

Photoresponsive polymeric systems:

1. Mixed monomolecular films of some synthetic polymers and indolinospiropyrans

Hal S. Blair and Ciaran B. McArdle

Dept. of Chemical Engineering, The Queen's University of Belfast, Belfast, Northern Ireland, UK

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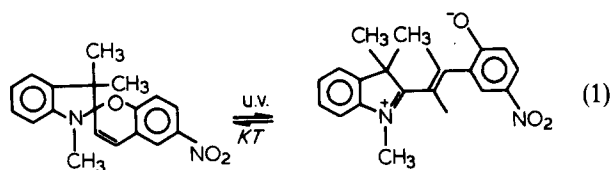
The properties of mixed monolayer films of photochromic indolinospiropyrans and poly(methyl methacrylate) (PMMA), poly(vinyl stearate) (PVSt), and poly(2-vinyl pyridine) (P2VP) have been studied. It was found that reversible photoinduced changes in monolayer surface-pressure with time occurred in collapsed systems and in mixed films in which the photochrome had been forced out of the polymer monolayer. Mixed films of P2VP and a spiropyran of particular structure could have their inherent stability increased under the action of ultraviolet irradiation on aqueous subphases. This effect appeared to be related to the formation of a physically crosslinked photomerocyanine-polymer two-dimensional network.

(Keywords: photochromism; photoresponsive; spiropyran; polymer; monolayers)

INTRODUCTION

Rideal *et al.*¹ considered the photochemical reaction of macromolecules in Langmuir films more than forty years ago, when they studied the effect of ultraviolet radiation on protein monolayers to obtain information on biological reactions to radiation. More recently there has been a renewed interest in the photochemical properties of polymer monolayers and several papers have appeared in the literature within the past three years²⁻⁵. These publications describe in particular photochromic phenomena in two-dimensional polymeric systems, a subject which has already received considerable attention in the bulk solid and liquid states^{6,7}. The present paper describes photoresponsive effects in mixed monolayers of polymers with photochromic indolinospiropyrans.

Spiropyrans are well known organic photochromes, the indolino derivatives being the most common group⁸. Equation (1) shows the 'normal' or positive photochromic reaction of a typical spiropyran.



This reaction involves a heterocyclic cleavage of the 1,2 single bond of the pyran ring followed by the rotation of the two halves of the molecule to give planar zwitterionic forms which are stabilized by resonance. This process is accompanied by a colour change because the spiro form (SP) lacks conjugation whereas the planar photo-produced zwitterionic species are in fact merocyanine dyes (PMC).

In view of the photoresponses occurring when such photochromes are chemically or physically incorporated into bulk polymeric systems⁶, it was of interest to investigate the possibility of photoresponsive effects in analogous two-dimensional systems.

EXPERIMENTAL

Materials

Polymers: The polymers used were commercial samples (Aldrich) of high molecular weight poly(methyl methacrylate) (PMMA), poly(vinyl stearate) PVSt and poly(2-vinyl pyridine) (P2VP).

Spiropyrans: The spiropyrans were synthesized as described previously⁹. The products have the structures and names shown in *Figure 1*. The melting points of SP1 and SP2 were 86° and 94°C respectively. The notation PMC refers to the photomerocyanine forms of the spiropyrans.

Spreading solutions: Gold label spectrophotometric grade benzene and chloroform (Aldrich) were used as solvents. The solutions contained accurately weighed quantities of polymer and photochrome and were stored for 24 h in the dark before use. The polymer concentration used was 1 mg cm⁻³.

Monolayer subphases: The aqueous subphase was doubly distilled water, the second stage distillation was from alkaline permanganate solution. Sub-phases of high and low pH were prepared from the buffer systems as described by Long¹⁰.

Instrumentation

Determinations of surface pressure/area isotherms (π -A

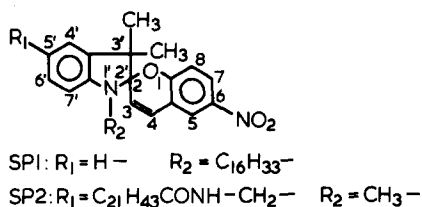


Figure 1 Structures of spiroopyrans SP1 and SP1

curves) were, performed with a Lauda MGW automatic recording film balance (Lauda-Königshofen FGR). Mixed polymer-photochrome solutions were delivered to the previously cleaned water surface from an all glass Agla micrometer syringe (Wellcome Diagnostics, Kent) and a period of 5–10 min was allowed for solvent evaporation before compression. In π -A experiments, the mixed films were compressed at a rate of about 0.9 cm min^{-1} . In the case of P2VP systems, the films were re-expanded at this rate after the initial compression in order to establish hysteresis effects. All experiments were conducted at 21°C under different conditions of illumination. π -A determinations were repeated several times to ensure reproducibility and control experiments were conducted with the polymers only to ensure that ultraviolet radiation had no adverse effects on their monolayers.

