Translated from *Uspekhi Khimii*, **46**, 292-319 (1977) U.D.C. 541.641 : 541.14

# Photochromic Polymers

V.D.Ermakova, V.D.Arsenov, M.I.Cherkashin, and P.P.Kisilitsa

The chief methods of preparation and the photochromic properties of polymers containing covalently bound photochromic groups in the main or a side chain of the macromolecule are surveyed. The properties of such polymers differ from those inherent in analogues of low molecular weight or in mechanical mixtures of the latter compounds with polymers. The difference in behaviour is explained by the steric and polar influence of the macromolecule on the initial and the photo-induced forms of the photochromic compound. A list of 55 references is included.

CONTENTS

I. Introduction 145
II. Phototautomerisation with migration of hydrogen 145
III. Redox polymers 146
IV. *cis* - *trans*-Isomerisation of azo-groups 148
V. Polymers based on spiropyrans 152
VI. Conclusion 156

## I. INTRODUCTION

The phenomenon of photochromism—a reversible change in colour under the influence of light of definite wavelength—is observed in many classes of organic compounds, and during recent years has been intensively studied in connection with the wide prospects for its application. Photochromic materials may be used to obtain images and as memory units in electronic computers and light filters of variable density, automatically varying the transmission according to the conditions of illumination[1,2].

Comparatively recently several papers have appeared on the preparation and study of a new class of photochromic compounds—polymers containing covalently attached photochromic groups in the main or a side chain. Methods for preparation and the photochromic behaviour of polymers containing mainly spiropyran groups have been surveyed by Smets[3].

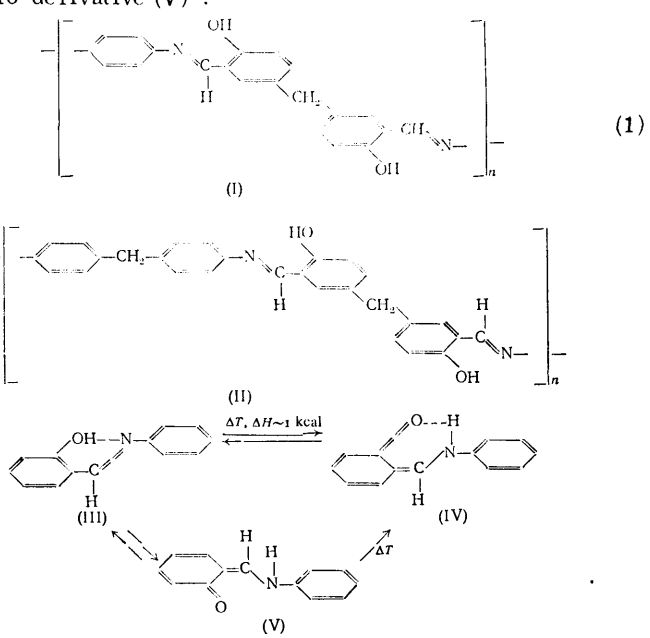
The photochromism of the simpler organic compounds may be due to isomerisation, heterolytic and homolytic bond cleavage, tautomerism, redox reactions, dimerisation, and triplet transitions. Various aspects of the photochromism of organic substances have been covered in a number of reviews and monographs[4-6]. The development of photochromic polymers is based on the assumption that the same mechanisms underly their action.

Distinctive features of the photochromism of polymers are the restricted mobility of the photochromic groups contained in the macromolecule, the dependence of their properties on the conformation, and the influence of the polarity of the comonomer. The present Review considers the main methods of preparing polymers containing covalently linked photochromic groups, the kinetic and spectral behaviour of the polymers in solutions and in films as functions of their chemical nature and structure, and also the photochemical reactions of the polymers. In order to study the steric and polar influence of the macromolecule on the behaviour of the photochromic groups, the properties of copolymers are compared with those of relatively simple photochromic compounds (model compounds), and also with solid solutions of photochromic compounds in a polymer matrix (photochromic matrix polymers).

The Review does not cover many papers on matrix polymers in which attention was paid mainly to investigating the mechanism of photochromic transitions in relatively simple compounds, with the polymers used merely as media for such investigations.

## II. PHOTOTAUTOMERISATION WITH MIGRATION OF HYDROGEN

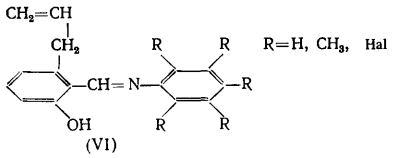
The photochromism and thermochromism of polyazomethines containing a salicylidenanil group in the main polymer chain (I) and (II) was studied by Laverty and Gardlund[7]. The phototautomerisation of anils involves intramolecular migration of hydrogen from an *o*-hydroxy-substituent (III) to the azomethine group to form a *trans*-keto-derivative (V)[7]:



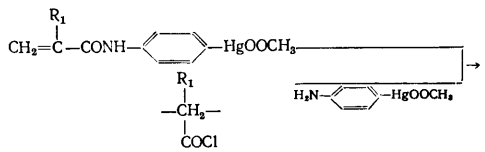

(1)

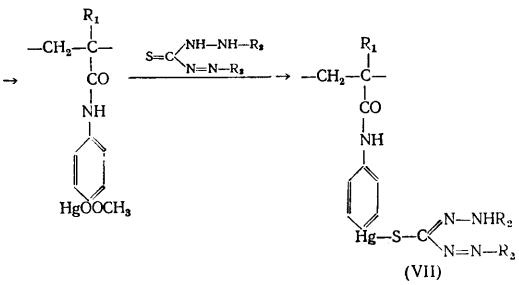
The *trans*-keto-form of the anil isomerises thermally into the *cis*-keto-form (IV), which is converted into the *cis*-enol (III) before equilibrium is established. The polymers (I) and (II), which are insoluble in the usual organic solvents, are not photochromic: they exhibit only the thermochromic transition (III) → (IV), but the bathochromic shift when heated from 25 to 100°C is merely 20 nm.

Photochromic polyazomethines can be obtained[8] by the copolymerisation of styrene and methyl methacrylate with the unsaturated salicylidenanil derivative

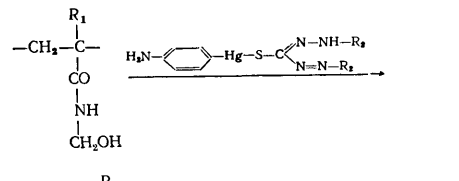


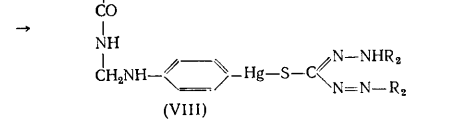

Photochromic transitions in copolymers of the two monomers with unsaturated derivatives of mercury dithiozonates were subjected to detailed investigation by Kamogawa et al.[9,10] Such polymers were obtained by various polymer-like conversions[9-12]:



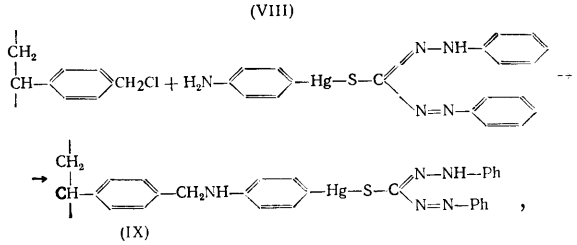




(2)
(3)



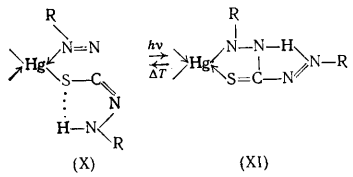

(4)




(5)

where $R_1$ = H, $CH_3$ and $R_2$ = $C_6H_5$, 2-$C_{10}H_7$, *p*-$C_6H_4Br$, *p*-$C_6H_4Cl$, *p*-$C_6H_4CH_3$, *o*-$C_6H_4CH_3$, *o*-$C_6H_4OCH_3$, *o*-$C_6H_4CF_3$.

The photochromism of metal dithiozonates is due to geometrical isomerisation of the ligand about the C=N bond with migration of hydrogen (X) → (XI):




(6)

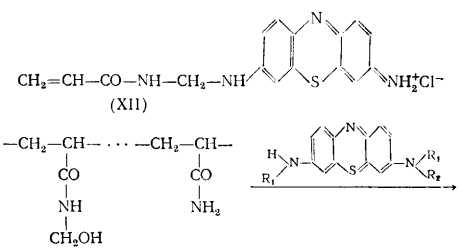
In the copolymers (VII)–(IX) the initial form (X) absorbs at 500 nm, but the photoinduced (XI) in the region of 600 nm. Photocoloration and thermal decoloration are described by first-order equations. The rates of forward and reverse reactions depend on the composition of the copolymer, the chemical structure of substituents in the dithiozonate group, and the viscosity of the system.

The steric influence of the macromolecule depends on the mobility of the comonomer. The rate of thermal fading of copolymers of (VII) with styrene is lower than that of copolymers containing more mobile residues (the copolymer with methyl acrylate)[9]. Both forward and reverse reactions are slowed down by the introduction into the dithiozonate group of electron-accepting substituents ($R_2$ = *o*-trifluoromethylphenyl) or substituents that cause steric hindrance ($R_2$ = 2-naphthyl, *o*-tolyl)[10]. Electron-donating and electron-accepting substituents produce bathochromic and hypsochromic shifts respectively in the spectra of initial and photoinduced forms.

