

Photoresponsive polymers: 2. The monolayer behaviour of photochromic polymers containing aromatic azobenzene residues

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The monolayer characteristics of photochromic azo containing addition and condensation polymers have been investigated under different conditions of illumination. Possible orientations of the polymers in the monolayers have been proposed. It was found that *trans*→*cis* photoisomerization of these materials was not always possible in the Langmuir films and photoinduced changes in monolayer area with time were followed for those polymers which showed uninhibited photoisomerization.

(Keywords: photoresponsive polymers; monolayers; azo polymers; photochromism; photoisomerization)

INTRODUCTION

In a previous paper¹ the properties of mixed monolayers of some polymers with photochromic spiropyrans were described. The present article describes the properties of some macromolecular azo containing monolayers and reinvestigates the aromatic azopolyamides which were considered briefly in a preliminary report² with less sensitive apparatus.

EXPERIMENTAL

Materials

(i) *4-Palmitoylaminoazobenzene (4-PB)*. The structure of 4-PB is shown in Figure 1(a). The model compound was prepared by condensation of palmitoyl chloride with 4-aminoazobenzene in the presence of triethylamine in benzene. The fatty substituted dye melted at 120°C. Key bands in the infra-red spectrum in wave-numbers were: 3280 (NH stretch), 2910, 2840 (–CH₂– stretch, asym. and sym), 1655 (Amide I), 1540 (Amide II), 1468 (–CH₂– deformation), 720 (+(CH₂)_n rock, n>4). Optical spectra in hexane: *trans*-4PB λ_{max}=330 nm, *cis*-4PB λ_{max}=250 nm.

(ii) *4-Acryloylaminoazobenzene (AAB)*. The structure of AAB is shown in Figure 1(b). The photochromic monomer was prepared by a procedure similar to that described by Eisenbach^{3a}. The monomer was purified by recrystallization three times from ethanol:water (1:1) mixture. AAB melted at 167°C (literature 167°C^{3b}).

(iii) *Homopolymerization of AAB*. The homopolymer of AAB is coded PAAB. AAB (3 g) in acetone (30 cm³) containing AIBN was injected into a pyrex polymerization tube. The mixture was degassed by three alternate freeze-pump-thaw cycles and sealed in the tube under vacuum. Polymerization was effected by heating at 60°C for 96 h. The polymer (PAAB) was purified by three

precipitations into methanol and then dried in a vacuum oven at 30°C for several hours.

Like AAB, PAAB exhibited *trans*→*cis* photoisomerization in solution on irradiation at about 366 nm. The optical spectra for the monomer and its polymer are shown in Figure 2.

(iv) *Copolymerization of AAB with methyl methacrylate (MMA)*. A series of copolymers coded MX, M1, M2, M3 were prepared having photochrome mole fractions of 0.623, 0.022, 0.019 and 0.006 respectively as estimated from optical spectra.

Copolymerization was conducted in toluene in the presence of AIBN at 60°C for 20 h with the requisite monomer concentrations. Copolymers were purified by reprecipitation in methanol. All samples were photochromic.

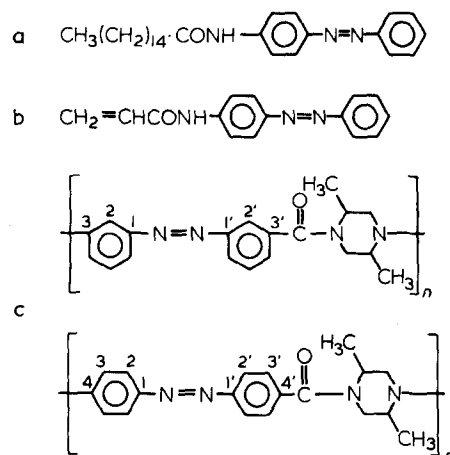


Figure 1 (a) structure of 4-palmitoylaminoazobenzene (4-PB); (b) structure of 4-acryloylaminoazobenzene (AAB); (c) structures of the azopolyamides; (upper) poly (3,3'-azodibenzoyl-*trans*-2,5-dimethyl piperazine) (3,3'-polymer) and (lower) poly (4,4'-azodibenzoyl-*trans*-2,5-dimethyl piperazine) (4,4'-polymer)

(v) *Azopolyamides*. The structures of the azopolyamides and their formal nomenclature and acronyms are given in Figure 1(c). The samples were a gift from Mr J. E. Riordan, Ulster Polytechnic⁴.