Irradiation of the monolayers was from above with a Hanau Fluotest-Forte ultraviolet lamp fitted with a blacklight filter (Original Hanau Heraeus GmbH, Hanau, FGR). This lamp has a high pressure mercury vapour burner (180 W) and a useful wavelength of 360 nm; it is capable of irradiating large areas. The lamp was mounted about 15 cm from the monolayer to minimize thermal effects. Careful checks were kept on the temperature of the subphase beneath the monolayer by monitoring subphase temperature with a platinum resistance thermometer (Lauda, US7-UA1). Dark conditions refer to the subdued light from a green 60 W safelight in an otherwise blacked out room.

Reversible cycling of surface-pressure was effected by compression of mixed PVSt-spiroopyran monolayers under u.v. light to pre-determined values by means of a constant pressure accessory unit (Lauda US8) to the film balance. The compression and irradiation were then simultaneously switched off and a time-base activated on an X-Y recorder (BBC Goerz Servogor 733, Goerz Electro GmbH, Wien, Austria) so that π -t data were monitored. After a given period the monolayers were re-irradiated with u.v. light. This u.v.-on/u.v.-off procedure was repeated several times.

RESULTS AND DISCUSSION

The results from the three different systems: PMMA; PVSt; P2VP-spiroopyran, will be discussed separately. The PPMA-spiroopyran mixed system was studied only briefly in order to compare and contrast the results obtained from mixed monolayers with those recently obtained from monolayers of a structurally related photochromic copolymer⁵.

PMMA-spiroopyran mixed monolayers

Interesting photoresponses in monolayers were measured recently by Rondelez and co-workers⁵ arising from the photochromic copolymer prepared from methyl

methacrylate and 6-nitro-1'- β -methacryloyloxyethyl-3',3'-dimethyl spiro [2H-indolimo-2,2'-benzopyran] (5.1 mol% spiroopyran derivative, MW: 21 500¹¹). These authors have stated that repartition of spiroopyran chromophoric side chains from the monolayer can be assigned unambiguously on the basis of three observations: (i) spiroopyran side chains apparently do not contribute to surface area or pressure, (ii) the surface pressure of the copolymer is independent of subphase pH under dark conditions, and (iii) individual spiroopyran molecules cannot spread spontaneously. That complete repartition of spiroopyran side chains from a true monolayer occurs for these reasons seems unlikely in the light of our experiments with PMMA-spiroopyran systems. Figure 2 represents the π -A isotherms obtained for mixed films of PMMA with SP1 in various proportions. It can be seen that the difference between dark and u.v. isotherms for any particular polymer-photochrome composition, depends upon the concentration of the spiroopyran in the mixed film. However, the variation in the dark isotherms at different spiroopyran concentrations is relatively small. Thus, the spiroopyran chromophore seems to make little contribution to surface pressure or area in these mixed systems in the dark also. However, the isotherms give no obvious indication of phase separation of the photochrome from the polymer or of incompatibility. Similar results were obtained with mixed films of PMMA and a non-surface active spiroopyran 6-nitro-1'- β -hydroxyethyl-3',3'-dimethyl spiro [2H-indolino-2,2'-benzopyran] which is the precursor to the photochromic comonomer.

Sutherland and Miller¹² have suggested that monolayers of PMMA may contain voids because the polymer molecules are slow to assume the conformation which places the maximum number of polar groups in the interface. The occurrence of spiro chromophores, either as side chains or simply mixed in, in monolayer voids could explain why these molecules do not make an obvious contribution to surface area in PMMA films.

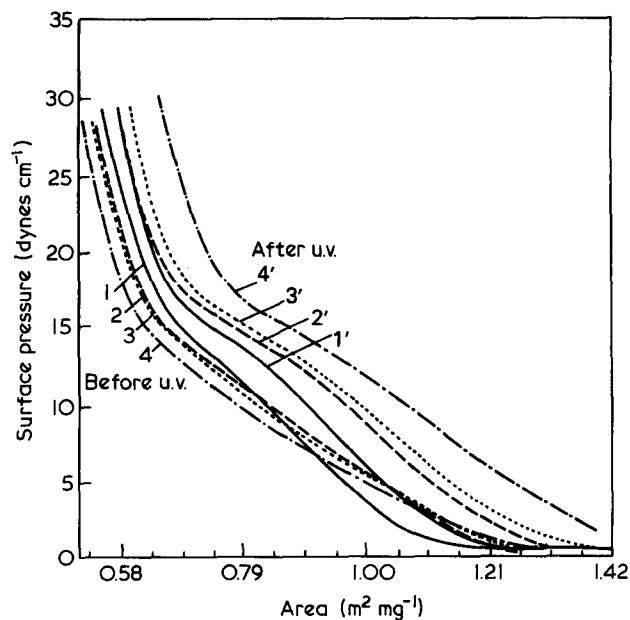


Figure 2 π -A isotherms for PMMA-SP1 mixed monolayers on an aqueous subphase at 21°C . Concentrations of the photochrome with respect to the polymer 10, 20, 30, 40% w/w corresponding to curves (1)–(4). Curves (1')–(4') were recorded after u.v. irradiation