Photoconversion and decolorisation are greatly retarded in films of copolymers of (VII)–(IX) owing to the considerable steric hindrance to *cis–trans*-isomerisation. This is confirmed by the shortening by a factor of 50 in the half-period of the dark reaction of copolymers of (VII) with styrene when the temperature is raised from 15 to 65°C, and also by the lowering of the glass point $T_{gl}$ of the polymer and the increase in the rate of photochromic conversions of the copolymers with increase in the content of butyl acrylate groups[9].

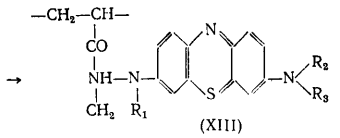
## III. REDOX POLYMERS

The reversible photodecolorisation of thionine introduced into a polymer chain in the presence of a reductant ($Fe^{2+}$), which was accompanied by photochemical redox reactions, was first observed by Kamogawa[13]. Photochromic polymers have been obtained also by the copolymerisation of a thionine monomer (XII) with acrylamide[14] and by chemical reactions on polymers[14-16]:




(8)†

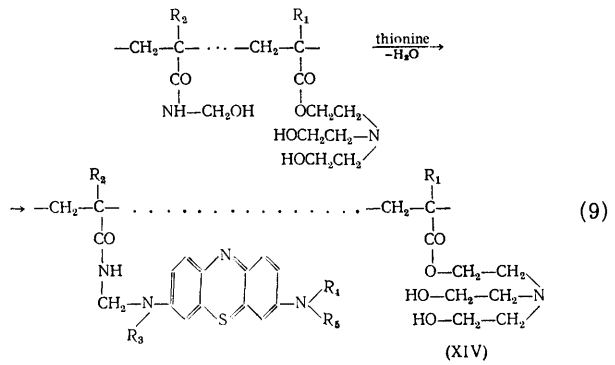
† Equation (7) is absent from the Russian text (Ed. of Translation).



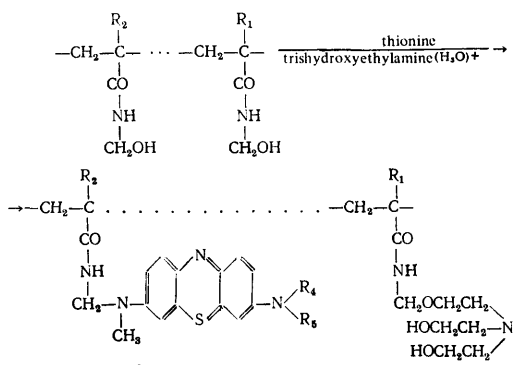
(XIII)

$R_1=R_2=R_3=H$; $R_1=H$, $R_2=R_3=CH_3$; $R_1=R_2=R_3=CH_3$; $R_1=R_2=H$, $R_3=CH_3$; $R_1=CH_3$, $R_2=R_3=H$

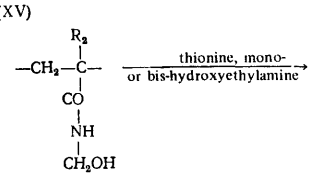
Polymers containing thionine dye and hydroxyethylamine residues have been synthesised[16]:

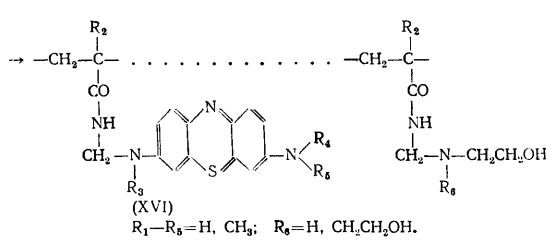


(XIV) (9)



(XV) (10)

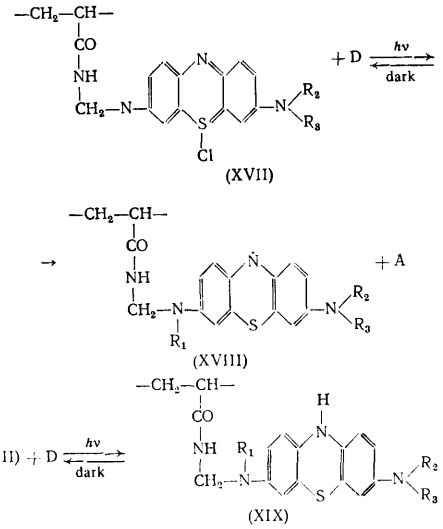




(XVI) (11)

$R_1$—$R_5$=H, $CH_3$; $R_6$=H, $CH_2CH_2OH$.

In the solid state thionine polymers fade reversibly (absorption diminishes in the region of 600 nm) on exposure to visible light. Kamogawa[15] attributed this reaction to photoactivated reduction of the coloured form of thionine (**XVII**), in the presence of an electron donor D, to the colourless semiquinone form (**XVIII**), which disproportionates rapidly into the colourless leuco-thionine (**XIX**) and the coloured thionine (**XVII**) forms:



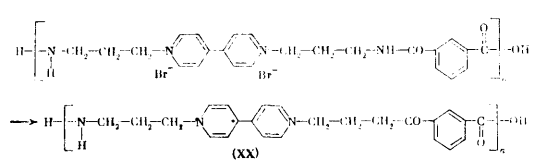
(XVII) (XVIII) (XIX) (12)

The reverse reaction takes place in the dark, and involves slow oxidation of leuco-thionine successively to the semiquinone and to the coloured thionine form in the presence of an electron acceptor A.

Introduction of electron-donating components such as $Fe^{2+}$ ions, poly(vinyl alcohol), hydroxyethylamines, certain enzymes (e.g. papain) confers considerable photosensitivity on the polymers. However, the mechanism of reaction (12) is probably more complicated, since the photochromic behaviour of thionine systems depends in considerable measure on the moisture content of the polymer film. It is suggested[15] that water molecules adsorbed on active groups in the polymer, just like atmospheric oxygen, are involved in redox reactions. Increasing the concentration of the donor D in the polymer chain somewhat enhances the sensitivity to photochromic reactions, but hydroxyethylamine residues inserted into the polymer chain are comparable with the monomeric analogues in effectiveness[16].

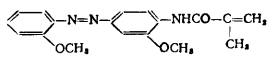
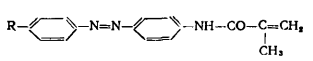
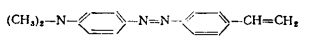
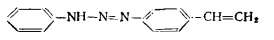
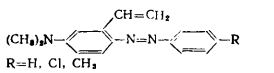
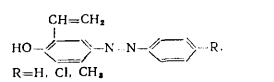
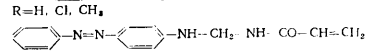
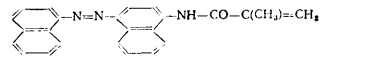
The rate of fading is somewhat affected by the method of preparation of the thionine polymers. Increasing the acidity of the polymer films (**XV**) diminishes the electron-donating power of the hydroxyethylamine residues, with a consequent slower rate of fading of the polymer[16]. The rate of restoration of the colour diminishes on introduction of the iron(II)–(III) system as carboxylate salts[15].

Photochromic redox polymers containing an *NN'*-dialkyl-4,4'-bipyridinium group (a viologen) have recently been prepared and studied[17]. New polyviologens (**XX**) and (**XXa**) possessing film-forming properties have been obtained by the interfacial polycondensation of *NN'*-bis-aminoalkyl-4,4'-bipyridinium salts with di-, tri-, or tetra-functional acid derivatives. On chemical and electrical reduction or exposure to light the polymer films become coloured owing to formation of a viologen radical:



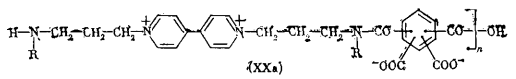
(XX) (13)

**Table 1.** Photochromic polymers containing azo-groups, obtained by radical copolymerisation.

| Copolymer | Photochromic monomer | Comonomer or comonomer mixture (mole %) | $10^{-3}$ *M* | Photochrome, mass % | Ref. |
|---|---|---|---|---|---|
| (XXI) a |  | $CH_2=C(CH_3)-COOH$ | — | 3.6 | 20 |
| b | | $CH_2=CH-COOH$ | 50—200 | 1.2 | 20 |
| (XXII)* a | | $CH_2=C(CH_3)-COOH$ | 150 | — | 21 |
| | | | | | 24 |
| b |  | $CH_2=C(CH_3)-COOH$ $CH_2=C(CH_3)-COOCH_3$ (60 : 40) | 225 | — | 21 |
| c | | $CH_2=C(CH_3)-COOCH_2CH_2N(CH_3)_2$ | 75 | 0.8—1.0 | 21 |
| d | | $CH_2=C(CH_3)-COOH$ $CH_2=C(CH_3)-COOCH_2CH_2N(CH_3)_2$ (50 : 50) | 88 | — | 21 |
| e | |  | 0.15** | 5*** | 27 |
| f | | $CH_2=C(CH_3)-COOCH_3$, $CH_2=C(CH_3)-COOC_2H_5$ | 0.12—0.16** | 9—10*** | 27 |
| g | | $CH_2=C(CH_3)-COOH$ | — | — | 24 |
| (XXIII) a |  |  | 0.13* | 2.5—2.9** | 14,25 |
| b | | $CH_2=C(CH_3)-COOCH_3$ | 0.15* | 0.7—1.3** | 14,25 |
| (XXIV) |  |  | — | — | 14 |
| (XXV) |  R=H, Cl, $CH_3$ |  | — | — | 14 |
| (XXVI) |  R=H, Cl, $CH_3$ | $CH_2=C(CH_3)-COOCH_3$ and $CH_2=CH-COOC_2H_5$ | — | — | 14 |
| (XXVII) |  |  | — | — | 14 |
| (XXVIII) |  | $CH_2=C(CH_3)-COOCH_3$ | 0.26* | 3*** | 27 |

* R = $N(CH_3)_2$ and $^+N(CH_3)_3$ for copolymer (XXIIg); R = H for the remaining copolymers (XXII).
** Intrinsic viscosity of the polymer.
*** Photochrome content, mole %.

