

PHOTOCHROMIC BEHAVIOUR OF POLYMERIC SYSTEMS AND RELATED PHENOMENA

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ABSTRACT

The different photochromic systems which have been used in polymer chemistry are mainly based on *cis-trans* isomerization of azomethines and azocompounds which were built into the polymeric backbone, or attached as sidegroups. These systems are reviewed and briefly commented upon. Special attention is paid to spirobenzopyran derivatives of which the photochromism is very important and characterized by a strong negative solvatochromism. Different spirobenzopyran photochrome-containing polymers are considered:

- (1) copolymers with vinyl monomers, e.g. methyl methacrylate-styrene.
- (2) polypeptides such as polytyrosine and polylysine.
- (3) polycondensation products.

Their behaviour in solution is discussed and the existence of different isomeric mesoxy amines demonstrated.

In the solid state when these photochromes are used in a polymeric matrix, they permit detection of secondary glass transition phenomena; by contrast, when attached on a copolymer, they permit accurate determination of T_g . In crosslinked systems the copolymers show a reversible photochromic behaviour. Finally a comparison of these photochromic phenomena with thermal racemization of some new optically active polymers is presented.

INTRODUCTION

Substances which undergo reversible colour formation under irradiation with light are called photochromic compounds. The fundamental processes which depend on this phenomenon can be very different. For inorganic species such as metal oxides and halides, they are usually related with the presence of some impurities or crystal defects which interact with the electrons liberated under the influence of light. For organic compounds, photochromism is mostly linked with molecular structural modifications, e.g. valence isomerization, tautomerism, bond scission (homolytic and heterolytic), *cis-trans* isomerization and dimerization reactions; sometimes even chemical reactions may be involved, for example, redox reactions. It is the purpose of the present lecture to discuss some systems, which have been used recently in the domain of polymer chemistry, and to concentrate more on details in the use of spirobenzopyran derivatives which were the basis of our own experiments. As a general rule, it can be assumed that the incorporation of photochromic groups into a polymer molecule may deeply affect the photochromic behaviour on account of polar and steric effects

due to the proximity of the polymer chain and on account of internal viscosity effects which may restrict segmental motions. On the other hand, in order to be conclusive, the results obtained with photochromic polymers should be compared with those of mixtures of the corresponding polymers with the homologous low molecular weight photochromes.

There is therefore a first experimental condition, which should be fulfilled, if one expects a strong difference between the photochromic behaviour of the systems to be compared, namely the phenomenon which is involved should include an appreciable change of configuration of the photochromic group, for example an important movement of one moiety of the molecule with respect to the other one; valence tautomerism would therefore *a priori* be much less interesting than *cis-trans* isomerization.

Thus, most data in the literature on photochromic polymers are concerned with *cis-trans* isomerization phenomena either in the case of azomethines, or that of azo-compounds, such groups being attached to a polymeric chain as sidegroups, or incorporated in the main chain. These data will be now discussed successively.

1. PHOTOCROMIC POLYAZOMETHINES

The photochromism and thermochromism of some *hydroxylated polyazomethines* has been studied recently by Laverty and Gardlund¹. The reaction scheme is represented by equation 1, where the hydrogen bonded anil (I) can be photoisomerized into the *trans*-keto derivative (III). This *trans*-keto form isomerizes thermally to the *cis*-keto isomer (II), which itself can return to the *cis*-enol (I) by hydrogen jump through the equilibrium $I \rightleftharpoons II$ ($\Delta H \cong 1$ kcal).

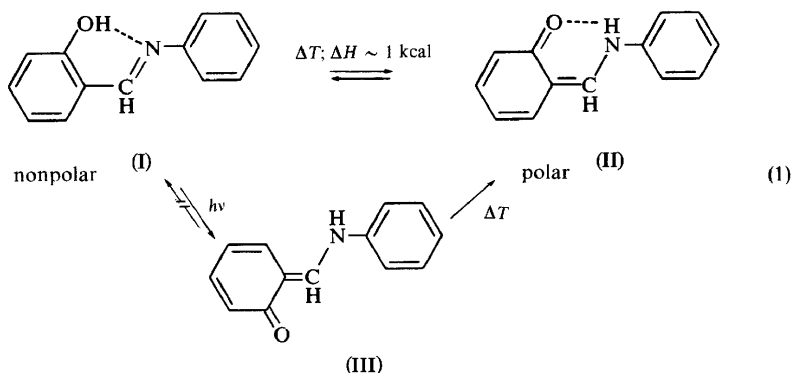


Figure 1

The authors prepared different polyazomethines, e.g. from methylene-bis-salicylaldehyde and *p*-phenylenediamine (IV) and *p,p'*-methylene dianiline (V). The polymers were insoluble in most organic solvents, but soluble in concentrated sulphuric and concentrated formic acid.

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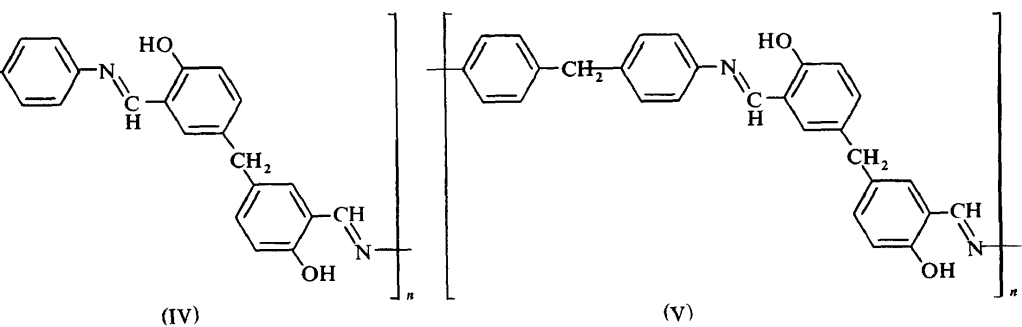
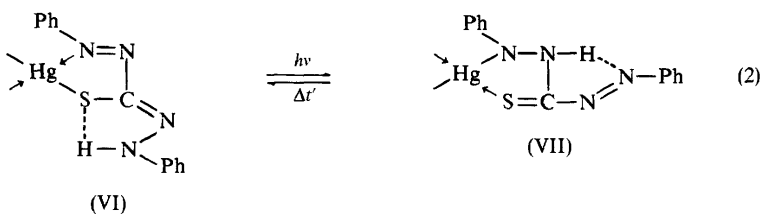


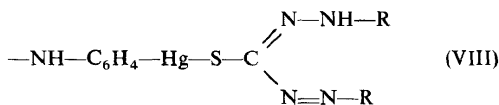
Figure 2

Although not photochromic, these polymers behave thermochromically on account of the easy proton shift; the bathochromic effect between 25° and 100°C is, however, very small. The movements and energy required to produce the *trans*-form of the polymer backbone were assumed to be prohibitive.

Cis-trans isomerization of an azomethine group followed by a rate-determining proton shift is also proposed for the orange-blue photochromism of *mercurydithizonate*, and was applied very recently to photochromic polymers by Kamogawa². Following Meriwether *et al.*^{3,4} reaction scheme 2 can be written:



The copolymers contained *p*-amino phenyl-mercuric-diphenylthiocarbazonate side groups (VIII), with styrene or methylacrylate as comonomers:



The spectral recovery occurs thermally. On the basis of decoloration half-lifetimes, the reaction is about a hundred times slower in a film, than in solution; moreover, a higher glass transition of the copolymer (styrene comonomer) causes a longer decoloration time than that for copolymer with methylacrylate.