Their contribution to surface pressure will also go unnoticed until the polymer molecules begin to interact at which stage bulky spiro molecules whether chemically or physically incorporated will disrupt packing and lower the film stability. In the mixed films instability was observed even at 10 dynes cm^{-1} and there appears to be an indication from π -A data that the copolymeric system also becomes unstable at 11 or $12 \text{ dynes cm}^{-1.5}$.

The independence of surface pressure of the copolymeric (and mixed systems on subphase of low pH under dark conditions is to be expected since the spiro forms do not interact with HCl in the subphase in the dark and at room temperature¹³. However, it is known that spiro forms will interact with gaseous HCl in toluene and ethanolic solutions at -78°C ¹⁴. Under these conditions a 'closed' salt (2) formed which can readily isomerize to the more stable 'open' salt (1). It is important to note that the open salt form (1) can then be photochemically reconverted to the closed form, i.e. species (1) exhibits negative photochromism¹⁵. The reaction is described in Figure 3.

The statement that individual spiropyran molecules cannot spread spontaneously to form monolayers must be qualified since monolayers of pure SP2 have been obtained under dark conditions indicating that the spiro chromophore can interact with the aqueous subphase⁹.

It seems therefore probable that the photoresponses reported by Rondelez *et al.* arise from monolayers which are unstable or perhaps even collapsed, (surface concentration 1.39 mg m^{-2} , $\pi = 11 \text{ dynes cm}^{-1.5}$ and mixed and copolymer films appear unstable above about 10 dynes cm^{-1}). The dark recovery of surface pressure noted by these authors at pH 1.5 cannot be due to thermal ring closure of the protonated photomerocyanine side chains since such species are well known to be negatively photochromic and hence in the dark they are stable¹⁶. This would indeed suggest that the observed decay of surface pressure with time is a consequence of film instability.

PVSt-spiropyran mixed monolayers

In view of the discussion above it seems likely that when spiropyran chromophores are present in a collapsed overfilm reversible responses may occur. It was therefore of interest to examine polymer-spiropyran mixed systems in which the spiropyran chromophores could be pushed out of the polymer monolayer into the overfilm. Previous results with mixed monolayers of octadecanol and SP1¹³ indicated that this photochrome was very incompatible with the long chain fatty alcohol and was easily phase separated from its monolayer. It was anticipated that polymers capable of forming vertically oriented monolayers such as PVSt¹⁷, would give similar behaviour when chosen as a mixing component for SP1. SP2-octadecanol monolayers did not show clean phase separations because

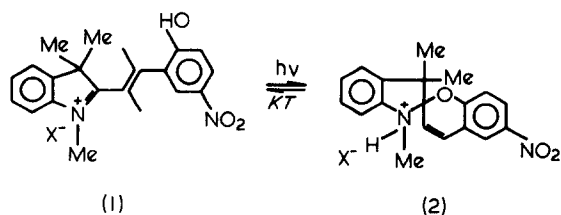


Figure 3 Negative photochromic reactions of protonated opening form of an indolinospiro

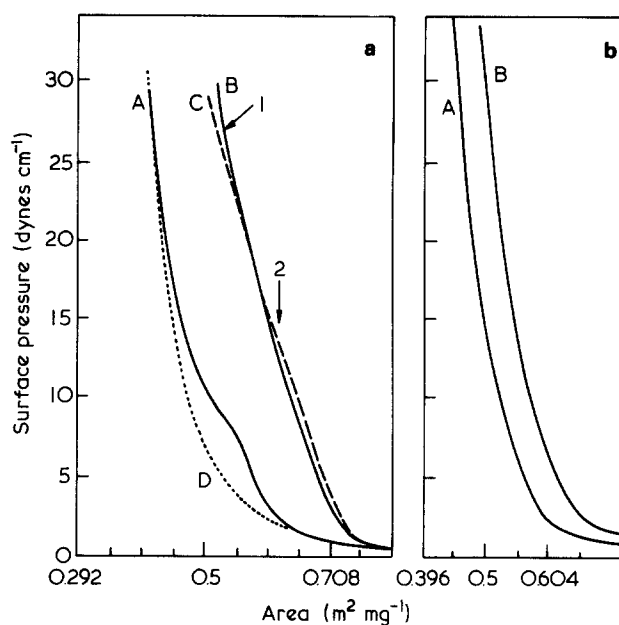


Figure 4 π -A curves for mixed PVSt-spiropyran films (a) PVSt-SP1 system (30% SP1 w/w) curve A mixed film isotherm recorded in the dark on aqueous and acidic (HCl) subphases; curve B same system under u.v. conditions on aqueous subphase, point 1 representing onset or phase separation of PMC1 form; curve C same system under u.v. conditions on HCl subphase, point 2 representing phase separation of protonated PMC1 species. (b) PVSt-SP2 system (30% SP2 w/w) on aqueous subphase before (A) and after (B) ultraviolet irradiation