With pyromellitoyl chloride a betaine type of polymer is formed:



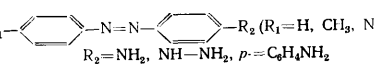
(XXa)

(R = H, $CH_2CH_2CH_3$)

Decolorisation of the films takes place in air in the dark after 8 h, or under the influence of water after 1 min.

## IV. *cis–trans*-ISOMERISATION OF AZO-GROUPS

The principle of *cis–trans*-isomerisation about the N=N bond has been utilised for the preparation of photochromic polymers containing an azo-group. Copolymers containing an azo-group in the side-chain have been obtained by the radical copolymerisation of vinyl derivatives of azo-compounds with unsaturated monomers. Similar photochromic copolymers can be prepared also by chemical modification of poly-*o*-hydroxystyrene with diazonium salts of aniline derivatives or of a ternary copolymer of *N*-hydroxymethylacrylamide with derivatives of *p*-aminoazobenzene[14,18]



$R_2 = NH_2$, NH—$NH_2$, *p*-$C_6H_4NH_2$

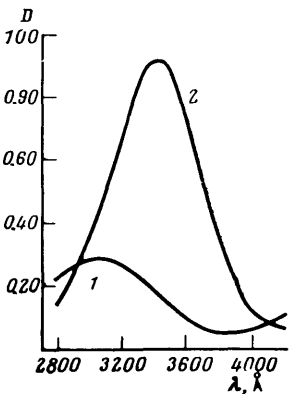


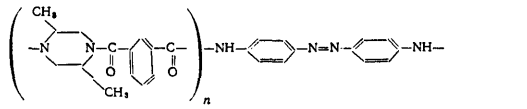
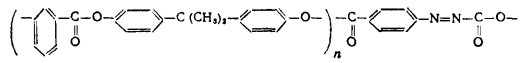
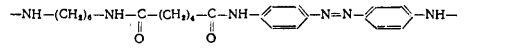
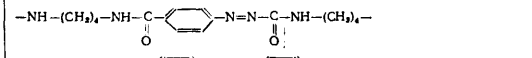
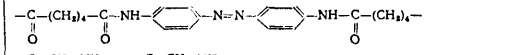
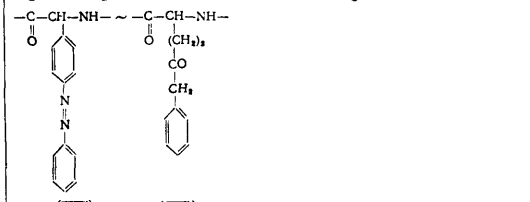
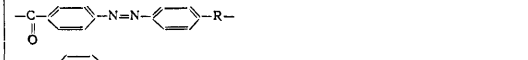
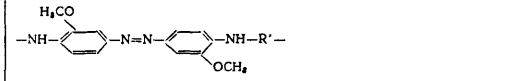
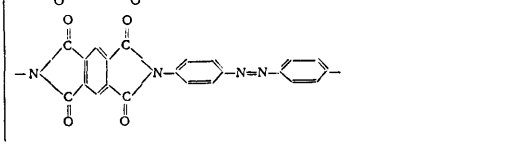

**Figure 1.** Absorption spectra of *p*-acetamidoazobenzene (0.01 M at pH 8): 1) initial form; 2) photoinduced form.

Polycondensation has been used to introduce an azo-group into the main chain of the polymer. Data on the structure and the composition of copolymers obtained by radical copolymerisation and copolycondensation are summarised in Tables 1 and 2 respectively.

Initial and photoinduced forms of the azo-group usually have absorption bands close together in the near ultraviolet or the visible spectrum (Fig. 1).

Goodman and Falxa showed[19] that the photoisomerisation of azo-groups on introduction into a polypeptide chain (XXXIII) (Table 2) is accompanied by a change in the optical activity of the isomers. The photochromic properties of polymeric azo-compounds are strongly influenced by the conformation of the macromolecule. This effect is especially clearly developed in polyelectrolytes containing an azo-group in the side-chain. Polymers of this type were first obtained by Lovrien[20] (XXIa, b) and later by Fink[21] (XXIIa, c, d) (Table 1).

Table 2. Photochromic polycondensation polymers.

| Polymer | Repeating unit | Ref. |
|---|---|---|
| (XXIX) |  | 27 |
| (XXX) |  | 27 |
| (XXXI) |  | 27 |
| a (XXXII) |  | 26 |
| b |  | |
| (XXXIII) |  | 19, 33 |
| (XXXIV) |  | |
| a |  | 32 |
| b |  | |
| c |  | |
| (XXXV) |  | 32 |
| a |  | |
| b |  | |
| (XXXVI) |  | (29) |

Both photoinduced and dark reactions are influenced by conformational transitions of polyelectrolyte macromolecules depending on their degree of ionisation, so that the isobiestic wavelength in the absorption spectra of copolymers of acrylic acid and 4-acrylamido-2,2′-dimethoxyazobenzene (XXIa, b) depends on the pH and becomes considerably shorter with increase in the reduced viscosity (pH 5–7) owing to uncoiling of the polyelectrolyte chains[20]. This is responsible also for the diminution in the rate of the dark reaction of (XXIb) at pH 6–10, although the rate of transition of the model monomeric azo-compound increases in the same pH range because of the catalytic effect of hydroxide ions[20].

The pH dependence of the rate of the dark *cis–trans*-isomerisation of azo-groups is influenced by the type of polyelectrolyte[21]. At pH < 8–9 the macromolecule of the polyanion of (XXIIa, b) is coiled up, which slows down the isomerisation; conversely, this transition is facilitated when the macromolecule has straightened out (pH > 8–9). The rate constant of the dark reaction of (XXIIa, b) has its minimum value at pH = 8–9. The opposite dependence is observed for the polycation (XXIIc), for which the minimum rate constant occurs at pH 5–6. The polyampholyte (XXIId) is similar in behaviour to the model photochromic compound, for which a minimum rate constant is observed at pH ≃ 7. The uncoiling of the polypeptide (XXXIII) macromolecule in trifluoroacetic-acid solution increases the yield of the *cis*-isomer on photoexcitation relative to that observed in dioxan solution, in which the polypeptide has a coiled conformation[19].

On the other hand, photoisomerisation of constituent azo-groups in the polyelectrolyte changes the conformation of the macromolecule and hence the viscosity of the polymer solutions (the "photoviscous effect")[22], which opens up the possibility of photocontrolling the conformation of a polyelectrolyte by means of photochromic compounds. An example of one of the two main mechanisms distinguished by Lovrien[22] is provided by a copolymer of methacrylic acid such as (XXIIa). In the absence of irradiation the balance between two types of interaction—van der Waals cohesion of hydrophobic lateral *trans*-azo-groups and electrostatic repulsion of like charges—determines the degree of coiling of the polyelectrolyte. On *trans–cis*-photoisomerisation the hydrophobic interaction of the azo-groups diminishes owing to the increased polarity of the *cis*-isomer, leading to uncoiling of the macromolecule and increase in the viscosity of the polyelectrolyte solutions.

An example of the second type of system is a macromolecule of polymethacrylic acid with adsorbed ligands of a charged azo dye (e.g. anions of Chrysophenine). The addition of photochromic ligands uncoils the polyelectrolyte macromolecule as a consequence of interaction of like charges. On *trans–cis*-conversion the increased dipole moment of the *cis*-isomer makes the ligand more hydrophilic, which leads either to its desorption from the macromolecule or to an increase in the dielectric constant along the chain. In either case the macromolecule coils up: i.e., in contrast to the first mechanism, solutions of the polyelectrolyte will become less viscous after exposure‡. With degrees of ionisation of polymethacrylic acid < 0.075 (pH < 4.9) the addition of ligands—Chrysophenine anions—coils up the polymer chain and lowers the dissociation constant (p$K$) of the carboxy-groups on *trans–cis*-photoisomerisation[23].