Instrumentation and techniques

Surface pressure–area (π - A) isotherms were measured on an MGW Lauda Film Balance. The film balance was fitted with an *XYt* recorder. The subphase in each case was doubly distilled water.

Spectroscopic grade benzene (Aldrich, Gold Label) was used as spreading solvent for all samples except the azopolyamides when spectroscopic grade chloroform was used. Solutions were delivered to the water surface from an Agla micrometer syringe (Wellcome, Kent).

Irradiation was conducted with a Hanau Fluotest Forte analytical U.V. lamp (180 W, principle wavelength 366 nm) fitted with a 'black light' filter.

RESULTS AND DISCUSSION

Monolayer characterization

The monolayer behaviour of the model compound 4-PB was considered for two reasons. Firstly to obtain information about the orientation of the azo group at the air/water interface and secondly to check the photochemical stability of the hydrocarbon–CONH–azo chromophore system. The latter check was important since molecules such as stearyl anilide ($C_{17}H_{35}$ –CONH– C_6H_5), benzylstearylamine ($C_{17}H_{35}$ –CONH– $CH_2C_6H_5$) and β -phenylethylstearylamine ($C_{17}H_{35}$ –CONH– $(CH_2)_2-C_6H_5$) are known to undergo photo-decomposition in monolayers^{5,6}.

The π - A curves for 4-PB are shown in Figure 3 for the *trans* and *cis* isomers. It was found that *trans*→*cis* photoisomerization was inhibited in monolayers of 4-PB and so the *cis* isomer was produced by preisomerizing the *trans* spreading solution.

The zero pressure extrapolated area ($A_{\pi=0}$) for the *trans* isomer suggests that after compression the azo chromophore is oriented with its long axis perpendicular

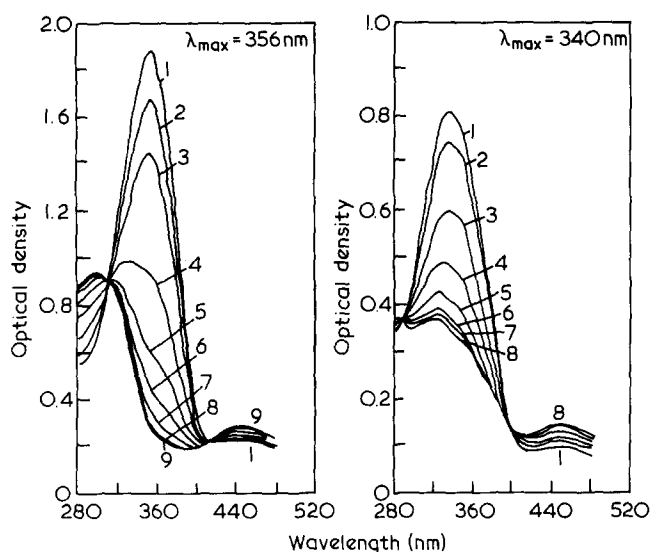


Figure 2 Absorption spectra for AAB monomer (left) and its homopolymer PAAB (right) in benzene before and after u.v. irradiation. Curves (1) dark, curves 2–9 after 1, 5, 10, 15, 20, 25, 30 and 40 s irradiation (366 nm)

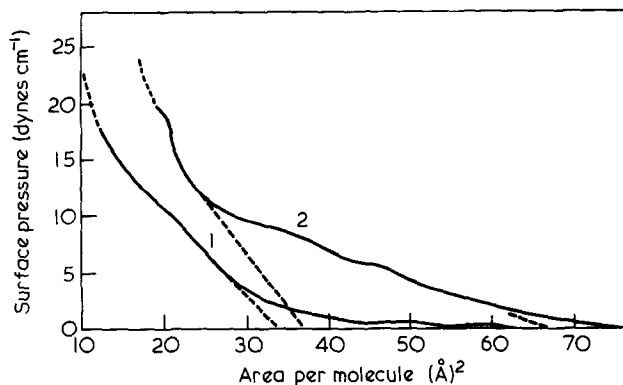


Figure 3 Surface pressure–area isotherms for *trans*-4-PB (1) and *cis*-4-PB (2). Subphase: pure water. Temperature: $20^\circ \pm 1^\circ C$