2. PHOTOCHROMIC AZOBENZENES

Cis-trans isomerization of *azo compounds* as the photochromic principle has been used by several authors and first as *sidegroups* by Lovrien and Waddington⁵. Indeed, they synthesized photochromic polyelectrolytes by

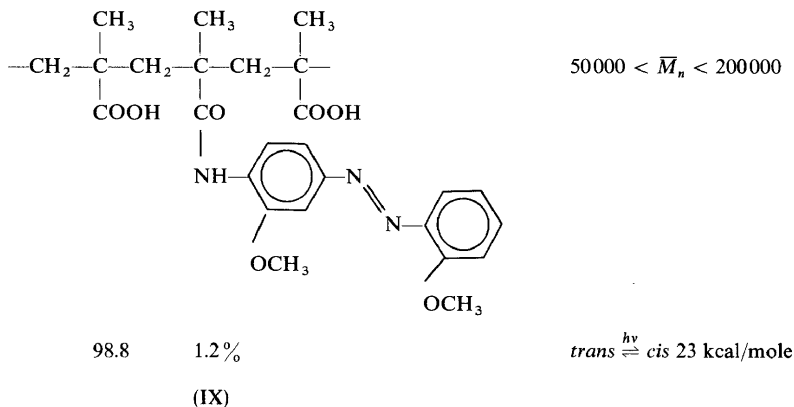


Figure 3

copolymerization of acrylic-methacrylic acid with a few per cent of azo-dye acrylamide monomers (1.2 to 3.6 per cent). Under the influence of light *trans-azo* compounds are transformed into their *cis*-isomer, the energy of

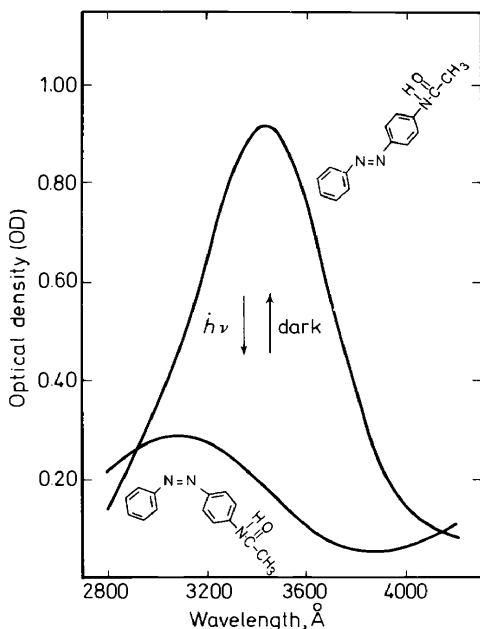


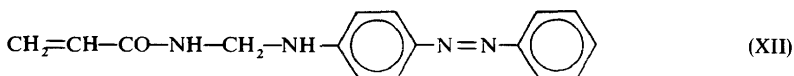
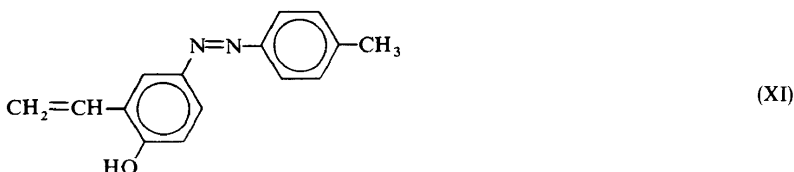
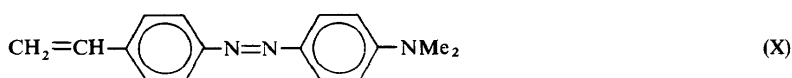
Figure 4. Photochromism of *p*-acetamino-*trans*-azobenzene (0.01M) at pH 8 [R. Lovrien and J. C. B. Waddington, *J. Amer. Chem. Soc.* **86**, 2315 (1964)]

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activation of the reverse reaction (*cis* → *trans*) being about 23 kcal/mole, while the enthalpy difference is about 5.7 kcal/mole. The photochromism of the model compound, *p*-acetamino-azobenzene is illustrated by *Figure 4*.

In the case of covalently bound dyes, irradiation response and dark recovery are linked to the charge and conformations of the polyacid chain; thus the 'isosbestic' crossing point wavelengths depend on the pH, and decrease markedly when the intrinsic viscosity increases on account of the uncoiling of the charged macromolecule, i.e. around pH = 6.

Kamogawa and co-workers⁶ synthesized copolymers of vinylamino azobenzene and styrene (X), polyvinylhydroxy-azobenzenes (XI), copolymers of 4-acrylamidomethyl-aminoazobenzene (XII) with styrene, butylacrylate and methyl methacrylate.

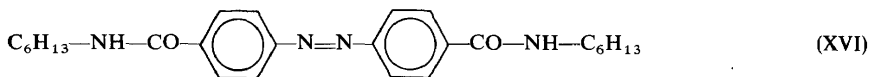
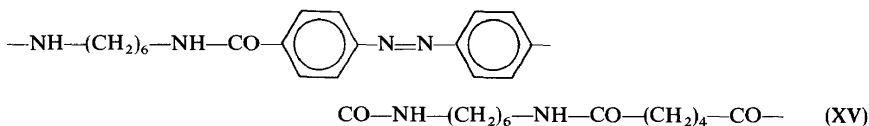
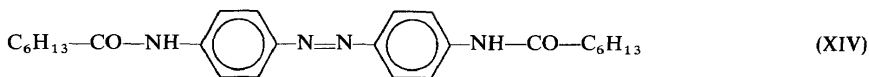
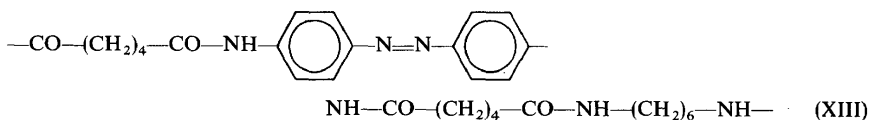


The authors measured the decoloration recovery halftime values of the polymers and compared them with those of the model compounds. Sometimes more favourable results were obtained for the polymers; they were explained on the basis of the aggregation of azobenzene molecules in a film or solution which is prevented by incorporation of an azobenzene component in a copolymer chain by separation with inert comonomers. On the other hand, incorporation in the polymeric chain causes steric hindrance for *cis*-*trans* isomerization; these two effects may compensate each other, the total behaviour resulting from the balance between them.

The authors also compared the photochromic behaviour of the copolymers in solution and in film; as expected, the *cis*-*trans* isomerization is slower in the film state, especially if the comonomer constitutes a rigid chain component (styrene and methyl methacrylate compared to butylacrylate).

Tabak and Morawetz⁷ examined the *cis*-*trans* conformational transitions in solution of *polyamides* containing *azobenzene* residues in the *backbone*, and compared these isomerizations with those of corresponding model compounds, namely compounds XIII/XIV and XV/XVI.

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For XIII/XIV the isomerization rate of the polymer X is only 15 per cent lower than that of XIV; it is independent of the concentration of the azobenzene residues in the chain and corresponds strictly to a first order reaction.

Copolymer XV did not obey first order kinetics and is best represented by the following equation:

$$C/C_0 = \alpha \exp(-k_1 t) + (1 - \alpha) \exp(-k_2 t)$$

in which C and C_0 are concentrations of azo-*cis*-form at time t and zero time respectively.

The two rate constants k_1 and k_2 do not vary with the azobenzene content; the fraction of the azobenzene units isomerizing at the faster rate do not change with a change in the reaction temperature, k_1 being equal to about three times k_2 ; k_1/k_2 , however, decreases with increasing acidity of the medium.