Photocontrol of the conformation of polymethacrylic acid in solution at degrees of ionisation of 0.2 (pH 4.5–5.5), at which the polyelectrolyte macromolecule uncoils, is

‡ It is undoubtedly of interest to study such processes, since this would open up the possibility of using membranes and photochromic polyelectrolytes for the photoregulation of biological processes.

possible with the use of cationic ligands based on *p*-phenylazophenyltrimethylammonium iodide or the copolymers (XXIIa)[24]. Solutions of polymethacrylic acid with cationic ligands exhibit a decrease of 0.2 in the p$K$ on *trans–cis*-photoisomerisation, caused by a change in the degree of coiling of the polyelectrolyte molecules. The photochromic copolymers (XXIIa) also display an induced photochemical jump in p$K$ when the azo-groups pass into the *cis*-form. Since

$$pK = pH + \lg[(1+\alpha)/\alpha],$$

the degree of ionisation of polymethacrylic acid modified by photochromic groups, and hence the conformation of the polyelectrolyte, should be controlled photochemically in buffered solutions.

A usual consequence of the addition of azobenzene groups to a polymer chain is steric hindrance to *cis–trans*-isomerisation, which is apparent in a diminished rate of photochromic transitions of copolymers in comparison with model compounds[14,21,19,25]. An increased rate of thermal isomerisation relative to the reaction with model compounds has been observed with the copolymers (XXIIIa), (XXV), and (XXXII)[14,26]. Such anomalous behaviour was attributed to diminished aggregation of azobenzene groups when separated by an inert comonomer. This is supported by the decrease in the rate of photochromic transitions with increase in the aggregation of azobenzene molecules due to polar groups capable of forming hydrogen bonds, e.g. in the copolymer (XXIV)[14].

Thus the effects of aggregation of azobenzene groups and steric hindrance by the macrochain tend to balance each other, and the photochromic behaviour of the macromolecule will depend on the relation between them. Another view[26] is that the introduction of azobenzene groups into the main chain of the polyamide (XXXII) does not impede isomerisation, since the time required for conversion of the macromolecular conformation into a form corresponding to the transition state in the *cis–trans*-isomerisation of azo-groups is comparable with the time of isomerisation of these groups in a model compound.

The steric effect of a polymer chain on *cis–trans*-isomerisation is evident also in the dependence of the rate of photochromic transitions on the mobility of the macromolecule. The rate of the thermal *cis–trans*-isomerisation of copolymers on methyl methacrylate with *p*-dimethylamino-*p'*-vinylazobenzene (XXIIIb) in benzene solution exceeds that of copolymers with styrene (XXIIIa) because of the greater mobility of poly(methyl methacrylate). For the polystyrene macromolecule, which has a straight conformation in benzene solution, isomerisation processes in side-chains are difficult[25]. Analogous results were obtained by Kamogawa et al.[14]: the rate of the thermal *cis–trans*-isomerisation of copolymers falls with decrease in the flexibility of the macromolecule—polystyrene and poly(methyl methacrylate) compared with poly(butyl acrylate).

Since the mobility of a macromolecule in solution depends on the interaction of the polymer with the solvent, the rate of a photochromic transition is influenced by the parameter $\chi$ of this interaction. The higher value of $\chi$ for polystyrene than for poly(methyl methacrylate) in benzene is responsible for the lower *cis–trans*-isomerisation rate constant of vinyldimethylaminoazobenzene in copolymers with styrene than in those with methyl methacrylate (XXIIIa) and (XXIIIb)[25]. The decrease in the rate constant with increase in the content of vinyldimethylaminoazobenzene in the copolymer (XXIIIb) is also explained by an increase in $\chi$. The departure from this relation observed for simultaneous increase in the content of this monomer and increase in the concentration of the copolymer in the solution is probably due to inter- and intra-molecular transfer of excitation energy[25].

The loss of mobility of a macromolecule in a film results, as would be expected, in a considerable decrease in the rates of photochemical transitions relative to those observed in solution, especially if the polymer has a rigid chain[14,27]. Sometimes the longer-wavelength absorption band of the polymer undergoes a bathochromic shift in a film in comparison with the maximum in solutions[14].

However, it was found[27] that, after a photostationary state had been reached in a film, the dark *cis–trans*-isomerisation of photochromic copolymers containing azobenzene groups—whether in side-chains (XXIIe), (XXIIf), and (XXVIII) or in the main chain (XXIX)–(XXXI)—takes place at a constant rate differing little from that in dilute solutions of analogous polymers. This unexpected phenomenon was explained in terms of the fundamental postulate of the theory of rate processes that the transition state in a reaction is in equilibrium with the initial state, and the reaction velocity is unaffected by the reduced mobility of the reactants imposed by increase in the viscosity of the medium.

In solutions of polymers photochemical *trans* $\rightleftharpoons$ *cis*[25,19] and thermal *cis–trans*-isomerisation[21,25,26,19] are usually first-order reactions. The latter type of isomerisation in dilute formic-acid solutions of the polyamide (XXIIa) containing azobenzene groups in the main chain diverged from this rule[27]. Its kinetics are described by the equation

$$c/c_0 = \alpha \exp(-k_1 t) + (1-\alpha)\exp(-k_2 t)$$

where $c_0$ is the concentration of the *cis*-isomer at zero time, $c$ is its concentration at time $t$, and $k_1$ and $k_2$ are rate constants of the *cis–trans*-isomerisation of the azobenzene groups. Here $k_1 \simeq 3k_2$, with the latter approaching the isomerisation constant of a model compound. The presence of rapidly isomerising azo-groups in the polyamide is probably connected with their oxidation to azoxy-derivatives. This view is supported by the decrease in the ratio $k_1/k_2$ in a more acid medium.

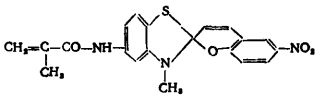
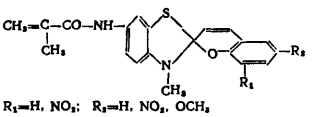
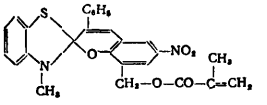
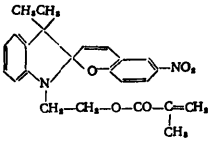
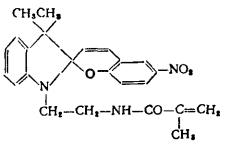
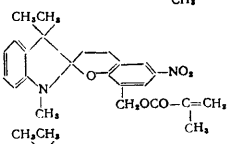
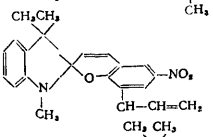
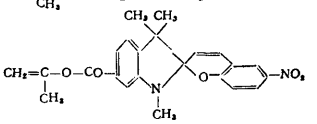
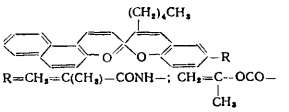
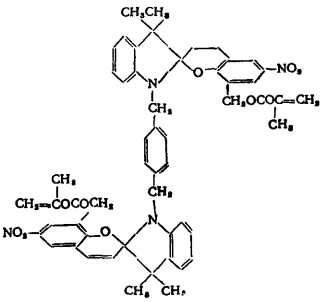
Kinetic investigation of the thermal *cis–trans*-isomerisation in a film of polymers containing azobenzene and azonaphthalene groups in side-chains—(XXIIe), (XXIIf), and (XXVIII)—revealed a relation between the glass point and the departure from first-order kinetics[27]. A first-order equation was obeyed by polymers in a state of rubber-like elasticity. A proportion of rapidly isomerising azoarene groups and the associated departure from first-order kinetics appear at temperatures below the glass point. Such anomalous behaviour of polymer films was attributed[27] to the non-equilibrium character of the vitreous state, which causes a non-uniform distribution of free volume in the polymer. Similar results were obtained for solid solutions of 2,2'-azonaphthalene or *p*-ethoxyazobenzene in polystyrene[28]. The content of *cis*-isomers in the photostationary state decreases with increase in the viscosity of the medium, but the kinetics of the dark reaction deviates from a first-order equation at temperatures below the glass point.

It has recently been reported[28] that the photoisomerisation of polymers containing azo-groups in the main chain may be accompanied by mechanical changes. When poly-*pp'*-azobenzene–pyromellitimide (XXXVI) was subjected to temperature cycles involving heating to 200°C under constant pressure, shrinkage and expansion of the film were

observed. With the length of the film maintained constant, on the other hand, the stress applied to the film during exposure increased with time.