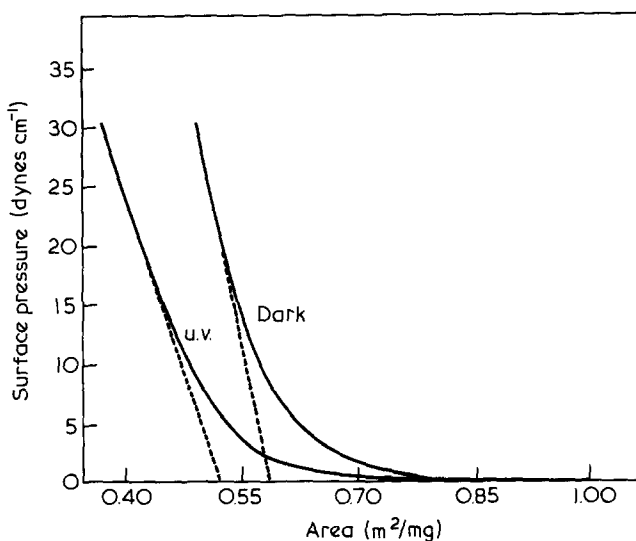


Figure 4 Surface pressure–area isotherms for PAAB under u.v. and dark conditions. Subphase: pure water. Temperature $20^\circ \pm 1^\circ C$

to the water surface. Azobenzene itself in such an orientation gives a cross-sectional area of 25.2 \AA^2 which is reasonably close to the 32 \AA^2 shown by the palmitoyl-amino derivative which is expected to occupy a slightly higher area.

Examination of molecular models suggests that the *cis* isomer of 4-PB should have a projected area of $65 \pm 3 \text{ \AA}^2$ in the plane of its unsubstituted ring and a projected area of $30\text{--}36 \text{ \AA}^2$ when its $-N=N-$ bond is vertically oriented. It will be noted that the final area occupied by the *cis* isomer is greater than that of the *trans* isomer. This result is in agreement with the observations of Gegiou *et al.*⁸ who suggest that the order of molecular volume for stilbenes is *cis* > twisted transition state > *trans* and that a similar situation should exist for the closely structurally related azobenzenes. This result explains the inhibited *trans*→*cis* photoisomerization of 4-PB on the water surface since this is a sterically unfavourable process. A similar result was reported by Whitten⁹ concerning the photoisomerization of thioindigo dyes in monolayers.

Figure 4 shows the π - A curves for homopolymer PAAB. It is apparent in this case that the isotherm recorded under u.v. conditions has a lower $A_{\pi=0}$ value than that given in darkness. This result is the opposite of that found for 4-PB and *trans*→*cis* photoisomerization is uninhibited in the monolayers of PAAB. Thus the *cis*-PAAB isotherm resulted when PAAB was irradiated with

u.v. light on the water surface. It should be noted that it was impossible to spread pre-isomerized PAAB solution since u.v. irradiation of benzene solutions of PAAB caused precipitation of the polymer. Photoreversible precipitation and resolubilization of an azobenzene-styrene copolymer has been reported very recently by Irie *et al.*¹⁰ and occurs because of the photoinduced change in dipole moment across the azo bonds in the photochromic polymers, the dipole moments being 0.5 D for *trans* and 3.1 D for *cis* azobenzenes¹¹. Since polymer-solvent interactions were clearly markedly affected by u.v. irradiation, it was anticipated that polymer-polymer interactions in monolayers would also be substantially influenced.

It is reasonable to assume that *trans*-PAAB adopts a configuration in which the bulky photochromic side chains alternate along the backbone and that the backbone is held at the interface by its numerous hydrophilic amide side groups. In this configuration the molecule has considerable breadth ($>27 \text{ \AA}$). Photoisomerization of the side chains leads to a reduction in the breadth of the macromolecule and the reduced lateral dimensions of *cis*-PAAB require monolayer area to be decreased before polymer-polymer interactions develop surface pressure for the *cis* isomer. The $A_{\pi=0}$ value for *cis*-PAAB is 10% lower than for *trans*-PAAB.

That photoisomerization was inhibited in 4-PB monolayers but not in those of PAAB indicates that the orientation of the chromophoric groups as well as the local steric environment dictates whether or not the process is favourable in monomolecular films.

In the AAB-MMA systems, the monolayer behaviour of the copolymers bore a closer resemblance to that exhibited by 4-PB rather than to that shown by PAAB. Thus, *trans*→*cis* photoisomerization was inhibited for the copolymer monolayers and the *cis* isotherms occurred at higher molecular area than the *trans* isotherms. The relative positions of the two curves was markedly influenced by photochrome concentration. The π - A curves for sample MX are shown in Figure 5. For sample M2 the u.v. and dark isotherms were coincident.