The model compound XVI decolorizes with a rate constant corresponding to the slow azo-groups of the copolymer XV.

In order to explain these effects, Tabak and Morawetz admit that the time required for the change of chain conformation to a form which corresponds to the transition state of the azo-group must be comparable to the relaxation time of the *cis-trans* isomerization in the absence of such restraints.

It must, however, be pointed out that the experiments of these authors were all carried out in formic acid as solvent, and only in dilute solutions.

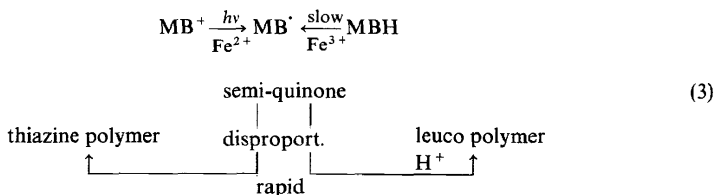
3. PHOTOCHROMIC POLYTHIAZINE REDOX SYSTEM

Very interesting results were also described recently by Kamogawa in the domain of the redox photochromism, i.e. the reversible colour changes associated with reversible photochemical oxidation-reduction reactions⁸. It is well known that thiazine derivatives such as methylene blue are photo-bleached in the presence of reducing agents like ferrous ions; thus methylene

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blue can be reduced into the semi-quinone, which disproportionates rapidly into a colourless leuco derivative and methylene blue.

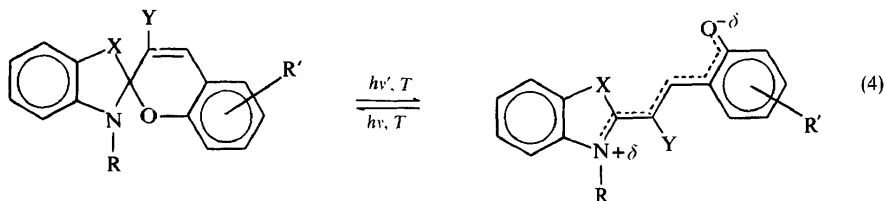
The reverse reaction consists of slow oxidation of the leuco compound into semi-quinone, and consequently into the dye, under the influence of the iron(III) ions. This reaction principle has been applied for the synthesis of photochromic polymers⁹, as shown by reaction scheme 3.



Thus several compounds were obtained from *N*-hydroxy methylacrylamide sidegroups of acrylamide copolymers by reaction with thiazine compounds; the systems include various reduction agents, such as polyvinyl alcohol, ferrous ions, or mercapto derivatives and their photochromism depends strongly on the moisture content of the polymer.

4. PHOTOCROMIC POLYSPIROBENZOPYRANES

We have concentrated our efforts on spirobenzopyran derivatives¹⁰, where the photochromism consists of scission of the C—O-pyran bond followed by a rotation of one part of the molecule so as to approach coplanarity (reaction 4)¹¹.



when $X = \text{CMe}_2$, $Y = \text{H}$; when $X = \text{S}$, $Y = \text{Me}$;
 $h\nu'$: ultra-violet light; $h\nu$: visible light.

The open ring merocyanines are characterized by a very strong solvatochromism¹² affecting their maximum absorption wavelength as well as their decoloration rates¹³⁻¹⁵; moreover, they are very sensitive to steric effects, especially in the benzthiazol series^{16, 17}. These facts were the main reason for choosing these benzopyrylspirans for incorporation in macromolecules^{17, 18}. From the synthetic point of view, photochromic spirocyan polymer can be obtained either by copolymerization of unsaturated photochromic monomers with vinyl comonomers, or by polycondensation of bifunctional compounds.

Photochromic sidegroups can also be attached to a polypeptide chain, by reaction of a haloalkyl- or haloacylphotochrome with a hydroxyl- or amino-

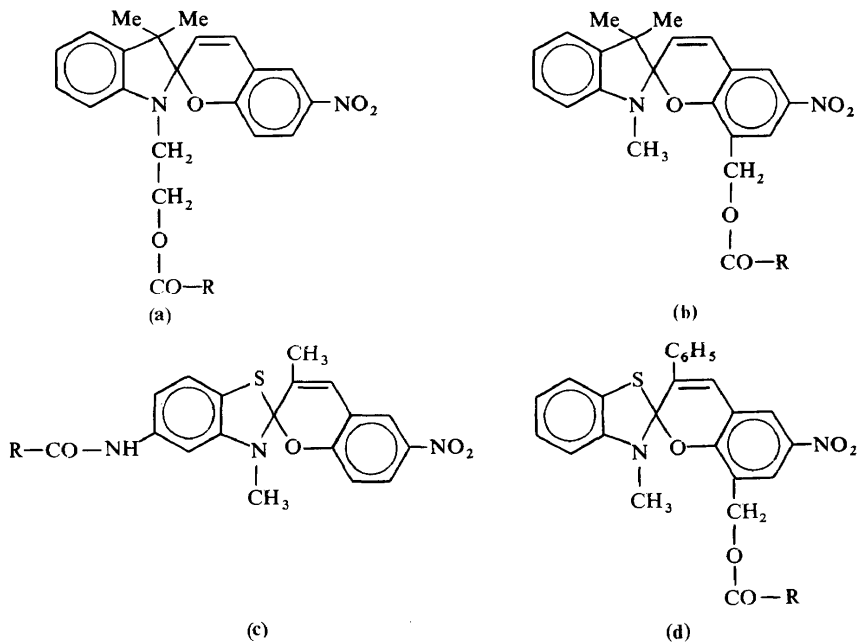
group-containing polymer; thus by condensation of the free phenol groups of polytyrosine with *N*(δ -iodo-butyl) spirobenzopyran, a photochrome polypeptide was obtained. In these first cases, the photochromes are attached as sidegroups on the main chain, of which the influence depends on the distance of the photochrome to the chain, on the nature of the comonomer, and on the site of attachment in the photochrome itself. If the comonomer is acrylic or methacrylic acid, irradiation response and dark recovery will probably be linked to the degree of neutralization and the conformation of the polyelectrolyte.

In the polycondensates, where the photochromes are incorporated into the main chain, the synthetic approach is much more difficult, from the additional point of view of the synthesis of bifunctional dimers as well as that of the polycondensation. Indeed the insertion of substituents appropriate for further condensation is often tedious, and their choice necessarily limited on account of their influence on photochromic behaviour. On the other hand, the polycyclic structure of the photochromes causes a decrease of solubility of the condensation products, which precipitate frequently before attaining a high molecular weight; in this respect copolycondensation seems to be more likely to be satisfactory.

We will consider successively different types of such photochromic polymers.

(a) Photochromic spirobenzopyran copolymers

Several substances were synthesized by copolymerization of methyl methacrylate (90 molar per cent), e.g. with *N*-(β -methacryloxyethyl)-1,3,3-trimethyl-6'-nitro-indoleninobenzopyrylospiran (a), 1,3,3-trimethyl-6'-nitro-



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8'-methacryloxymethylene-indoleninobenzopyrylospiran (**b**), 1,3'-dimethyl-5-methacrylamino-6'-nitro-benzothiazolinobenzopyrylospiran (**c**), and 1-methyl-3'-phenyl-6'-nitro-8'-methacryl-oxymethylene-benzothiazolinobenzopyrylospiran (**d**).

In these formulae R is isopropenyl (methacrylic copolymers) or isopropyl (isobutyric model substances). The photochromic behaviours of these copolymers and models in acetone solution are reported in *Table 1*, and illustrated by *Figure 5* for the copolymer —A.