Since the activation energy of compression of a film is insignificant, whereas the activation enthalpy of isomerisation of azo-compounds in solution is ~ 20 kcal mole$^{-1}$,

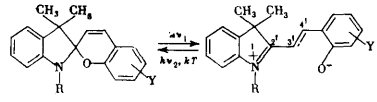
Table 3. Spiropyran polymers obtained by radical copolymerisation.

| Copolymer | Shiropyran monomer | Comonomer or comonomer mixture | Photochrome in polymer, mole % | $10^{-4}$ $M$ | Ref. |
|---|---|---|---|---|---|
| (XLII) a |  | methyl methacrylate | 3.3—21.5 | 0.77—9.0 | |
| b | | styrene | 10 | 0.55 | 34 |
| c | | methacrylonitrile | 10.2 | — | |
| d | | dodecyl methacrylate | 17.9 | 3.08 | |
| e | | 1- or 2-vinylnaphthalene | 9—13 | 0.19—0.87 | |
| (XLIII) |  $R_1$=H, $NO_2$; $R_2$=H, $NO_2$, $OCH_3$ | methyl methacrylate | 10 | — | 35 |
| (XLIV) |  | methyl methacrylate | 10 | 42.6 | 3 |
| (XLV) a |  | methyl methacrylate (MMA) | 0.6—50 | (—100) | 3,35,36,37, 38,39 |
| b | | styrene | 2.5 | — | 37,40 |
| c | | MMA-*p*-acrylamidophenol-*p*-azidoxy-carbonylbenzoic acid | 3.2 | — | 37 |
| d | | 2-vinylnaphthalene | 2.1 | 0.28 | |
| e | | 9-vinylanthracene | 50.6 | 0.12 | |
| f | | 5-methacryloyl-2-methoxybenzaldehyde | 3.3 | 0.27 | |
| g | | 4-vinylpyridine | 2.1 | 0.53 | 40 |
| h | | acrylonitrile | 2.0—3.3 | 0.17 | |
| i | | 2-hydroxyethyl methacrylate | 2.2 | 0.15 | |
| j | | 1-methacryloylmethyl-*o*-carborane | 2.5 | 0.30 | |
| k | | homopolymer | 100 | 0.16 | |
| (XLVI) |  | n-propyl or isobutyl methacrylate | — | — | 3 |
| (XLVII) a |  | styrene | 1.5—100 | — | 41 |
| b | | methyl methacrylate | 2.1 | 37.9 | 3,41 |
| (XLVIII) |  | methyl methacrylate | 0.2—0.8 | 12—26 | 35,38 |
| (XLIX) |  | methyl methacrylate | 5 | — | 37 |
| (L) |  R=$CH_2$=C($CH_3$)—CONH—; $CH_2$=C(—)—OCO— | methyl methacrylate | — | — | 42 |
| (LI) |  | methyl methacrylate, ethyl acrylate | 0.5—1 | — | 3,30 |

Agolini and Gay[29] suppose that the rate of expansion or contraction is determined by the elastic properties of the polymer rather than by the rate of *cis–trans*-isomerisation. This seems a very probable interpretation in view of data obtained[27] for polyamides and polyesters containing azoarene groups and the absence of a direct relation between the rates of isomerisation of the polymer and of expansion or contraction of the film. Water-swollen membranes of a copolymer of 2-hydroxyethyl methacrylate and ethylene dimethacrylate with adsorbed molecules of Chrysophenine shrink by 1.2% on illumination, and return to their original dimensions in the dark[30,31]. This phenomenon was explained[30,31] by a change in the conformation of the polymer chain resulting from the difference between the solubilities of *trans*- and *cis*-isomers in the hydrophobic part of the macromolecule.

## V. POLYMERS BASED ON SPIROPYRANS

The photochromism of polymers containing spiropyran residues has been subjected to most detailed investigation. Ultraviolet irradiation causes dissociation of the carbon–oxygen bond, with coloration of the colourless photochromic systems[34]. The reverse process of ring closure takes place either in the dark or under the influence of visible light in the region of absorption by the merocyanine form:



(14)

Polymers containing spiropyran units in the side-chain have been obtained by the copolymerisation of unsaturated photochromic monomers with vinyl comonomers (Table 3), as well as by chemical reactions on polymers.

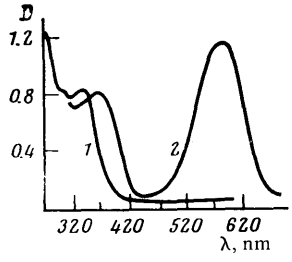
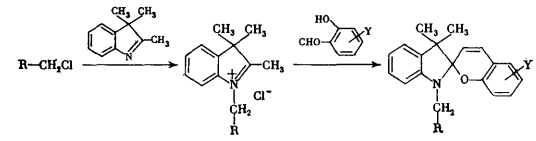


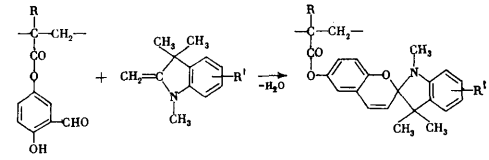

**Figure 2.** Absorption spectra of forms of copolymer (XLVa): 1) initial; 2) photoinduced.

The absorption bands of the coloured form $\lambda_{max}^{vis}$ are located over the range 470–600 nm depending on the structure of the spiropyran and the nature of the comonomer. Fig. 2 shows typical spectra of initial and photoinduced forms of an indolinospiropyran copolymer.

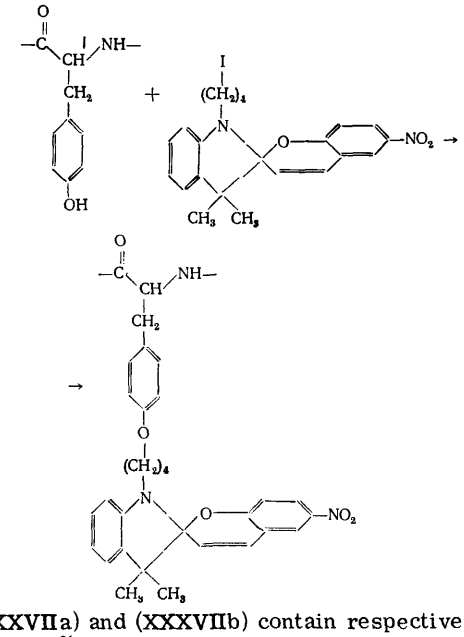
Polymers may be obtained by reaction between chloromethylated polystyrene and Fischer's base[43]:



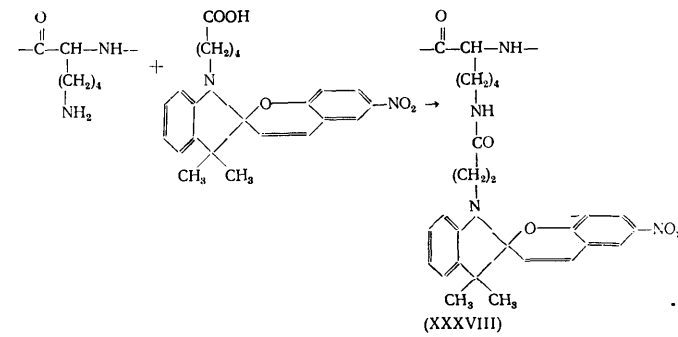
(R represents a macroradical and Y different substituents—$NO_2$; $NO_2$, $NO_2$; $NO_2$, $OCH_3$; $NO_2$, Hal). An alternative reaction is[44]



where R = H, $CH_3$, Hal and R′ = $CH_3$, $NO_2$, Hal, AlkO, AlkS). Some Japanese workers[45] have obtained photochromic polymers by the action of "live" polymers, such as the polystyrene or the poly-$\alpha$-methylstyryl anion, on a spiropyran having a chloromethyl, bromoaryl, or ester group as reactive centre. Photochromic polypeptides were obtained[46] by the reaction of $N$-$\omega$-halogenoalkylindolinospiropyrans with poly-L-tyrosine:

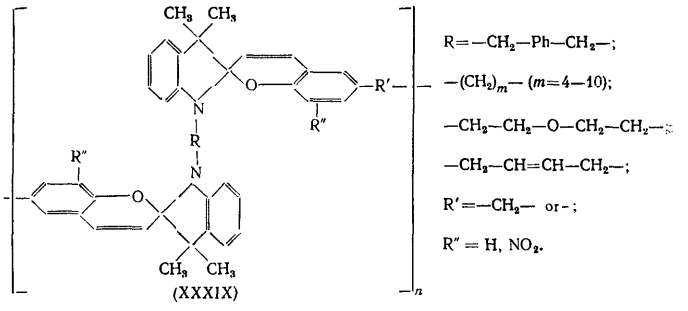


where (XXXVIIa) and (XXXVIIb) contain respectively 54.7 and 72.3 mass % of the photochrome. Alternative reactants are an $N$-carboxyalkyl derivative of indolinospiropyran and polylysine[3]:



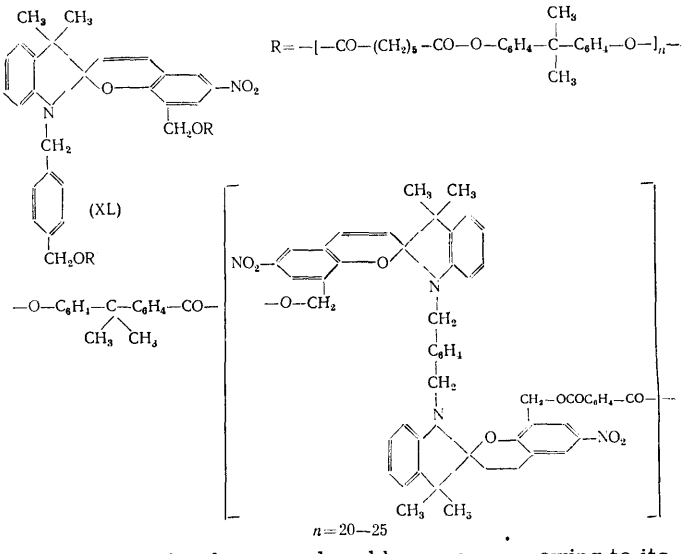
(XXXVIII)

Smets[3,47] used the polycondensation of bisindolenines with bis-salicylaldehydes to introduce photochromic groups into the main chain of the polymer:




(XXXIX)

Because of the sparing solubility of the condensation products (XXXIX), only oligomers having $n = 5$–$10$ were obtained. The copolycondensation of a bishydroxymethyl derivative of indolinospiropyran or a bisindolinospiropyran or of bisphenol A with pimeloyl chloride or a mixture of iso- and tere-phthaloyl chlorides gave polyesters (XL) and (XLI) containing respectively 4.0 and 9.5 mass % of the photochrome[3,30]:




The merocyanine form produced by exposure, owing to its zwitterionic nature, possesses strong negative solvatochromism (especially in benzothiazolinospiropyrans), which affects both $\lambda_{max}^{vis}$ and the rate of decolorisation. As a consequence, the specific effect of the polymer chain on the photochromic transitions of spiropyran units can be determined by comparing the photochromism of simple spiropyrans with that of their copolymers.