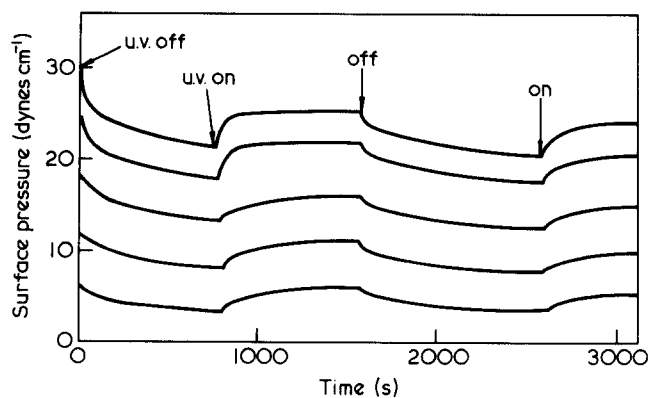


Figure 5 Reversible photoresponses of PVSt-SP1 (30% SP1 w/w) on an aqueous subphase. The mixed film was initially compressed to the pre-set values indicated on the π -axis at $t=0$ under ultraviolet light

the SP2 structure enables more compatible mixed monolayers to be formed^{9,13}.

Figures 4-7 indicate the results obtained from PVSt-SP1 systems. The π -A isotherms for the PVSt-SP2 system is shown for comparison in Figure 4b but was not suitable for further study since as expected phase separation of SP2 did not occur. The reversible photoresponse cycles corresponding to alternate periods of u.v. irradiation and darkness are shown in Figures 5-7. In experiments with PVSt-SP1, the mixed monolayers were compressed to surface pressures corresponding to regions before, during and after SP1 had been pushed out of the PVSt surface film. These surface-pressures were selected from the π -A data shown in Figure 4. No significant photoinduced increase in surface-pressure was apparent before phase separation, but during and after this process, reversible photoresponses were observed. At surface

pressures above ~ 15 dynes cm^{-1} , the magnitude and rate of the photoresponse was seen to increase and the stability of the PVSt film decreased as evidenced by the immediate drop in surface-pressure on cessation of u.v. irradiation (see Figures 5 and 7). The difference in photoresponses above and below 15 dynes cm^{-1} were taken to originate from phase separated and collapsing bulk systems respectively. Figure 6 shows that the photoresponse can be cycled quickly and that variation of irradiation conditions can alter the overall rate at which the film collapses.

The change in magnitude and rate of photoresponse was more apparent when the experiment was conducted on hydrochloric acid subphases as shown in Figure 7. In this Figure, competition between film collapse and photogeneration of surface pressure can be seen even during periods of continuous irradiation above 15 dynes cm^{-1} . The differences between the photoresponses above

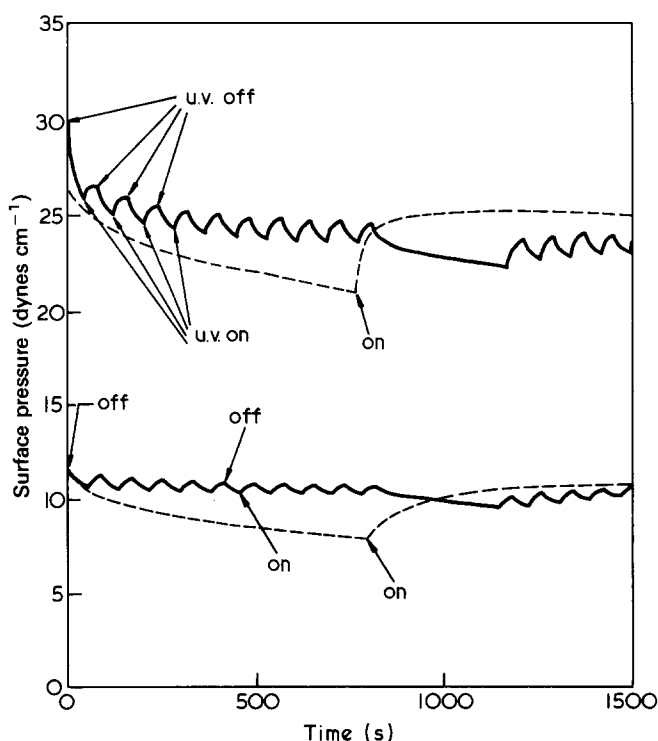


Figure 6 Indication of the speed at which the photoresponses of a PVSt-SP1 (30% SP1 w/w) can be cycled and how variation of method of irradiation changes the overall decay rate of surface pressure in the dark. Dotted curves are the initial cycles from Figure 5 shown for comparison