Interpretation of copolymer configurations at the interface is more complicated than in the former systems because of the additional considerations arising from the methacrylate side chains in these polymers. The compressible region of the *cis*-4PB isotherm shown in Figure 3 results from interaction of the polar hydrophilic *cis*-azobenzene (dipole moment 3.1D) with the aqueous substrate. Because of the similarities in photoreaction behaviour at the water surface, and in view of the relative positions of the *cis* and *trans* isotherms for 4-PB and MX, it is presumed that the configuration of copolymer monolayers embodies *cis*-azobenzene side chains oriented similarly to those found in the *cis*-4PB model compound monolayers.

The π - A isotherms for the 3,3'- and 4,4'-azopolyamides are shown in Figures 6 and 7. The large differences in monolayer behaviour of these polymers originates from the structural differences in their molecules. Numerous subtle variations in macromolecular configuration are possible for these polymers by virtue of their conformationally flexible piperazine subunits. To simplify interpretation of results it is assumed that the 3,3'- and 4,4'-(*trans*) azopolyamides exist in an extended conformation in solution and that their *trans* 2,5-dimethyl piperazine residues have a preference for diaxial substitution. This assumption is reasonable in view of the

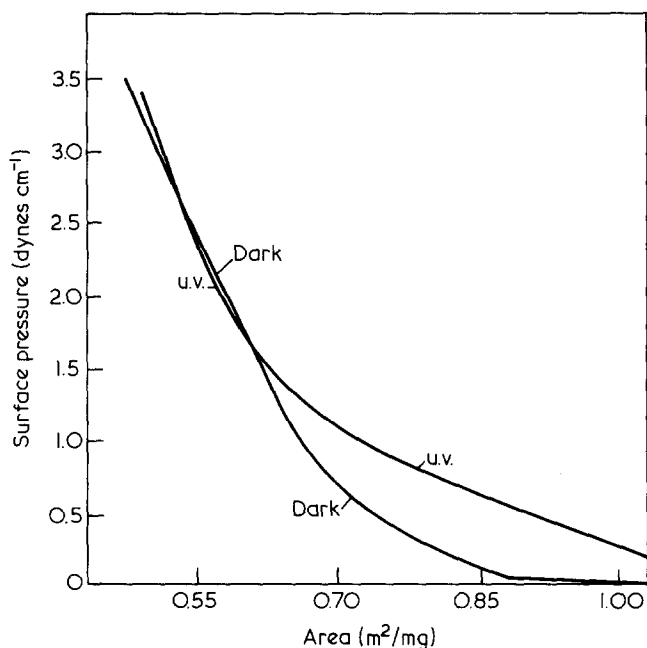


Figure 5 Surface pressure-area isotherms for AAB-MAA copolymer MX (mole fraction photochrome: 0.623) before and after u.v. irradiation. Subphase: pure water. Temperature $20^\circ \pm 1^\circ\text{C}$

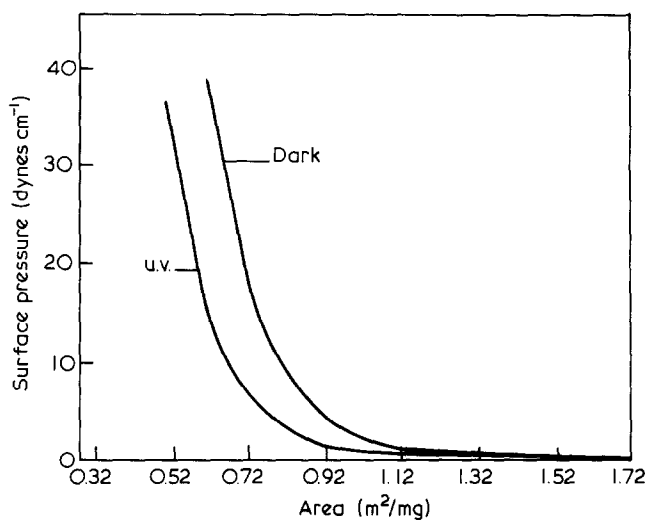


Figure 6 Surface pressure-area isotherms for 3,3'-azopolyamide before and after u.v. irradiation. Subphase: pure water. Temperature $20^\circ \pm 1^\circ\text{C}$