The kinetic and spectral behaviour of spiropyran polymers differs depending on whether the polymer is in solution or in the solid state. Furthermore, differences have been found in the behaviour of polymers into which spiropyran groups have been introduced chemically and of solid solutions of the corresponding photochromic monomers in the homopolymers.

## 1. Photochromic Transitions in Solution

The steric and polar effects of the macrochain depend on the polarity of the solvent[34,36]. In strongly polar media (e.g. dimethylformamide, pyridine) the copolymers (XLIIa–e) (Table 3) exhibit strong negative solvatochromism similar to that of model compounds[34]. The thermal decolorisation of such copolymers obeys a first-order kinetic equation. The activation energy in dimethylformamide solution varies from 24.9 to 25.6 kcal mole$^{-1}$ depending on the comonomer, which compares with the value of 22.1 kcal mole$^{-1}$ for the model benzothiazolinospiropyran.

The photochromic polypeptides (XXXVIIa, b) also undergo first-order thermal decolorisation in dimethylformamide[46]. In strongly polar protic solvents (ethylene glycol and formamide) both polytyrosine (XXXVII) and its model compound, the latter obtained by reaction between 1-(4-iodobutyl)-3,3-dimethyl-6′-nitrospiro(indolino-2,2′-[2*H*-1]-benzopyran) and the methyl ester of *N*-acetyltyrosine, exhibit reverse photochromism, a phenomenon due to the high content of the merocyanine form in thermal equilibrium with the spiropyran[46].

In solvents of low polarity (acetone, dichloromethane, oxolan) the copolymers (XLIIa–e) and (XLVIIa, b) differ considerably from the model compound in photochromic behaviour[34,41]. In such solvents the polar influence of the comonomer becomes appreciable. Interaction of the merocyanine form of the spiropyran with the comonomer is confirmed by the hypsochromic shift in $\lambda_{max}^{vis}$ of the copolymers relative to the lower spiropyrans[34,40,41], which increases with the polarity of the comonomer. If the macromolecule is not solvated, the merocyanine form may also interact with spiropyran units to produce a hypsochromic shift in $\lambda_{max}^{vis}$ and a decrease in the rate of decolorisation with increase in the spiropyran content of the copolymer[34,41].

Thermal decolorisation of the copolymers (XLIIa–e), (XXXVIIa, b), (XLVIIa, b), and (XXXIX) in solvents of low polarity, in contrast to that of model compounds, diverges from first-order kinetics, and can be represented by the sum of at least two first-order reactions[3,34,41,46]. The variation in optical density of the $\lambda_{max}^{vis}$ band can be described by the equation

$$D = a\exp(-x_1 t) + b\exp(-x_2 t) \quad . \qquad (15)$$

which presupposes the existence of several *trans*-isomers—with respect to the central bond 3′–4′ in Eqn. (14)—of the merocyanine form, the rate of whose interconversion is far smaller than their rate of decolorisation. In formula (15) $a$ and $b$ are the contributions of each geometrical isomer to the optical density at $t = 0$, while $x_1$ and $x_2$ are their decolorisation rate constants.

The above regularities have been attributed[34,41] to the steric and polar effects of the macromolecule in raising the potential barrier separating the geometrical isomers. The polar influence of the comonomer diminishes with increase in the polarity of the medium, so that, when a polar precipitant (t-butyl alcohol) is added to a solution of the copolymer (XLIIa) in chlorobenzene, the first-order kinetics of decolorisation are restored up to degrees of conversion of 60%.[34]

As a consequence of incomplete solvation of polytyrosine macromolecules by solvents of low and high polarity the photochromism of solutions of copolymers (XXXVIIa, b) is almost independent of the polarity of the solvent, in contrast to that observed for the model compound. The specific effect of the polypeptide chain is evident also in the appearance of two absorption maxima in the visible range, due to different geometrical isomers of the merocyanine form[46].

Equilibrium between spiropyran and merocyanine forms is established in solutions of copolymers (XLVc–j) of indolinospiropyran with comonomers differing in polarity and in three-dimensional structure[40]. The equilibrium constant depends on the polarities of the solvent and of the comonomer.

Furthermore, the spectra of the homopolymer (XLVk) and of the copolymers (XLVc–e) contain a band due to a *cis*-cisoid isomer ($\lambda_{max}$ = 470 nm) formed immediately after dissociation of the carbon–oxygen bond in the pyran part of the molecule. The absence of such a band in the spectrum of the model compound, as well as in those of mixtures of the corresponding homopolymers with the model compound, suggests that steric hindrance by the macromolecule to interconversion of colourless and coloured forms is responsible for the appearance of this isomer. A polar solvent, as well as a polar comonomer, promotes rapid transition through the stage of formation of the *cis*-cisoid isomer, and stabilises the merocyanine form (*trans*-isomer)[40].

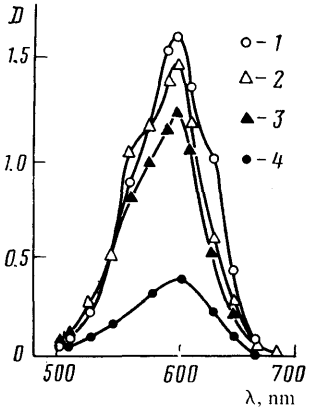



**Figure 3.** Absorption spectra of coloured form of copolymer (XLVc) (0.3 mM solution in benzene) after: 1) 40 μs; 2) 0.66 ms; 3) 0.1 s; 4) 15 s.

The use of flash photolysis[48] to investigate photochromic processes, including those accompanied by formation of short-lived intermediates on photoexcitation of copolymer (XLVc), confirms the existence of geometrical isomers of the merocyanine form having different lifetimes. The mechanism of photoconversion of the copolymer involves the formation of a short-lived *cis*-cisoid isomer ($\lambda_{max}$ = 490 nm), which passes rapidly (lifetime < 1 s) into more stable interconvertible geometrical isomers having absorption maxima at 560, 600, and 640 nm (Fig. 3). At times exceeding 1 s the spectrum still contains the band due to the thermally stable isomer ($\lambda_{max}^{phot} \simeq$ 600 nm), the decrease in whose optical density monitors the kinetics of the dark decolorisation after long periods of time.

The thermal decolorisation rate constants of copolymers in solution depend on many factors—the structure of the spiropyran, the nature of the comonomer, and the polarity of the solvent[34,41,39] (Tables 4 and 5). The copolymers (XLVIIb) and (XLIX) fade more slowly than do model compounds. The opposite effect is observed with the copolymers (XLVa) and (XLVI). This confirms that the rate of decolorisation is affected by the site at which the photochrome is attached to the polymer chain[39]. In the case of the benzothiazolospiropyran (XLIV) the rate of decolorisation of the copolymer is about half that of the model compound. Steric hindrance to rotation of the polymer chain about the 3′–4′ bond operates here[3].

**Table 4.** Photochromic behaviour of copolymers of spirobenzopyrans with methyl methacrylate (sp.) and their model compounds (mod.) in acetone solution[3,39].

| Structure | (XLVa) | | (XLVIIb) | | (XLIIa) | | (XLIX) | | (XLVI) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | mod. | sp. | mod. | sp. | mod. | sp. | mod. | sp. | mod. | sp. |
| $\lambda_{max}^{vis}$, nm | 577 | 577 | 567 | 567 | 526 (506) | 478 (504)* | 569 | 569 | 572 | 572 |
| $10^3 k_1$ (20°C), $s^{-1}$ | 8.2 | 9.9 | 1.3 | 1.0 | 1.7 (4.8) | 1.7** (3.8) | 2.0 | 1.05 | 2.8 | 4.7 |
| $E_a$, kcal mole$^{-1}$ | 22.3 | 22.4 | 24.3 | 24.5 | (22.1) | (25.6) | 21.6 | 23.0 | 24.7 | 24.5 |

*In all cases parentheses enclose values in dimethylformamide.
**Apparent initial rate constant.