Table 1. Photochromic behaviour of spirobenzopyran copolymers (cop.) and their model compounds (mod.) in acetone solution

Structure	a		b		c		d	
	mod.	cop.	mod.	cop.	mod.	cop.	mod.	cop.
λ_{max}	577	577	567	567	526 (506)	478 (504)*	569	569
k_1 20°C $\times 10^3 \cdot \text{sec}^{-1}$	8.2	9.9	1.3	1.0	1.7 (4.8)	1.7‡ (3.8)	2.0	1.05
E_a	22.3	22.4	24.3	24.5	(22.1)	(25.6)	21.6	23.0
$\bar{M}_n \times 10^{-3}$		213		379		64		426

* values in dimethylformamide.

‡ apparent initial rate constants.

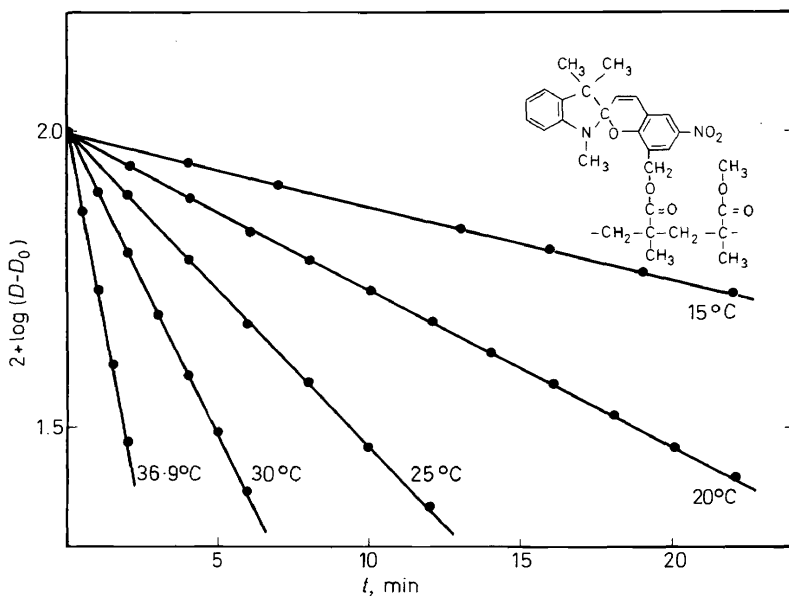


Figure 5. Decoloration of copolymer-A in acetone

It can be seen from these data that the decoloration rate constants are about equivalent for the copolymers and corresponding models, except for the series **d** with a 3'-phenyl group, where the copolymer's rate is only half that of the model; it shows already the influence of steric hindrance of the polymeric chain on the rotation possibility around the 3'-4'-bond. While the maximum absorption wavelengths for copolymers and models are identical for compounds **a**, **b** and **d** in acetone solution, for compound **c** this only applies in highly polar solvents, e.g. dimethylformamide. In such conditions, the decoloration kinetics correspond to a first order reaction rate up to high degrees of conversion.

Copolymer **c** has been submitted to further detailed study by P. H. Vandewijer on account of its peculiar behaviour in relatively low polarity solvents like acetone, dichloromethane and tetrahydrofuran¹⁸. By following the variation of optical intensity as a function of time, a strong deviation from a first order relationship was observed; the decoloration curve can be represented by the equation

$$D = a \exp(-X_1 t) + b \exp(-X_2 t)$$

This equation assumes the existence of two photochrome isomers of which the rate of interconversion is low compared to that of decoloration, and of which *a* and *b* represent their contribution to the optical density at zero time.

Table 2. Decoloration kinetics of a methylmethacrylate-5-methacrylamino nitro spirobenzopyran copolymer in solution

Solvent	Temp. °C	$k^* \times 10^3$ sec ⁻¹	$X_1 \times 10^3$ sec ⁻¹	$X_2 \times 10^3$ sec ⁻¹	% isomers	
					<i>a</i>	<i>b</i>
Acetone	20.5	1.7	1.7	0.27	36	64
Dichloromethane	20.0	3.4	5.7	0.48	66.7	33.3
Tetrahydrofuran	22.2	38.0 [‡]	4.6	0.70	68	32

* rate constant for the model compound.

‡ extrapolated value.

It must be noticed that λ_{\max} shifts towards shorter wavelengths during decoloration, and that the optical density becomes a function of the wavelength and the duration of irradiation. The kinetics of decoloration in low polarity solvents permit demonstration in this way the existence of two (or more) isomeric merocyanines, and confirm the results generally obtained only at low temperatures by Fischer, Wippler, Lashkow *et al.*¹⁹.

It is also understandable that it will be in low polarity solvents that copolymers of the 5-methacrylamino photochrome (compound **c**) with other comonomers as styrene, methacrylonitrile, α - and β -vinylnaphthalene will behave differently, the differences being most pronounced with the most polar comonomers.

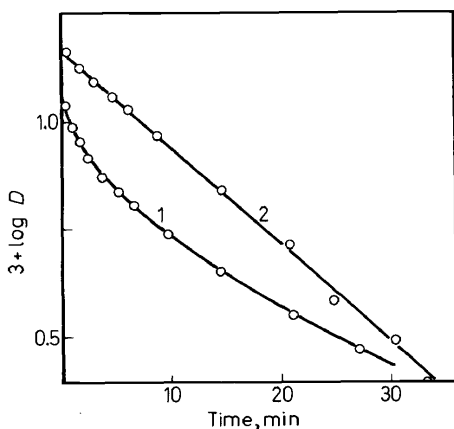


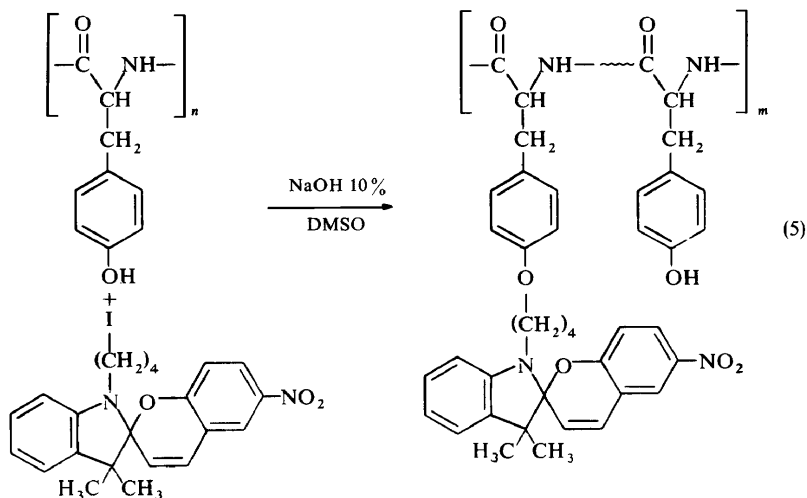
Figure 6. Influence of *t*-butanol on kinetics of decoloration reaction of copolymer 2 in chlorobenzene at 15°C: (1) pure chlorobenzene; (2) chlorobenzene containing 10 vol. % *t*-butanol

The solution photochromism of spiropyran (**c**) built into a methyl methacrylate copolymer was also examined in the presence of a non-solvent; it was indeed assumed that it could be affected by coiling up of the macromolecule. In fact, the behaviour is essentially dependent on the polarity of the medium on account of the very strong negative solvatochromism of these compounds. This effect can be illustrated by *Figure 6*, which represents the influence of the addition of *t*-butanol on the decoloration kinetics in chlorobenzene at 15°C. It can be seen that first order kinetics are restored by the addition of the precipitant. On the other hand, as expected, the behaviour of the model substance as well as that of the copolymer are strongly affected if one changes the overall viscosity of the medium; an increase of viscosity provokes a strong deviation from first order kinetics. All these effects have been analysed and discussed previously in detail¹⁸.

The departure of compound (**c**) from first order kinetics in solvents of relatively low polarity seems to be general where the photochromic group is linked to the polymeric chain through a methacrylamino-phenyl group. Thus a copolymer of methyl methacrylate and *N*-methyl-benzthiazol(2-2')spiro-3'(p-methacrylamino)phenyl-6' nitro benzopyran decolorizes not only in at least two successive steps, but where the rate constant k_2 is much slower than that of the model. It should, however, be pointed out that the activation energies of decoloration are similar (E_{model} : 25 kcal/mole; for the polymer the first and second step have respectively values of E_{a1} : 24.3 and E_{a2} : 26 kcal/mole). The monomer (**a**), 1-(β -methacryloxyethyl)-3,3-dimethyl-6'-nitro-indolinospiryran has also been copolymerized with acrylic acid. In dimethylformamide solution the rates of decoloration of the copolymer are practically identical with those of the model; in dioxane, however, the rates are only one-half of them. On neutralization of the acrylic acid with piperidine in dimethylformamide solution, the rate decreases progressively with an increasing degree of neutralization (up to 40 per cent) very likely on account of a stabilization of the merocyanine open form.

(b) Photochromic spirobenzopyranpolypeptides¹⁸

It seems interesting to investigate the photochromic behaviour of spiro-pyran sidegroups when they are attached to a polypeptide chain. Indeed it could be expected that accumulation of charged merocyanine groups along the chain would alter the chain conformation, and conversely that this conformation, if respected, will influence the photochromism itself. Thus two photochromic polytyrosines P_1 and P_2 containing 54.7 and 72.3 weight per cent photochromes, were prepared following the reaction scheme 5.



Their molecular weights were 10000 (P_1) and 4000 (P_2), i.e. 10 and 5.5 photochromic units per chain. Their behaviour was compared to that of the *N*-acetyl-tyrosine methyl ester derivative. Very strong differences have indeed been found: (i) the polypeptides showed a much less pronounced solvatochromism than their model; moreover, their absorption spectra always presented two absorption maxima instead of one for the model (see Table 3); (ii) in acetone and tetrahydrofuran, the decoloration kinetics

Table 3. Absorption maxima of photochromic polytyrosines (P_1 and P_2) and model substance (M) after ultra-violet irradiation

Solvent	E_T^*	Absorption maxima, nm		
		M	P_1	P_2
Ethylene glycol	56.3	530	520, 553 †‡	Ins
Methanol	55.5	534	Ins§	Ins
Dimethylformamide	43.7	567	526, 560	527, 560
Acetone	42.2	578	522, 558 ‡	525, 560 ‡
Pyridine	40.2	590	530, 568	530, 568
Tetrahydrofuran	37.4	591	529, 563 ‡	529, 563 ‡

* E_T = Dimroth's solvent polarity values.

† λ_{max} determined on the non-irradiated solution.

‡ Saturated solution (conc. < 0.1 g/l).

§ Ins = insoluble.

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of model and polymers deviate from a first order relationship; the variation of the optical density with the time is given by

$$D = ae^{-x_1t} + be^{-x_2t} \quad (\text{see Table 4})$$

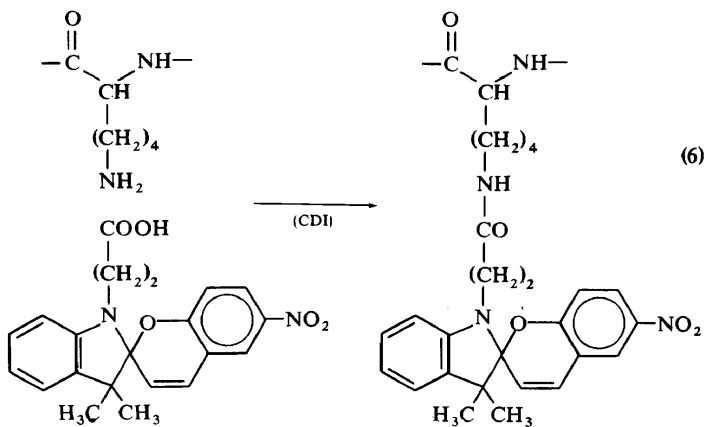
Table 4. Decoloration rate constants X_1 and X_2 of M, P_1 and P_2 in acetone and tetrahydrofuran at 20°C

Photochrome	$X_1 \times 10^2, \text{min}^{-1}$		$X_2 \times 10^2, \text{min}^{-1}$	
	Acetone	Tetrahydrofuran	Acetone	Tetrahydrofuran
$[M] = 3.3 \times 10^{-4} \text{ mole/l.}$	89.0 ± 0.7	39.8 ± 0.4	17.36 ± 0.02	23.9 ± 0.5
P_1 , saturated soln*	21.9 ± 0.7	18.9 ± 0.1	3.32 ± 0.03	5.43 ± 0.07
P_2 , saturated soln*	28.6 ± 0.1	22.6 ± 0.2	4.02 ± 0.02	5.96 ± 0.60

* In acetone. <0.1 g/l.; in THF. ca. 0.2 g/l.

The model discolours much more rapidly than the polymer; and the existence of two isomers, which are not convertible into each other, must therefore be admitted.

A photochromic polylysine has also been prepared recently by reaction of polylysine with 1-β[3,3-dimethyl-6'-nitro-spirobenzopyran indolenino] propionic acid in the presence of carbodiimide reagent (reaction scheme 6).



Its photochromism will be described in the near future and corresponds to that of polytyrosine.

(c) Photochromic condensation polymers

It was assumed that the incorporation of the photochromic groups into a polymeric backbone should affect most strongly their photochromism by lack of segmental mobility in these highly aromatic systems.

With this purpose in mind, several benzopyrylspiran dimers have been prepared by condensation of a bisindolenine with two molecules of substituted monosalicylaldehyde and inversely by condensation of a bissalicylaldehyde with two molecules of monoindolenines. Similarly the condensation of bisindolenines with bissalicylaldehydes should give polycondensation products; however, only oligomers were obtained on account of the low solubility of these polyaromatic compounds. The structures of these condensation products are given in *Figures 7 and 8*; the values of n varies from five to ten.

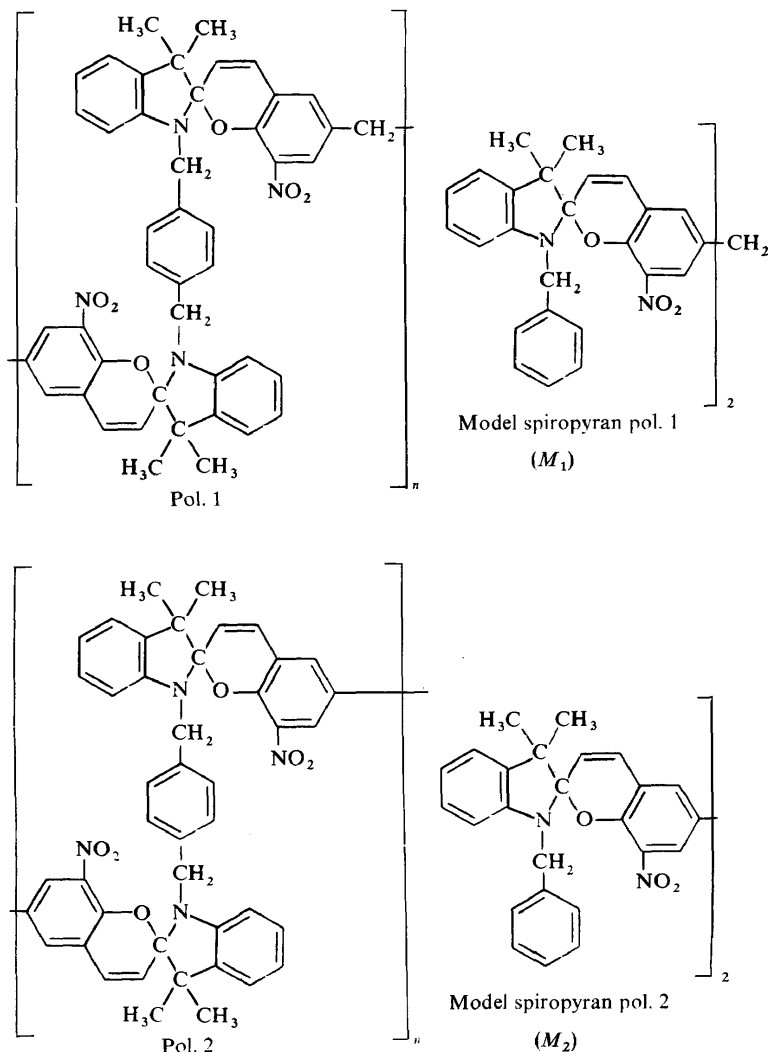


Figure 7

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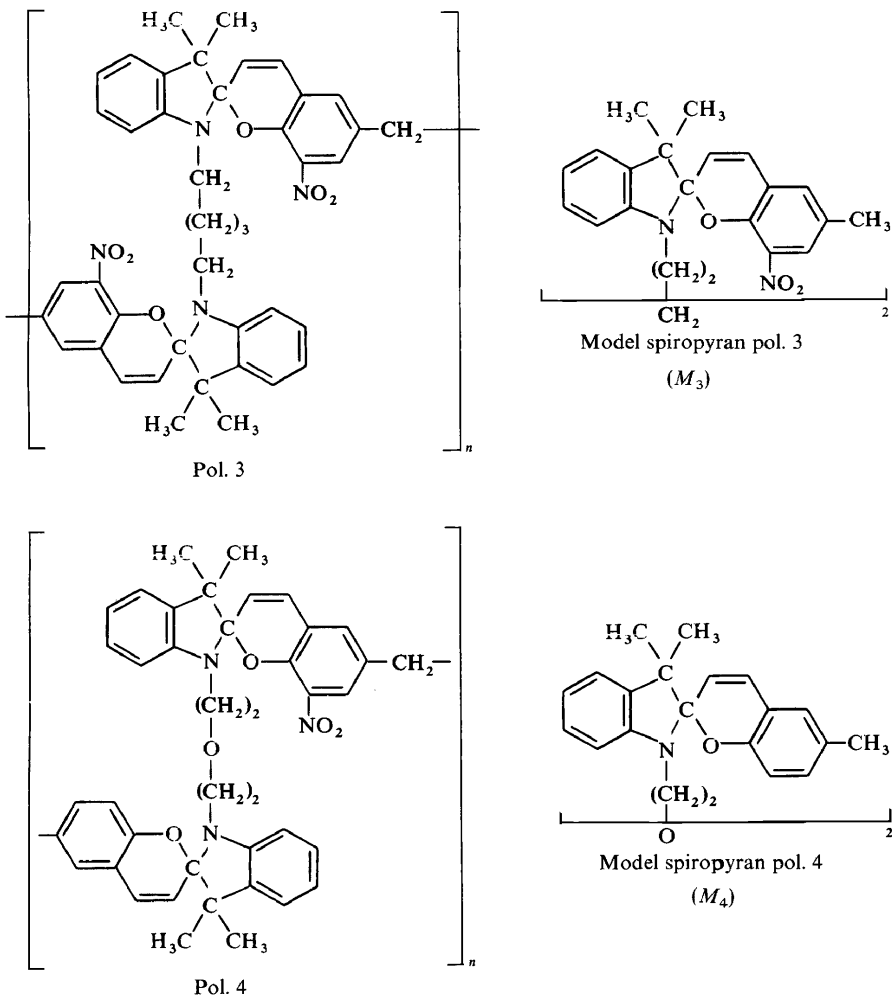
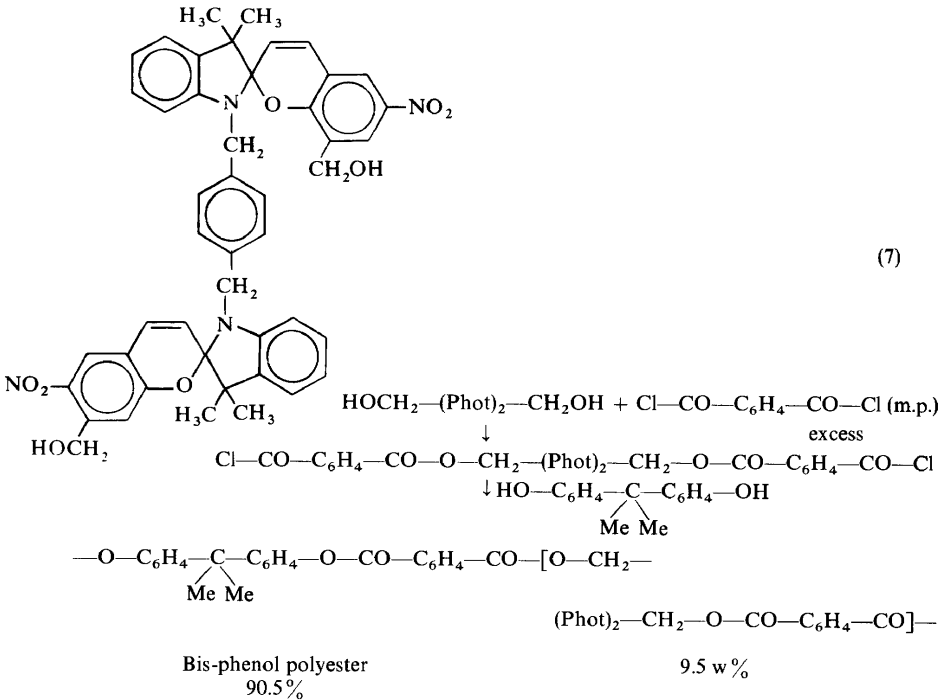


Figure 8

As a result the differences dimers/oligomers were much less pronounced, as could be expected. The rate of decoloration of the oligomers is nevertheless about half that of the corresponding dimers. Even in a solvent as polar as dimethylformamide their reaction kinetics deviate from a first order relationship, while the dimers behave linearly up to complete decoloration.

As to how far the existence of two or three isomers must be admitted in order to explain these kinetic deviations, is still questionable. A different behaviour of the photochrome endgroups compared to those inside the oligomeric chain could also be assumed.

In order to avoid these difficulties copolyesters have been prepared starting from a bismethylol photochrome, bisphenol-A and a mixture of iso- and terephthalylchloride following the reaction scheme 7.