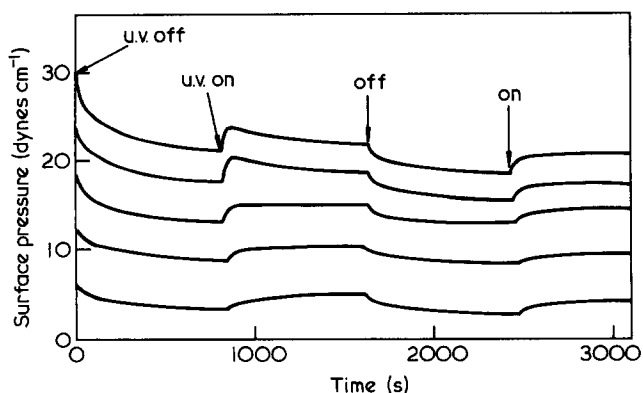


Figure 7 Reversible photoresponses for PVSt-SP1 (30% SP1 w/w) system on HCl subphase

15 dynes cm^{-1} observed on aqueous and acidic subphases are thought to be a consequence of the difference in compatibility between the photomerocyanine and the photomerocyanine hydrochloride of SP1 and the polymer after the photoproduct species is respread¹³. The u.v. π -A isotherms shown in Figure 4 were obtained by pre-isomerizing the spreading solution in the syringe before spreading on the water surface. These indicate that there is great compatibility between the polymer and the photoproduct on aqueous subphases than on acidic subphases, a result which was much more clearly shown in the octadecanol-SP1 model systems¹³.

P2VP-spiropyran mixed monolayers

To investigate how the structure and orientation of the polymer on the water surface might influence the photochromic properties of mixed polymer-spiropyran films, polymers such as polyvinyl acetate and P2VP which are known to form horizontally oriented monomolecular films^{18,19,20} were chosen as mixing partners for spiropyrans. Furthermore, hysteresis effects occur during compression-expansion cycles of the surface films of such polymers² which give an indication of the extent of polymer-polymer interaction on packing and unpacking of polymer chains. It was anticipated that the inclusion of a 'steric photochromic monolayer probe' would alter the hysteresis behaviour of such films under different conditions of illumination.

Poly(vinyl acetate)-spiropyran systems were studied initially, but this work was abandoned due to the difficulty in distinguishing between photo and thermal effects from the u.v. lamp since poly(vinyl acetate) showed great sensitivity to small increases in temperature. However, monolayers of P2VP are unaffected by temperature in the range 15°C-35°C²⁰ and since the temperature increase during a compression-expansion experiment was only ~ 2 -3°C after one hour, this polymer was ideally suited for study. Since P2VP is a polyelectrolyte influences of subphase pH were also investigated.

Figures 8 and 9 illustrate hysteresis in the π -A curves of mixed P2VP-SP1 systems at different photochrome concentrations under different conditions of illumination on neutral subphases.

Under dark conditions, it was found that the surface-pressure at which the film first became unstable increased slightly and the hysteresis loop became larger as the photochrome concentration increased up to about 30% w/w. Above this concentration no further enhancement of film stability was observed. Under ultra-violet conditions, the π -A curves were displayed to higher molecular area and there was a very marked increase in film stability as the photochrome content increased to 30% w/w. Two hysteresis loops could be distinguished under ultraviolet conditions, one at high surface pressures (>17 dynes cm^{-1}) and the other at lower surface-pressures for P2VP-SP1 films having greater than 10% w/w photochrome present. Both of these loops were narrower than those obtained under dark conditions.

Mixed films of P2VP and SP2 showed similar effects except that the ultimate surface pressure attained under ultraviolet light for these systems with an equivalent photochrome content, before collapse, was surprisingly lower than that for the P2VP-SP1 system. For example a P2VP-SP2 film with 30% w/w SP2 content became unstable at 24 dynes cm^{-1} under ultra-violet light,

compared to 32 dynes cm^{-1} for the equivalent P2VP-SP1 system.