**Table 5.** Kinetics of the decolorisation of copolymers of methyl methacrylate with 1-methyl-5-methacrylamido-6-nitrospiro(thioindolino-2,2′-[2*H*-1]benzopyran) (XLIIa) in solution[3].

| Solvent | *t*, °C | $10^3 k^*$, $s^{-1}$ | $10^3 x_1$, $s^{-1}$ | $10^3 x_2$, $s^{-1}$ | Isomer, %*** | |
|---|---|---|---|---|---|---|
| | | | | | *a* | *b* |
| Acetone | 20.5 | 1.7 | 1.7 | 0.27 | 36 | 64 |
| Dichloromethane | 20.0 | 3.4 | 5.7 | 0.48 | 66.7 | 33.3 |
| Oxolan | 22.2 | 38.0** | 4.6 | 0.70 | 68 | 32 |

*Rate constants for the model compound.
**Extrapolated value.
***The coefficients *a* and *b* from Eqn. (15).

The viscosity of the medium has a considerable influence on the kinetics of the photoconversion of copolymers[34,38]. Thermal decolorisation diverges from a first-order reaction as solutions of the copolymers become more viscous[34].

The introduction of the photochrome into the polymer molecules (XLVa) and (XLVIII) does not lower the quantum efficiencies of coloration and decolorisation.

The substantial decrease in mobility of photochromic groups on introduction into the main chain of the oligomers (XXXIX) halves the rate of decolorisation in comparison with the corresponding dimers, and the thermal process diverges from the first order even in polar solvents[3].

Solutions of benzothiazoline polymers (XLII) are less strongly coloured than are the indolinospiropyran copolymers (XLV). When a solution of the polymer (XLIII) is cooled, the fluorescence becomes more intense, while the efficiency of the photodecolorisation of coloured solutions diminishes[35].

## 2. Photochromism of Copolymers in the Solid State

The photochromism of copolymers in the solid state is of especial interest in connection with practical application. The rate of the thermal decolorisation of copolymer films and solid solutions depends significantly on the glass point of the polymer, especially when the spiropyran forms part of the macromolecule. This effect is most clearly developed in copolymers containing the photochrome in the main chain[30]. The rates of the dark decolorisation of copolymers and solid solutions of spiropyran monomers in a polymer matrix drop sharply (by factors of 100–500) at temperatures below the glass point[3,38,39,41,49,50]. The optical density of the absorption band of the copolymer $\lambda_{max}^{vis}$ decreases by 90% after a few minutes in solution, but after several months in a film[41]. A long-lived coloured state of spiropyrans has been obtained in polymer matrices containing reactive groups, which may undergo photochemical cross-linking[36].

The kinetics of the thermal decolorisation of copolymer films is described by a first-order equation at temperatures above the glass point, but diverges from it below this temperature. Such behaviour of films is consistent with the existence of two or more geometrical isomers, the rate of interconversion of which differs considerably depending on the mobility of the macromolecule at temperatures below and above the glass point[50,51]. In the latter case the rate is so high that decolorisation is a first-order reaction, whose velocity is comparable with that for solutions of spiropyrans[50]. Below the glass point isomerisation slows down considerably, and decolorisation can be regarded as the sum of two or more parallel first-order processes, each characterised by its own rate constant and activation energy[3,50].

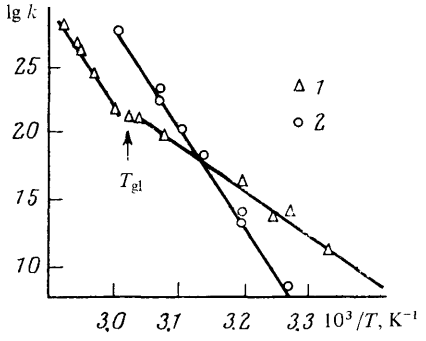



**Figure 4.** Temperature dependence of rate constant of dark decolorisation plotted in Arrhenius coordinates for: 1) copolymer (XLVI); 2) matrix mixture.

However, Lawrie and North[52], studying the rate of decolorisation of 1,3,3-trimethyl-6′-nitrospiro(indolino-2,2′-[2*H*-1]benzopyran) in various polymer matrices, concluded that the deviation from first-order kinetics for copolymers in a film below the glass point must be attributed to the non-uniform distribution of free volume in the vitreous state of the polymer and its relatively uniform distribution in the rubberlike elastic state. Thermal decolorisation of this spiropyran dispersed in a poly(methyl methacrylate) matrix is a first-order reaction below the glass point, owing to the short relaxation times (10–100 s) of the free volume in the polymer. The time of decolorisation of solid solutions of the above spiropyran increases in the sequence poly(methyl methacrylate) < poly(vinyl chloride) < polystyrene < poly-*p*-chlorostyrene owing to the intensifying polar and steric influence of the macromolecule[52].

The mechanism of the thermal decolorisation of three different indolinospirobenzopyrans in amorphous polymer matrices—poly(methyl methacrylate), poly-(n-butyl methacrylate), poly(vinyl acetate), and poly(vinyl n-butyrate)—has also been discussed in terms of a discrete distribution of free volume in a vitreous matrix[53]. The presence of two decolorisation rate constants, together with the change in activation energy below the glass point, is due to the existence of kinetic units of the macromolecule differing in ability to relax (e.g. end and side groups) and also to interaction of the photochromic molecule with the matrix[53].

The decolorisation of films of copolymers differs from that of solid solutions of a spiropyran in a polymer matrix: whereas the Arrhenius plot (Fig. 4) for a solid solution of 1-(2-methacryloyloxyethyl)-3,3-dimethyl-6′-nitrospiro-(indolino-2,2′-[2*H*-1]benzopyran) in poly(isobutyl methacrylate) exhibits a rapid increase in rate of decolorisation with rise in temperature, a film of the copolymer (XLVI) gives a curve with an inflexion near the glass point. The increase in the effective activation energy above this temperature is due to the additional activation energy of viscous flow[3]. The effect of a polymer matrix on the rate of decolorisation of spiropyrans is determined mainly by the polarity of the polymer and is fully consistent with the strong negative solvatochromism of the merocyanine ring system[3,50,52,39,53]. This fact, as well as the sensitivity of the merocyanine form to steric factors, enables benzopyrans to be used as indicators of molecular interaction of polymers[3,49,50,52].

Photochromic conversions in spiropyran copolymers in the solid state, in contrast to solutions, are accompanied by photodecomposition and oxidation. This phenomenon, which has been termed *fatigue*[54], is a result of two photoprocesses involving the colourless and coloured forms respectively. A scheme suggested[38] for photochromic conversions of copolymers (XLVa) and (XLVIII) can be written

$$C \xleftarrow{h\nu} A \underset{h\nu_1}{\overset{h\nu}{\rightleftarrows}} B \xrightarrow{h\nu} E,$$
$$\qquad\qquad\quad \downarrow h\nu_1$$
$$\qquad\qquad\quad F$$

where A and B are initial and coloured forms of the spiropyran, and C, F, and E are products of photodecomposition under the influence of ultraviolet radiation $h\nu$ and visible light $h\nu_1$. Fatigue of the copolyester (XL) at temperatures above the glass point is illustrated[55] by Fig. 5, which shows that the optical density of the coloured form in the photostationary state decreases after each period of exposure. This effect is considerably less well defined in a vacuum, which indicates that the process is influenced by oxygen.

It has recently been found[38] that the quantum efficiencies of the photodecolorisation of copolymers (XLVa) and (XLVIII) are one-third of those observed in solid solutions of spiropyrans in a polymer matrix. This is due to

inhibition of the relative rotation of parts of the spiropyran molecule, as a consequence both of the great structural viscosity of the medium and of the attachment of one part of the photochrome molecule to a polymer chain[38].

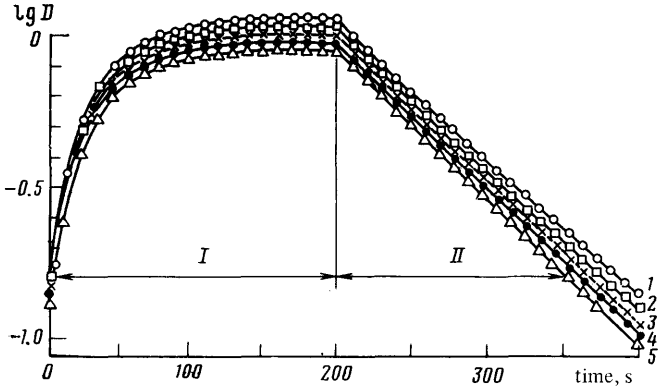



**Figure 5.** Photochromic behaviour of copolyester of bisindolinospiropyran at 65.3°C: I) period of irradiation; II) dark period; 1)–5) curves after first, second, etc. exposure cycles.

Interesting phenomena associated with the photochromism of spiropyran polymers—enhanced stability of copolymers with spiropyran groups during degradation induced by light and radiation[35] and a photomechanical effect[3,30]—have been discovered recently. The latter is observed on filaments and films prepared from photochromic cross-linked poly(ethyl acrylate) (LI). A shrinkage of 2–3% occurs on ultraviolet irradiation under strictly isothermal conditions; the original dimensions are regained in the dark. These photomechanical phenomena show good reproducibility, and are caused by the increase in entropy of the polymer chain resulting from the enhanced flexibility of open-chain merocyanines in comparison with rigid spiropyrans[30]. The amount of shrinkage depends on the applied stress, the temperature, the degree of cross-linking, and the position of attachment of the photochrome. The considerably lower activation energies than in dark decolorisation and shorter times of returning to the initial dimensions in the dark indicate that the photomechanical behaviour of photochromic polymers not only is controlled by isomerisation but also is connected, as in the case of azo-compounds[29], with the properties of the polymer matrix.