This copolyester contained 9.5 per cent weight photochrome, i.e. one unit for twenty bisphenolphthalate units. In cyclohexanone solution its decoloration rate at 29°C must again be explained by two successive rate constants which are equal to $k_1 = 30.6 \times 10^{-3} \text{ sec}^{-1}$ and $k_2 = 8.3 \times 10^{-3} \text{ sec}^{-1}$, while for the model compound k is equal to $19.5 \times 10^{-3} \text{ sec}^{-1}$.

On account of its polyester content, this copolyester can be cast easily into a film from its dichloromethane solution. When completely dry, these films no longer show photochromic behaviour; only on heating above the glass transition ($T_g \sim 194^\circ\text{C}$) do they become thermochromic. By contrast, swelling in the presence of dichloromethane vapours is already sufficient to restore their reversible photochromism and complete recovery.

(d) Photochromic copolymers in the solid state

Some very interesting results have been obtained from comparison of the photochromic copolymers with the corresponding mixture of their model substances.

(i) First of all, as had already been described by Gardlund²⁰, it must be remembered that the rate of decoloration of a spirobenzopyran is 400 to 500 times smaller in a polymethylmethacrylate matrix than in the homologous solvent, i.e. methylpivalate. In a polymeric matrix, the existence of three isomers, each characterized by a different rate constant, must be admitted, while in the pivalate due to rapid interconversion of the isomers, the rate constant corresponds only to the slowest isomer.

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(ii) The nature of the polymeric matrix plays a very important role, as can be seen from *Figure 9*. The rate of decoloration is much higher in polystyrene than in polymethylmethacrylate due to the negative solvatochromism. The activation parameters of the second and third decoloration steps for both matrices are the following :

	polystyrene	PMMA
E_{a_2}	16.3	22.5
E_{a_3}	17.6	24.4
ΔS_2^\ddagger	-18.8	+1.8
ΔS_3^\ddagger	-14.6	+3.9

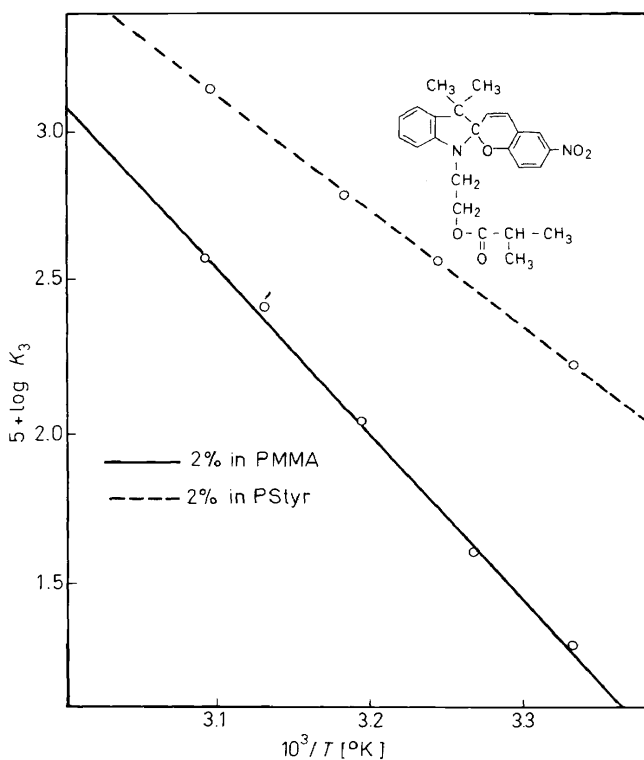


Figure 9. Influence of the polarity of the film

Not only the activation energies differ considerably, but the activation entropies have opposite signs in the two matrices. Similar results were found by Flannery¹³ with 1,3,3-trimethyl-6'-nitroindolinospiropyran solution, the entropy of activation being positive in polar solvents (ethanol, acetone) and negative in apolar, non-hydrogen-bonding solvents.

(iii) When a photochrome is dissolved (five per cent) in a given polymeric matrix, the behaviour is dependent on the glass transition of the polymeric

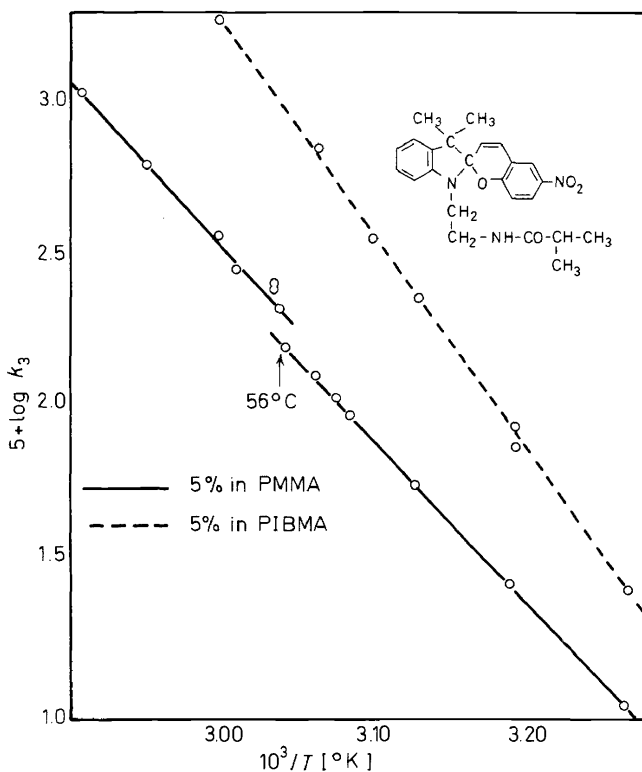


Figure 10. Influence of T_g on activation energy

substrate. This can be seen from the *Figure 10*. In polyisobutylmethacrylate ($T_g \sim 45^\circ C$) the rate is two to three times higher than that in polymethylmethacrylate, and the Arrhenius diagram is linear over the whole domain of temperature measurements. On the contrary, in polymethylmethacrylate ($T_g \sim 124^\circ C$) a 40 per cent increase of rate of decoloration can be found at $56^\circ C$ though the diagrams remain parallel. This acceleration corresponds to a secondary transition temperature of the polymer, at which the mobility inside the matrix increases. Several photochromes have been used in the same way for different polymers and confirm the reproducibility of the experiment and the validity of the conclusion. Thus a photochrome can be used for the detection of local motions in a polymer molecule, and can act as an indicator for the determination of secondary glass transition temperatures.

(iv) On the contrary, if the photochrome is bonded to the polymer chain, the behaviour is completely different (*Figures 11 and 12*). In this case, the Arrhenius plot of the decoloration reaction shows a marked kink at the glass

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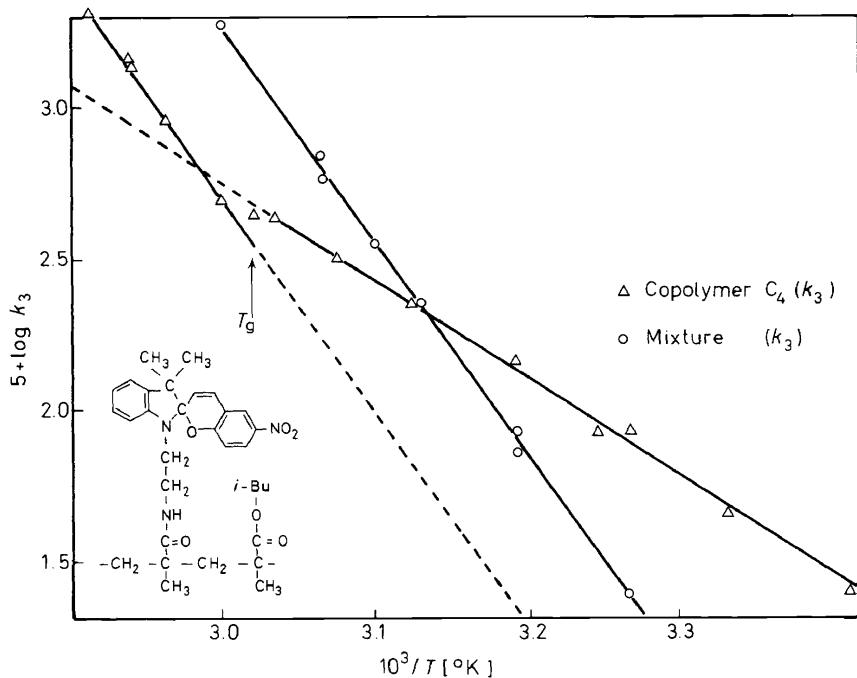