Figures 10 and 11 show how variation of subphase pH influences the π -A characteristics of the mixed films. Below pH 3.7, P2VP monolayers dissolve into the subphase, in the range 6.2-9.4 the π -A relationship is independent of subphase pH and above pH 9.4 there is slight expansion of the P2VP monolayer^{19,20}. It can be seen that on both high and low pH subphases, the mixed P2VP-SP1 monolayers become more compressible than before, achieve lower surface pressures before instability sets in, have large hysteresis loops under both conditions of illumination and under u.v. the reinforcement of monolayer surface pressure is not so apparent and the high pressure hysteresis loop disappears completely.

These results indicate that the interactions of photo-produced merocyanine with P2VP are quite different from those of the spiropyran with the polymer. Results from π -A data on neutral subphases suggests that PMCl (photomerocyanine of SP1) forms reinforce the P2VP monolayer. Similar reinforcement has been reported in mixed monolayers of poly(vinyl acetate) and fatty acids by Ries and co-workers²². That the extent of monolayer reinforcement is much less under dark conditions than under ultraviolet conditions in the P2VP-spiropyran systems suggests that photocontrol of monolayer stability is possible. Furthermore, the effect is dependent on both photochrome concentration and on photochrome structure.

It was observed that chloroform spreading solutions of P2VP-SP1 became slightly coloured even in the dark. Thus, P2VP solutions containing 10, 30, 50 and 100% w/w SP1 had optical densities of 0, 0.105, 0.185 and 0.315 at 575 nm, while no such colouration was seen with P2VP-SP2 solutions. The level of colouration of P2VP-SP1 solutions in the dark remained constant and was much less than that produced after irradiating the solutions with u.v. light. These observations would suggest that P2VP can stabilize the ring-open form of SP1 in polar solvents but not the ring-open form of SP2. This suggestion is supported by the results obtained from the monolayer experiments.

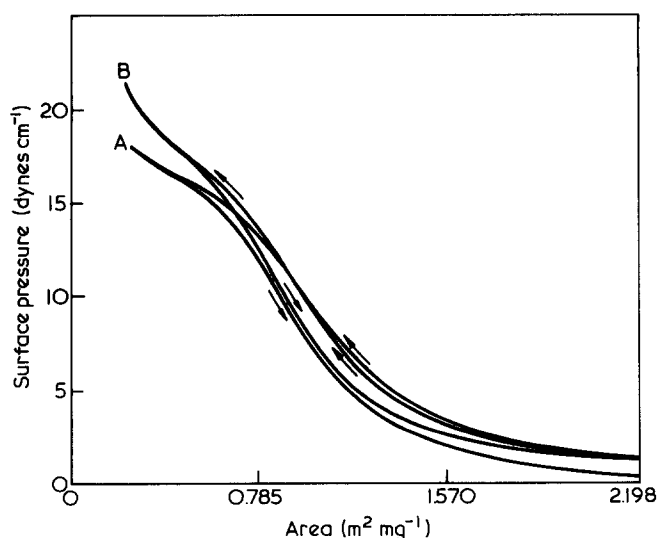


Figure 8 π -A isotherms for P2VP-SP1 (10% w/w) on aqueous subphase in dark (A) and in ultraviolet (B) conditions. Arrows represent either compression (decrease in surface area) or expansion (increase in surface area)

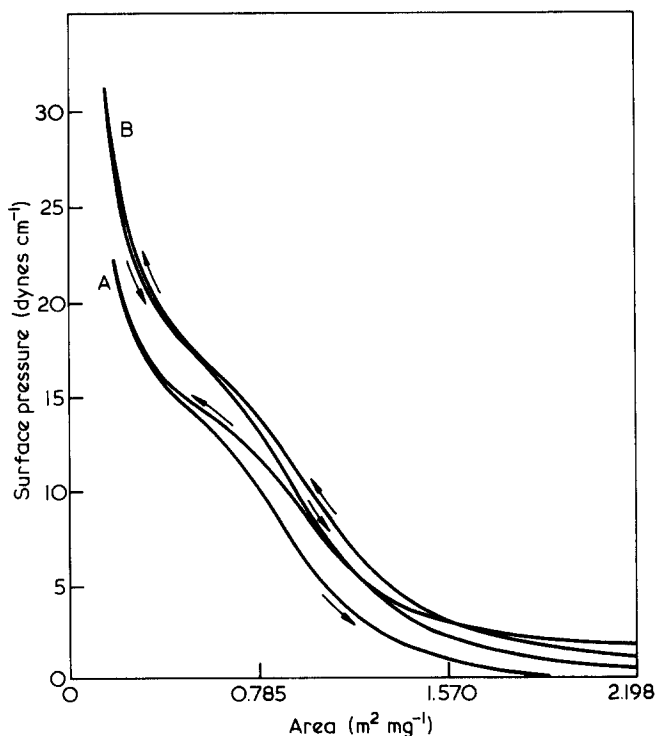


Figure 9 π -A isotherm for P2VP-SP1 (30% w/w) on aqueous subphase in dark (A) and u.v. conditions (B). The diagram shows enhancement in surface-pressure in ultraviolet light

Miller¹⁹ has studied the configuration and orientation of P2VP in monomolecular films and has concluded that this horizontally oriented polymer adheres to the interface via the polar nitrogen atoms of the pyridine rings. Thus the polymer backbone lies flat on the water surface while its pendant pyridine residues are vertically oriented. For P2VP unlike its isomer poly(4-vinyl pyridine), the pyridine residues tend to alternate in a *trans* configuration along the backbone.