## VI. CONCLUSION

Investigation of the spectral and kinetic properties of photochromic polymers, as well as the quantum efficiencies of their photodecolorisation, has revealed in several cases differences from the lower analogues. Furthermore, marked differences are observed in the behaviour of photochromic polymers in the solid state and in solution. With strong interaction between solvent and polymer the photochromic properties of the latter approach those of the simple analogues. When such interaction is less clearly defined, as e.g. in the case of copolymers of styrene and methyl methacrylate with indolinospiropyran in solvents of low polarity, the mechanism of the dark decolorisation of the polymers differs from that for the model compound, and is determined by the polar and steric influence of the macromolecule. The variation with solution pH in the conformation of polyelectrolytes containing azo-groups correlates with the rate constant of the dark reaction.

In the case of solid polymers the photochromic behaviour of groups forming part of the macromolecule depends on the physical state of the polymer. If an appreciable change in conformation of photosensitive groups, e.g. *cis–trans*-isomerisation, accompanies a photochromic transition, the latter is slowed down significantly in the solid, vitreous state because of strong steric hindrance. In the rubberlike elastic state deviations from the behaviour of the polymer in solution are less marked.

The behaviour of copolymers having covalently bound photochromic groups, especially when the latter form part of the main chain of the macromolecule, differs from that of matrix polymers. Smets[55] has recently shown experimentally that the rate constant of the dark decolorisation of a matrix mixture containing indolinospiropyran is only around 10% of the value for photochromic copolyesters.

Thus by varying the polymer structure and the orientation of the polymer matrix it is possible to obtain materials having various photochromic characteristics ($\lambda_{max}^{vis}$, rate constant of dark decolorisation—i.e. colour and stability of the image). These factors, together with the improved technology for obtaining photochromic materials from photochromic copolymers rather than introducing a low-molecular-weight photochromic compound into a polymer matrix, explain the increasing interest taken by research workers during recent years in the study of photochromic copolymers.

Nevertheless, despite the extensive study of the spectral and kinetic characteristics of photochromic transitions, little attention has been paid to the photochemical characteristics of polymers such as the quantum efficiency of photocoloration and photodecolorisation, as well as photosensitivity. Few papers have appeared on the mechanism of photoreactions in polymers. Because of the lack of such information it is impossible in several cases to assess the possibility of practical application of the synthetic photochromic polymers.

## REFERENCES

1. V.A.Barachevskii, M.A.Gal'bershtam, Yu.E.Gerasimenko, and Yu.N.Gerulaitis, Zhur.Vses.Khim. Obshch.Mendeleeva, 19, 85 (1974).
2. G.H.Dorion and A.F.Wiebe, "Photochromism—Optical and Photographic Application", Focal Press, London, 1970.
3. G.Smets, Pure Appl.Chem., 30, 1 (1972).
4. J.Vitry, Chim.et Ind., 102, 1333 (1969).
5. S.Dähne, Z.wiss Phot., 62, 189 (1968).
6. G.H.Brown (Editor), "Photochromism" (Technology of Chemistry, Vol.3), Wiley, New York, 1971.
7. I.I.Laverty and Z.C.Gardlund, J.Polymer Sci., B7, 161 (1969).
8. US P.3483162 (1969).
9. H.Kamogawa, J.Polymer Sci., A-1, 9, 335 (1971).
10. H.Kamogawa and H.Watanabe, J.Polymer Sci., Polymer Chem.Ed., 11, 1645 (1973).
11. Jap.P.44355 (1972).
12. Jap.P.44354 (1972).
13. H.Kamogawa, Kogyogijitsu, 4, 16 (1963).

14. H.Kamogawa, M.Kato, and H.Sugiyama, J.Polymer Sci., **A-1**, 6, 2967 (1968).
15. H.Kamogawa, J.Appl.Polymer Sci., **13**, 1883 (1969).
16. H.Kamogawa and H.Hasegawa, J.Appl.Polymer Sci., **17**, 745 (1973).
17. M.S.Simon and P.T.Moore, J.Polymer Sci.: Polymer Chem.Ed., **13**, 1 (1975).
18. Jap.P.7897 (1972).
19. M.Goodman and M.L.Falxa, J.Amer.Chem.Soc., **89**, 3863 (1967).
20. R.Lovrien and J.C.B.Waddington, J.Amer.Chem. Soc., **86**, 2315 (1964).
21. H.Fink, Plaste und Kautschuk, **18**, 645 (1971).
22. R.Lovrien, Proc.Nat.Acad.Sci.USA, **57**, 236 (1967).
23. G.van der Veen and W.Prins, Photochem. and Photobiol., **19**, 191 (1974).
24. G.van der Veen, R.Hoguest, and W.Prins, Photochem. and Photobiol., **19**, 197 (1974).
25. D.Braun and J.Berger, Makrom.Chem., **171**, 83 (1973).
26. D.Tabak and H.Morawetz, Macromolecules, **3**, 403 (1970).
27. C.S.Paik and H.Morawetz, Macromolecules, **5**, 171 (1972).
28. W.J.Priest and M.M.Sifain, J.Polymer Sci., **A-1**, 9, 3161 (1971).
29. F.Agolini and F.P.Gay, Macromolecules, **3**, 349 (1970).
30. G.Smets and F.Blauwe, Pure Appl.Chem., **39**, 225 (1974).
31. G.Van der Veen and W.Prins, Nature, Phys.Sci., **230**, 69 (1971).
32. R.C.Schulz, Pure Appl.Chem., **34**, 320 (1973).
33. M.Goodman and A.Kossoy, J.Amer.Chem.Soc., **88**, 5010 (1966).
34. P.H.Vandewijer and G.Smets, J.Polymer Sci., **C22**, 231 (1968).
35. V.A.Krongauz, E.L.Zaitseva, N.S.Kardash, and A.L.Prokhoda, in "Tezisy Dokladov I Vsesoyuznoi Konferentsii po Besserebryannym i Neobychnym Fotograficheskim Protsessam" (Abstracts of Papers at First All-Union Conference on Silverfree and Unusual Photographic Processes), Kiev, 1972, p.176.
36. G.A.Delzenne, Proc.Third Internat.Congr.Reprogr., London, 1971; Guildford, 1971, p.169.
37. BRD P.1949715 (1970); Chem.Abs., **73**, 25330 (1970).
38. N.S.Kardash, V.A.Krongauz, E.L.Zaitseva, and A.V.Movshovich, Vysokomol.Soed., **16A**, 390 (1974).
39. J.Verborgt and G.Smets, J.Polymer Sci., **A-1**, **12**, 2511 (1974).
40. V.D.Arsenov, V.D.Ermakova, M.I.Cherkashin, and P.P.Kisilitsa, Izv.Akad.Nauk SSSR, Ser.Khim., 2489 (1975).
41. M.Kikuchi, T.Kakurai, and T.Noguchi, Nippon Kagaku Kaishi, **8**, 1323 (1972).
42. US P.3666525 (1972).
43. K.G.Dzhaparidze, D.P.Maisuradze, V.O.Ananiashvili, Sh.A.Akhabadze, and D.L.Loladze, in "Tezisy Dokladov na II Vsesoyuznogo Soveshchaniya po Fotokhimii" (Abstracts of Papers at the Second All-Union Congress on Photochemistry), Sukhumi, 1974, p.166.
44. US P.3652675 (1972).
45. M.Kikuchi, T.Kakurai, and T.Noguchi, Kobunsi Robunsyu, **31**, 551 (1974); Chem.Abs., **82**, 73605 (1975).
46. P.H.Vandewijer and G.Smets, J.Polymer Sci., **A-1**, 8, 2361 (1970).
47. B.P.1278775 (1972).
48. E.I.Merkulov, A.V.Vannikov, G.M.Chernov, V.D.Arsenov, V.D.Ermakova, M.I.Cherkashin, and P.P.Kisilitsa, Izv.Akad.Nauk SSSR, Ser.Khim., 2492 (1975).
49. Z.G.Gardlund, J.Polymer Sci., **B6**, 57 (1968).
50. Z.G.Gardlund and J.J.Laverty, J.Polymer Sci., **B7**, 719 (1969).
51. J.B.Flannery, J.Amer.Chem.Soc., 30 [?90], 5660 (1968).
52. N.G.Lawrie and A.M.North, European Polymer J., **9**, 345 (1973).
53. M.Kryszewski, D.Lapienis, and B.Nadolski, J.Polymer Sci., **A-1**, 11, 2423 (1973).
54. M.Nakazawa, K.Esida, H.Kokado, and E.Inoue, Koche Kagaku Zassi, **74**, 137 (1971).
55. G.Smets, J.Polymer Sci., Polymer Chem.Ed., **13**, 2223 (1975).

Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow