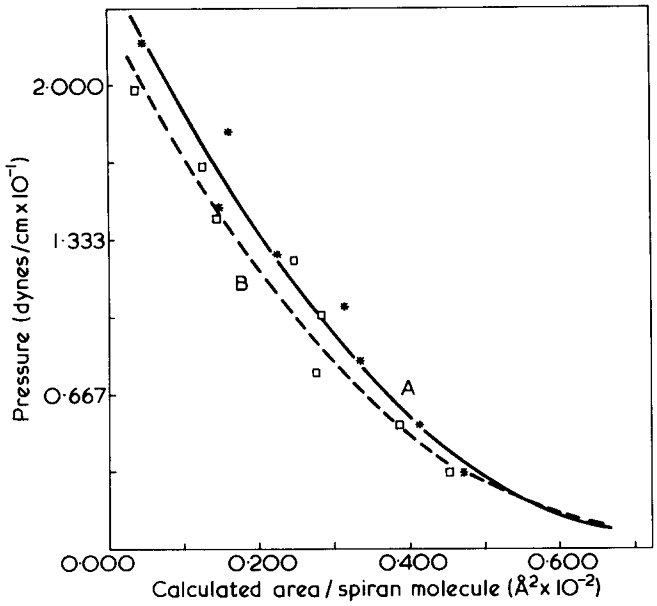

Figure 3 Pressure vs. calculated area/spiral molecule. 10% w/w spirobenzopyran

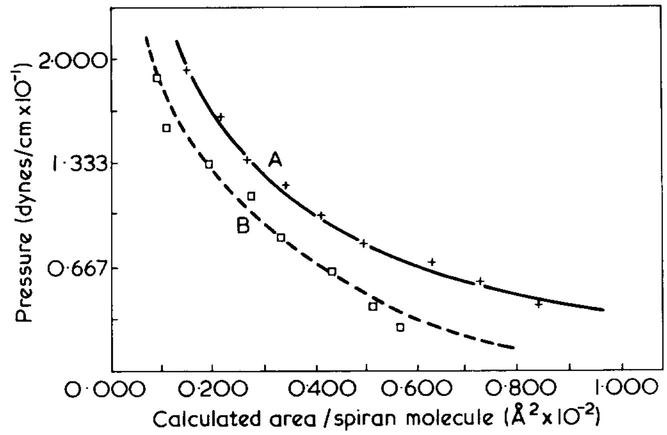

Figure 4 Pressure vs. calculated area/spiran molecule. 16% w/w spirobenzopyran

cally, then from the curves in *Figure 2*, π *versus* A curves can be obtained for the (V) component using the equation:

$$A12_{(\pi)} = n_1 A1_{(\pi)} + n_2 A2_{(\pi)}$$

where $A12$ is the average molecular area in the two component film, n_1 and n_2 are the mole fractions of components 1 and 2 present in the monolayer and $A1$ and $A2$ are the molecular areas in the two single component films at the same surface pressure (π).

Miscibility can be established by applying the surface phase rule, as developed by Crisp[10]. The procedure used is analogous to Gibb's derivation of the ordinary phase rule, and if surface tension, temperature and external pressure are allowed to vary, it leads to the equation:

$$F = C^B + C^S - P^B - q + 3$$

where F is the number of degrees of freedom, C^B is the number of components in bulk, and equilibrated through the system, C^S is the number of components confined to the surface, P^B is the number of bulk phases and q is the number of surface phases in equilibrium with one another. If there are two components constrained to remain in the monolayer, we can consider the application of the surface phase rule to mixed monolayers. At the liquid–gas interface we have $C^B = 2, C^S = 2$ and $P^B = 2$. Therefore:

$$F = 5 - q$$

and if there is only one surface phase, i.e. when there is complete miscibility, there should be 4 degrees of freedom: temperature; external pressure; surface pressure and the independently variable composition of the mixed film. In the event that the two components are immiscible there are two surface phases and 3 degrees of freedom, so that the composition of the phases is now fixed.

Clearly from *Figures 3* to *6* the area/spiran molecule varies with composition and would therefore suggest some degree of miscibility. However, the polymer–photochrome system described here is far from ideal. One problem is to decide just what constitutes a 'monolayer' of macromolecules, since it is quite possible that every individual polymer molecule could have one or some of its segments anchored in the interface while the rest of the long chain actually extends far into the adjacent bulk phase. If it is assumed that

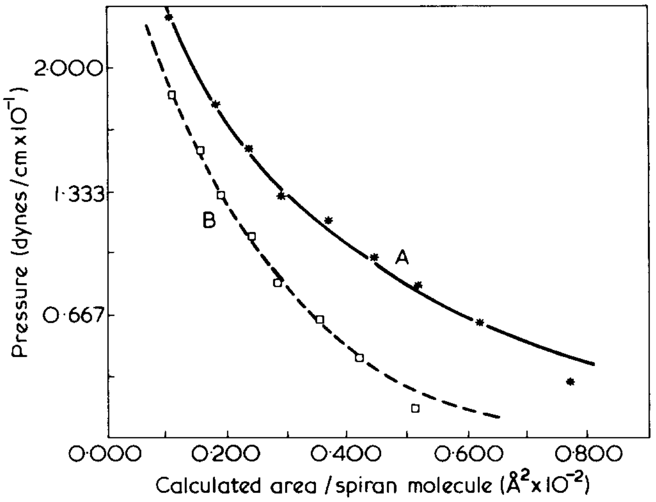

Figure 5 Pressure vs. calculated area/spiran molecule. 28% w/w spirobenzopyran

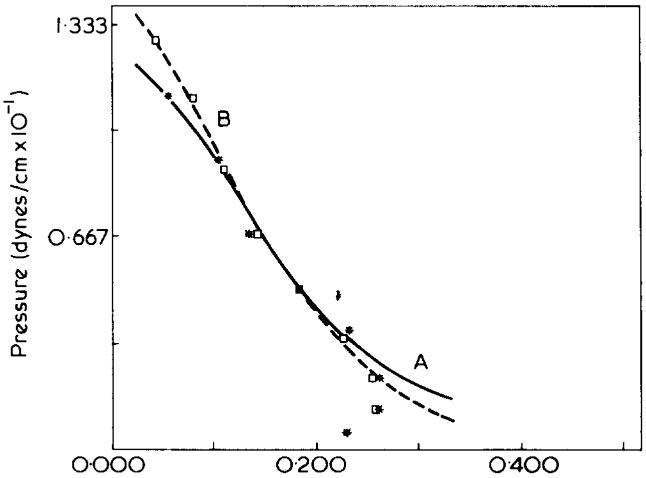

Figure 6 Pressure vs. calculated area/spiran molecule. 40% w/w spirobenzopyran

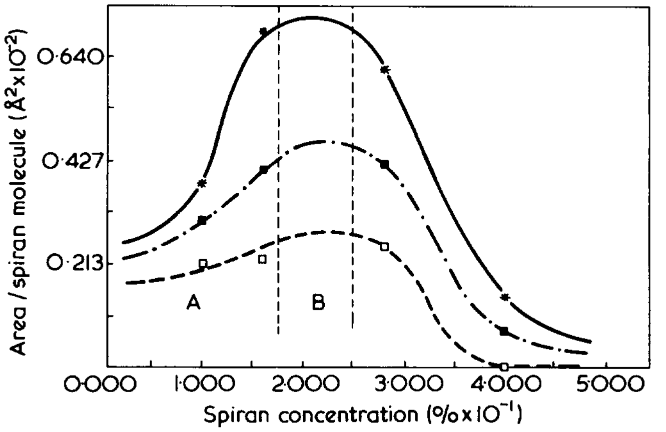

Figure 7 Area/spiran molecule vs. spiran concentration (%). ———, 6 dynes/cm; — · — · —, 10 dynes/cm; — — — —, 15 dynes/cm

there is some affinity between polymer and photochrome it may be possible for photochrome molecules to be held well out of the interface and also in a number of possible orientations, and therefore their contribution to the surface area is difficult to assess.

Another problem is the fact that the photochrome itself is not a compound which will spread and form a stable monolayer, but due to its possible affinity for the polymer molecule, it may be that spreading can be achieved at compositions below that which could be said to saturate the polymer. Clearly then, polymer–photochrome compositions having a higher percentage photochrome will not spread adequately due to the possible occurrence of crystallites and there will be a resultant decrease in average molecular area. This would seem to invalidate the surface phase rule assumptions. However, if its use is confined to compositions below this critical level there is evidence for miscibility. It would also seem reasonable to assume that at compositions above this critical level, small areas of photochrome would exist which upon compression would rapidly collapse at very low pressures.

Another factor which must also be considered is that a polymer chain, on compression, will not show a very regular packing and that the voids so produced could be quite capable of accepting a relatively small molecule, such as the photochrome molecule, without greatly affecting the surface pressure or indeed in some cases without affecting it at all. This again will result in a reduced area as calculated using the equation above.

The final factor to be considered is that the photochrome (V) will have a different molecular structure under ultraviolet light from that in the dark. Upon irradiation with ultra-violet light, pyran ring-opening takes place by C–O bond scission, followed by *cis–trans* isomerization about the double bond. This results in conversion of a colourless, bulky spiro compound, in which the benzopyran group adopts an attitude 90°C to that of the indoline group, to a polar planar merocyanine type molecule (VI) which could be expected to project a very different area to the interface. (It was the aim of this work to demonstrate this difference in structure by comparing the areas obtained and it is in the light of this that the results shown above are to be considered.) Indeed it must be stated that the areas for the photochrome, as calculated using this equation, are not absolute values but are values which take into consideration: (a) miscibility; (b) situation and orientation with respect to the interface; (c) irregular packing of the polymer chains; (d) molecular configuration of the spiro compound.

With reference to *Figure 3*. At low pressures, because of the irregular packing of the polymer chains, not only is the area/spiropyran molecule smaller than might be expected, but the difference in molecular configuration produced by irradiation does not have a marked effect. However, on further compression of the monolayer this difference becomes more apparent, although still relatively small.

On increasing the concentration of the photochrome to 16% a significant change under dark conditions is observed, whilst under u.v. irradiation there is little change (*Figure 4*). The change caused by *cis* and *trans* forms of the photochrome conformation is now becoming more apparent although it is still smaller than the true value. The fact that the area under dark conditions has increased may indicate that voids, due to irregular packing, having now been filled, more photochrome molecules are obliged to contribute to the surface area, whether actually in the interface or some distance removed from it. The small change in areas when the film is irradiated possibly indicates that the majority of spiropyran molecules are actually sites in the interface due to their polar nature.

Figure 5 shows the π *versus A* curve obtained when the concentration of spiropyran is raised to 28% and the effect of reduced spreadability is evident. At lower pressures the area is reduced as a result of this, however on compression of the monolayer, as the molecules are packed closer together, the effect is less obvious and there is indeed a slight increase in the area/spiropyran molecule.

When the concentration is increased to 40% a quite dramatic change occurs, both in the dark and under ultra-violet irradiation (*Figure 6*). In both cases a substantial reduction in calculated molecular area is observed, possibly due to the polymer being saturated with spiropyran molecules. This results in a reduced spreadability of the polymer–photochrome system combined with non-spreading of the excess photochrome component. The reduction in observed area/spiropyran molecule is much greater under dark conditions. This is possibly some indication of a sustained spreadability afforded by the ionic nature of the merocyanine form of the spiropyran molecule produced by ultraviolet irradiation. The results indicate clearly that the planar structure of the merocyanine form of the spiropyran presents a much smaller area to the surface than does the spiro form. There would also appear to be a movement of photochrome molecules of the merocyanine type towards the interface due to their ionic character. The effect of this is to reduce the observed change in area per spiropyran molecule by actually changing the concentration of spiropyran molecules in the interface. *Figures 7* and *8* show plots of areas

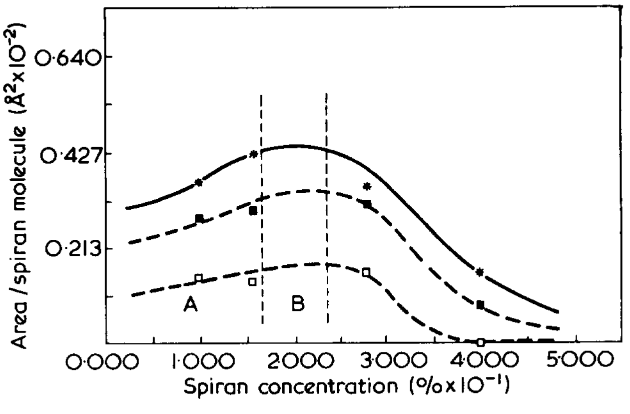

Figure 8 Area/spiran molecule vs. spiran concentration. ———, 6 dynes/cm; — · — · — 10 dynes/cm; — — — 15 dynes/cm

at fixed pressure against concentration, both in the dark and under radiation. Plots were made at three different pressures. The region labelled A represents a build-up of photochrome concentration to saturation of the polymer when voids in the polymer will be filled with photochrome molecules. Region B corresponds to the area where saturation has occurred. Here, the observed change in area will be at a maximum. Beyond B lies the region where the increasing photochrome concentration has a large effect on the measured area as described.

It is also apparent from *Figures 7* and *8* that there is a substantial difference in the slope of the curves in the region A. This is attributed to the photochrome's polar nature under ultra-violet radiation, ensuring that the majority of the molecules are in the interface and will therefore contribute to the area, whereas in the dark the photochrome is free to accommodate itself elsewhere in the polymer system.

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