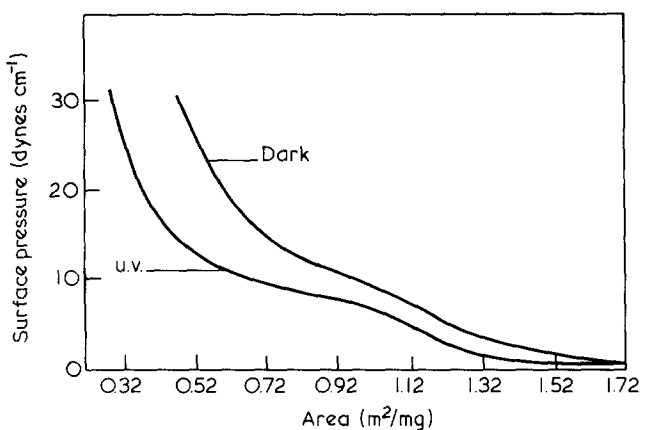


Figure 7 Surface pressure-area isotherms for 4,4'-azopolyamide before and after u.v. irradiation. Subphase: pure water $20^\circ \pm 1^\circ\text{C}$

structural analysis given by Montaudo *et al.*¹² on rigid polyamides containing piperazine residues.

The amide group in 1,4-dibenzoyl-2,4-dimethyl piperazine, which serves as a model for sections of the azopolyamide structures is almost planar and the carbonyl group conjugates strongly with the ring nitrogen but not the phenyl ring¹³. The phenyl ring is oriented at an angle of slightly over 50° to the plane of the amide bond¹³ and when incorporated into a macromolecule the phenyl substituents have restricted rotation¹². Thus piperazine residues play a predominant role in the determination of the overall configuration of the azopolyamides. Extension of the 1,4-dibenzoyl-2,5-dimethyl piperazine structure with azo systems leads to a narrow zig-zag configuration for the 4,4'-polymer under dark conditions as shown schematically in Figure 8(a). The 3,3'-polymer gives a more squat zig-zag configuration as a consequence of the *meta*-disubstitution of piperazine residues as represented in Figure 8(b).

The more extended structure of the 4,4'-polymer enables polymer-polymer interactions in monolayers to occur at higher molecular areas than for the 3,3'-isomer and also explains the greater compressibility of the 4,4'-azopolyamide films.

The u.v. isotherms for both azopolyamides occur at lower molecular areas than the 'dark' isotherms because of the substantial shrinkage in macromolecular dimensions that occur on irradiation of these polymers which contain isomerizable groups in every repeat unit. *Trans* → *cis* photoisomerization in monolayers was a favourable process for both 3,3'- and 4,4'-azopolyamides.

In *cis*-azobenzene the phenyl rings are oriented at

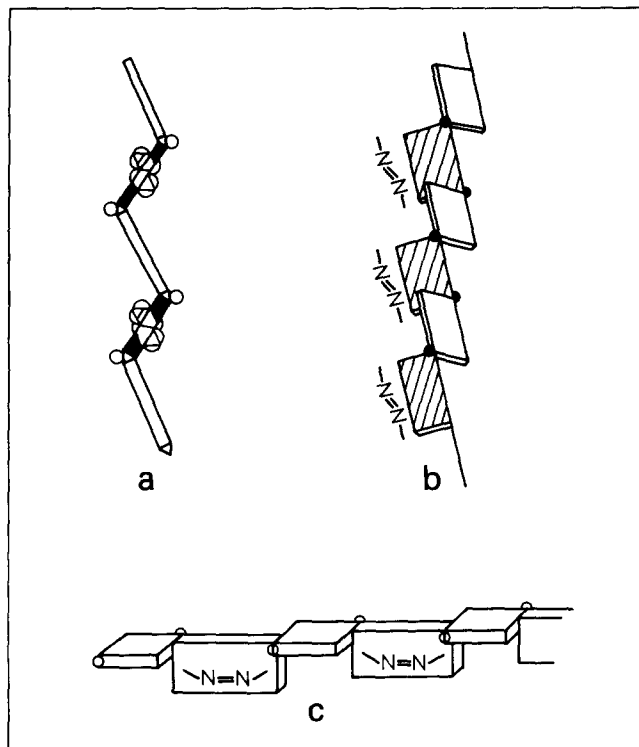


Figure 8 Schematic representation of azopolyamide conformations. (a) 4,4'-isomer with *trans* azobenzene units (viewed from above); (b) 3,3'-isomer with *trans* azobenzene units (viewed from above), and (c) 4,4'-isomer with *cis* azobenzene units