Examination of space filled molecular models showed that the PMCl form, which is a planar merocyanine dye with a fatty substituent more-or-less centrally located in its structure, can fit edgewise between the pyridine residues of P2VP so that its hydrocarbon chain is vertically oriented and there is good overlapping of the aromatic systems of the polymer and photochrome. Thus, PMCl can interlace between polymer chains thereby acting as a physical crosslink. There are various ways in which this interlocking can occur as shown in Figure 12, but as shown in diagram (C) enhancement of film stability could result, not only from the crosslinking effect, but also from the additional van der Waals interactions between the hydrocarbon chains attached to the photochrome. Such an effect might explain the dual hysteresis observed under ultraviolet conditions for the P2VP-PMCl system (Figure 9). The narrow hysteresis at high surface-pressures indicates unpacking of the hydrocarbon substituents on the photochrome, while the low pressure loop describes the polymer-PMCl-polymer unpacking as the film is expanded.

That PMCl may be forming a physical crosslink between P2VP chains is further supported by the observations obtained from the P2VP-SP2 system. The PMC2 form does not provide additional reinforcement of the monolayer in spite of its longer hydrocarbon substituent. This photochrome (PMC2) has the fatty

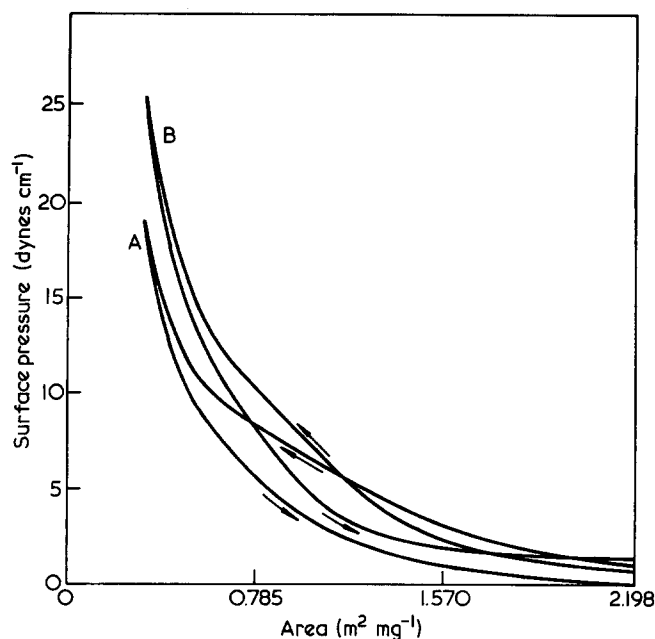


Figure 10 π -A isotherms for P2VP-SP1 (30% w/w) on citric acid/sodium citrate buffer (pH 3.97) in dark (A) and in u.v. conditions (B)

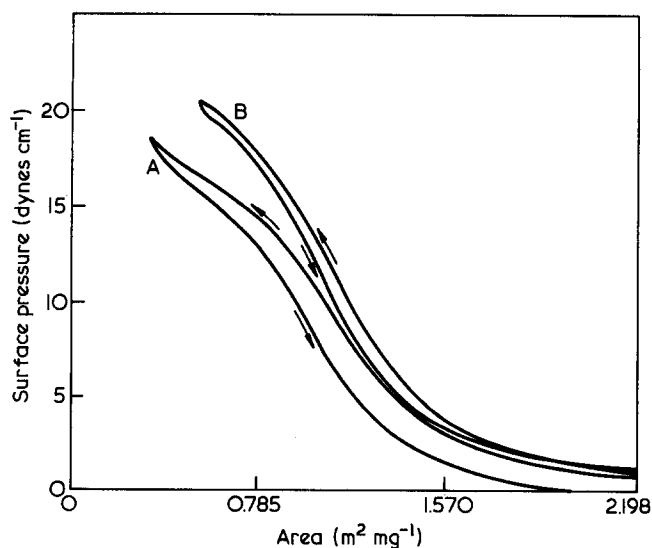


Figure 11 π -A isotherms for P2VP-SP1 (30% w/w) on subphase containing NaOH (pH 11.7) in dark (A) and in u.v. conditions (B)

substituent attached to the extremity of the long axis of the chromophoric system, *Figure 12d*, and when this is vertically oriented the hydrophilic chromophore lies directly beneath it as has previously been reported from experiments conducted on pure PMC2 monolayers⁹. Thus in the mixed P2VP-PMC2 system physical crosslinking is much less likely than for the P2VP-PMC1 system as reflected by the relatively low surface-pressure (24 dynes cm⁻¹ compared to 32 dynes cm⁻¹) at which the former mixed film becomes unstable. However, two well defined hysteresis loops occur also in the P2VP-PMC2 system indicating that there is still some degree of interaction between hydrocarbon chains (see *Figure 12e*).