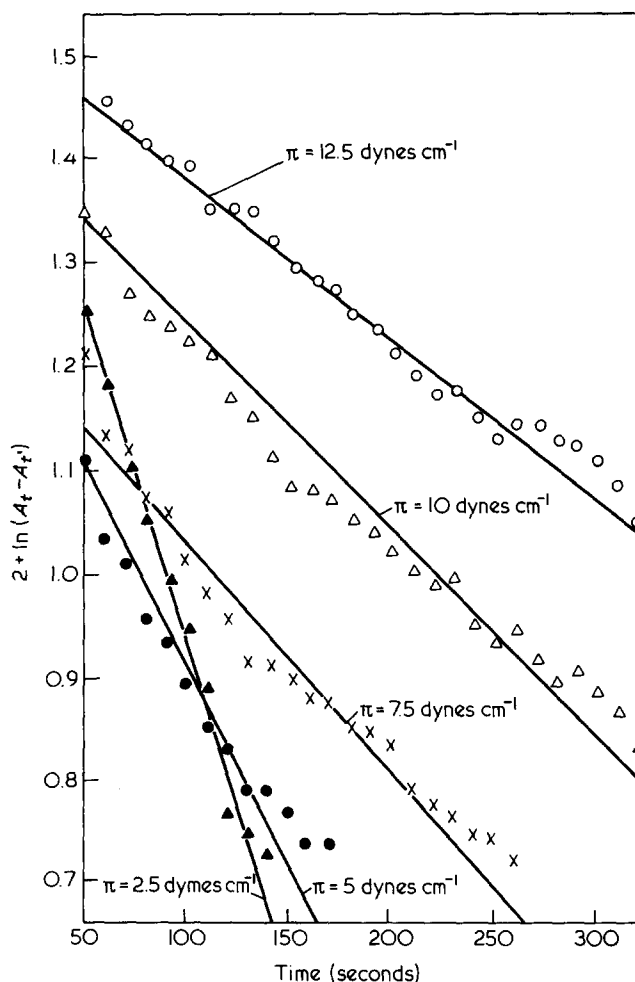


Figure 9 First-order rate plots describing contraction of 3,3'-azopolyamide monolayers after irradiation with u.v. light. Irradiation was effected when the individual surface films had been compressed to the surface pressures indicated. Subphase: pure water. Temperature $21^\circ \pm 1^\circ\text{C}$

about 53° relative to one another¹¹. Thus, since the phenyl substituents in 1,4-dibenzoyl-2,5-dimethyl piperazine are oriented at slightly over 50° relative to the amide bond, the presence of *cis*-azobenzene residues between piperazine units results in effectively removing the zig-zag from the *trans*-polymer structure and leads to an almost linear corrugated type structure shown schematically in Figure 8(c) for the 4,4'-polymer. Piperazine residues are situated at the maxima of the corrugations and reside in the interface; polar *cis*-azo groups are located at the troughs of the corrugations where they are solvated by the subphase. The situation for the *cis*-3,3'-polymer is similar although some zig-zag character is retained.

Photoinduced changes in monolayer area

In the systems where *trans* → *cis* photoisomerization was possible on the water surface, it was of interest to follow changes in the mono-molecular area with time at various constant values of surface pressure.

Monolayers of the 3,3'-azopolyamide compressed to specific surface pressures responded to u.v. irradiation in the way anticipated from consideration of the isotherms shown in Figure 6, i.e. irradiation of a *trans*-3,3'-azopolyamide film gave a smooth contraction in monolayer area with time. Area contraction data for this polymer are given in Figures 9 and 10. The contraction of

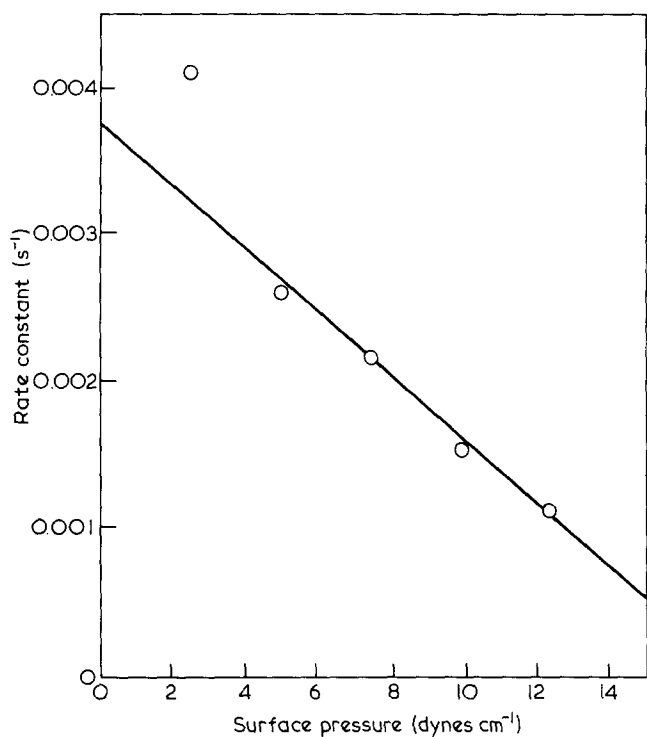


Figure 10 Relationship between rate constants for 3,3'-azopolyamide photo-induced area contractions and surface pressures. (See Figure 9). Subphase: pure water. Temperature $21^{\circ} \pm 1^{\circ}\text{C}$

area was seen to follow first-order kinetics and a trend of decreasing contraction rate with increasing surface pressure was apparent.

The 4,4'-azopolyamide and PAAB behaved anomalously. In both cases initial fast contractions in area ensued which were subsequently followed by area expansions at constant pressure values of less than 10 dynes cm^{-1} , in spite of the fact that u.v. irradiation was maintained throughout the experiments. Above 10 dynes cm^{-1} the initial period of contraction was followed by a more gradual contraction of monolayer area. It is likely that collapse of the polymer films above about 10 dynes cm^{-1} is responsible for the different behaviour above 10 dynes cm^{-1} as compared with that at surface pressures less than this value.

The initial fast contraction rates could not be quantified since the servomechanism controlling the compressing barrier can only permit the film to be compressed (area reduced) at speeds up to a maximum of about 6 cm min^{-1} which was not sufficient to follow the initial process. However, as an indication of the magnitude of the contraction, after 100 s of u.v. irradiation PAAB occupied an area 12% lower than that occupied before irradiation when the constant surface pressure imposed on the film was about 5 dynes cm^{-1} .

A chart recording of the anomalous $A-t$ behaviour of the 4,4'-azopolyamide is shown in Figure 11. In some cases there were oscillations in the $A-t$ traces. These were instrumental artefacts but could be suppressed by adjustment of amplifier gain¹⁴ in each given individual experiment. No such adjustments were made however so that qualitative comparisons could be made between data.

Photodegradation as a possible cause for the anomalous behaviour of PAAB and 4,4'-azopolyamide was considered. Mitchell and Rideal¹⁵ noted increases in surface pressure at constant area due to photofragmenta-

tion of peptide bonds in protein monolayers. Increases in surface pressure above a constant value would result in area expansion since the area would have to increase to restore the constant value. However, the model dye 4-PB showed no evidence of photodegradation since no photocontractions were apparent for this material. Furthermore the u.v. stability of the azopolyamides has been assessed by Riordan¹⁶ who found these polymers to exhibit pronounced resistance to photodegradation. Thus, azobenzene systems utilize absorbed u.v. energy to effect isomerization so that no energy is transferred to the photoliable-CONH- link. This behaviour contrasts the behaviour of for example, phenyl chromophores in protein side chains^{6,15}.

Thermal effects from the lamp were ruled out since the temperature of the monolayer was continuously monitored with a platinum resistance thermometer and no significant increases were noted.

To establish the authenticity of the anomalous expansile phenomena as a consequence of u.v. treatment, $A-t$ data were recorded for the 4,4'-polymer which has been isomerized before spreading; the results are shown in Figure 12. Comparison of Figures 11 and 12 indicate that the initial fast area contraction must be due to *trans*→*cis* photoisomerization on the surface, since this contraction is present in Figure 11 but not in Figure 12, the latter representing data recorded from a previously isomerized polymer spreading solution. The anomalous expansions noted when the 4,4'-polymer was isomerized on the surface were also much reduced when this polymer was pre-isomerized in solution then spread as shown in Figure 12.

Thus it would appear that when the initial fast period of contraction is not present, much of the anomalous expansile effects are removed. This would also explain why the 3,3'-azopolyamide responds differently from either PAAB or 4,4'-azopolyamide. The former does not give a fast contraction in monolayer area, rather the process is smooth and slower, and this polymer shows no expansile effects. Presumably dynamic relaxation

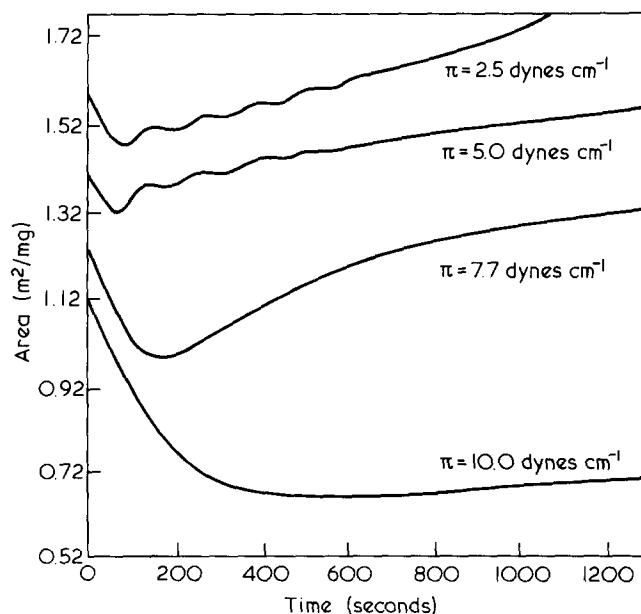


Figure 11 Chart recording of $A-t$ data for 4,4'-azopolyamide monolayers after irradiation on the water surface following compression to the surface pressures indicated. Subphase: pure water. Temperature $21^{\circ} \pm 1^{\circ}\text{C}$

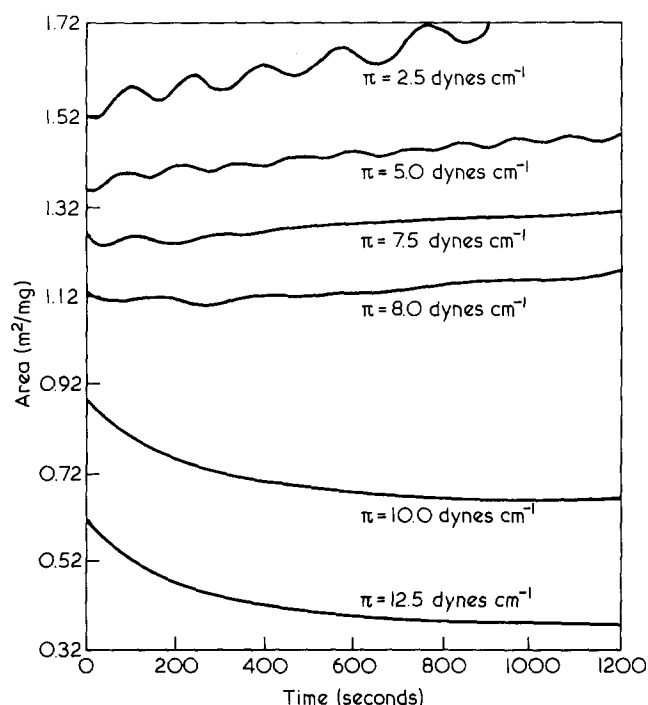


Figure 12 Chart recording of $A-t$ data for 4,4'-azopolyamide monolayers. The spreading solutions were pre-isomerized before spreading and u.v. irradiation was maintained throughout each experiment. Subphase: pure water. Temperature $21 \pm 1^\circ\text{C}$

phenomena occurring within the packed 4,4'- and PAAB monolayers after the dramatic photoregulation of their conformations, could generate deviations above the imposed constant values which would automatically be compensated for by retraction of the compressing barrier and hence monolayer expansion. This situation does not occur for the 3,3'-polymer because its photoregulation of conformation in monolayers is much slower and occurs to a lesser extent as a consequence of its structure. Indeed it has already been established that *trans*→*cis* photoisomerization is slower in solution for the 3,3'-polymer than for the 4,4'-polymer^{1,7a} and that the relative change in reduced solution viscosity on u.v. irradiation is much less for the former than for the latter polymer^{1,7,2}.

CONCLUSIONS

The ability to effect *trans*→*cis* photoisomerization of azobenzene residues in monolayers depends on the

orientation of the chromophores after film compression. Photoisomerization in monolayers was inhibited for 4-PB, and AAB-MMA systems but permitted for PAAB and for the 3,3'- and 4,4'-azopolyamides.

From measurements of photoinduced change in monolayer area with time it can be concluded that the rate of isomerization of azo residues in the 3,3'-polymer is slower than in the 4,4'- and PAAB polymers. This result compliments results obtained in bulk solution¹⁷. Anomalous expansions of 4,4'-azopolyamide and PAAB, under continuous irradiation, likely result from relaxation effects occurring within the packed monolayers after the substantial photoregulation of their configurations at the air/water interface.

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