That little reinforcement of P2VP-spiropyran mixed monolayers occurs under dark conditions is a consequence of the bulkiness of the spiro chromophore which precludes regular interlocking of the photochrome with the polymer chains. The slight increase in collapse

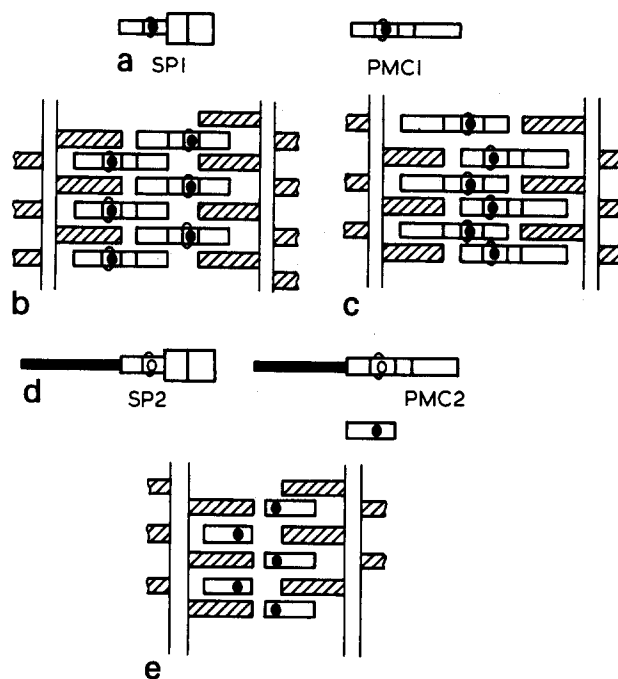


Figure 12 Schematic representation of proposed physical crosslinks formed by PMC1 and P2VP in an ideal model. (a) representation of spiro and photomerocyanine forms of SP1; (b) and (c) ways in which PMC1 can interlace P2VP chains; (d) representation of spiro and photomerocyanine forms of SP2. The end on view of PMC2 is also shown; (e) mixed P2VP-PMC2 system. Solid bars and circles represent fatty substituents, open circles represent methyl groups and lightly shaded areas represent pyridine residues

pressures in the dark with increasing spiropyran concentration shown in *Figures 8* and *9* likely result from the small quantity of PMC1 molecules which were initially stabilized by the polymer in the dark. No such surface-pressure enhancement in the dark was noted in the P2VP-SP2 isotherms with increasing SP2 concentration.

The lack of monolayer reinforcement and broader hysteresis curves noted in the experiments conducted at high and low pH (*Figures 10* and *11* result from the expansion of the polymer film at high pH and its partial dissolution at low pH both of which would decrease the ability of the photochrome (PMC1) to efficiently interlock between polymer chains.

It should be noted that the system described by *Figure 12* represents an ideal model. The real situation probably involves occurrence of the proposed physical crosslinks in some regions where irregularities in polymer structure such as buckled segments etc, assist the accommodation of the PMC1 molecules particularly when the system is under compressive force.

It would be of interest to examine the properties of poly(4-vinylpyridine)-SP1 monolayers since this polymer tends to have the pyridine residues along one side of the backbone when oriented on the water surface¹⁹. It would be anticipated that the monolayer reinforcement noted for the P2VP-PMC1 system would be less apparent for the P4VP-PMC1 system since the possibility of forming a physically crosslinked two-dimensional network would be precluded in the latter case.

CONCLUSION

Monolayer experiments conducted on polymer-spiropyran mixtures have shown that reversible

photoinduced changes in surface-pressure occur in collapsed and phase separated systems. These easily measured changes represent efficient photomechanical responses and may have potential application for transduction of light energy.

A membrane-like structure made up from a macromolecule (P2VP) and an ultraviolet sensitive fatty substituted derivative (SP1) may have its stability regulated by light. The additional stability after u.v. irradiation appears to result from the ability of the photoexcited form of the photochrome to take part in physical crosslinking of the two-dimensional polymeric matrix. Further considerations of the interactions between spiropyrans and poly(vinyl pyridines) in solution and in monomolecular films are currently under investigation.

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