Figure 11. Arrhenius plot of decoloration reaction

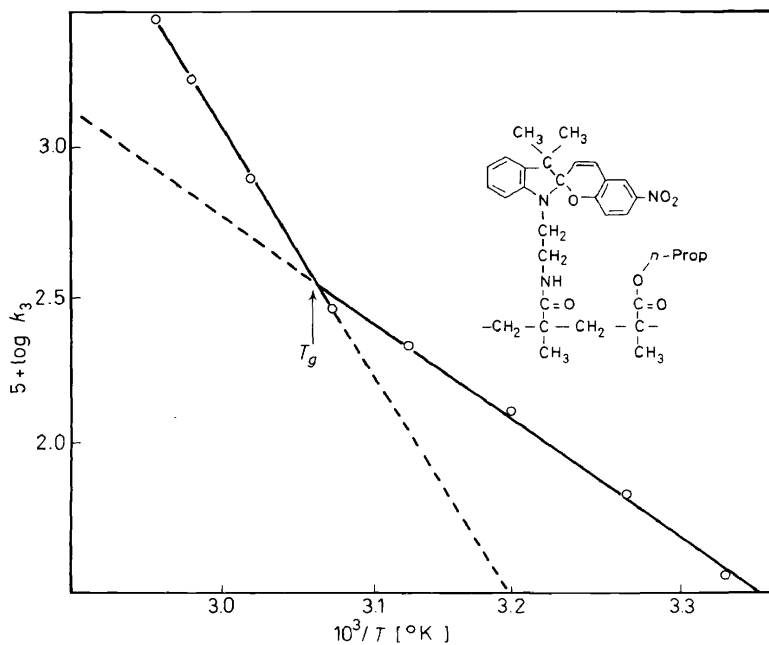


Figure 12. Arrhenius plot : copolymer 6 (k_3)

transition of the copolymer, respectively at 61° and 53°C for the isobutyl- and *n*-propylmethacrylate copolymers. These T_g were controlled by differential scanning calorimetry. The activation parameters for the second and third decoloration steps can be summarized in the following Table 5.

Table 5. Activation parameters of decoloration kinetics of photochromic copolymers

	Isobutylmethacrylate copolymer		<i>n</i> -Propylmethacrylate copolymer	
	below T_g	above T_g	below T_g	above T_g
E_{a2}	12.6	26.4	15.4	31.5
ΔS_2^{\ddagger}	-28.8	+12.4	-20.1	+27.7
E_{a3}	15.1	32.3	17.2	36.9
ΔS_3^{\ddagger}	-25.5	+25.8	-19	+41

The increase of overall activation energy above T_g is due to the additional activation energy for viscous flow. Very striking is the change of activation entropy values, which vary from strongly negative to highly positive values, by passing from below to above the glass transition temperatures respectively.

(v) Another very stimulating and new phenomenon which was observed recently with spirobenzopyran copolymers is the photomechanical behaviour of a crosslinked copolymer (Figure 13) of a bismethacryldiphotochrome

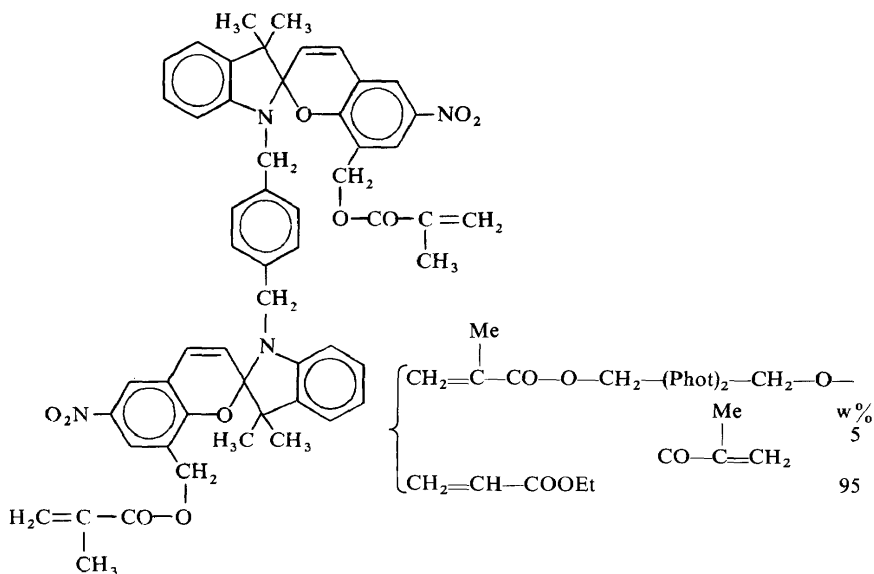


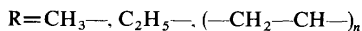
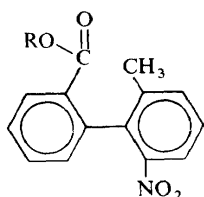
Figure 13

(five per cent) with ethylacrylate (95 per cent). It was found that on irradiation with ultra-violet light a dry thread of this polymer stretches with a relative elongation of about two per cent, and recontracts reversibly in the dark after a few minutes.

This phenomenon must be related to the observation described by Agolini and Gay²¹ in the case of aromatic imides containing an azo link; these compounds show a reversible photo and thermal contractile behaviour that may be associated with *cis-trans* isomerization of the dicarboxy azobenzene units. A similar observation was made recently also by Prins²² on β -hydroxyethylmethacrylate methylmethacrylate copolymers containing some sulphonic azodyestuff.

PHOTORACEMIZATION OF OPTICALLY ACTIVE POLYMERS

A phenomenon related to photochromism is the photoracemization of optically active polymers. Such experiments were undertaken by Schulz and Jung²³ who compared racemization kinetics between 100°C and 120°C of the polyvinyl and methyl/ethyl esters of the (+) 2-methyl-6-nitro-biphenyl-2'-carboxylic acid in dioxane solution.



While the low molecular ester shows a linear first order relationship on plotting ($\log \alpha_o/\alpha_t$ versus time), the polymer racemizes much more slowly; after some twenty per cent conversion, the racemization proceeds apparently in a second step the rate of which is more than ten times slower than the first one.

Similarly in our laboratory, P. Hermans has prepared polyesters and copolyesters of bisphenol-A with optically active (+) 2-bromo-dibenzo (a.e) cyclooctatetraene-6,11-dicarboxylic acid (BCT), of which the interconversion of enantiomers becomes important at 120°C. The principle of the racemization is based on the interconversion of both cyclooctatetraene conformations²⁴ (Figure 14).

The racemization behaviour of (BCT) esters and polyesters is summarized in Table 6. As can be seen from these data, the rates of racemization in dioxane solution are very similar for the diphenylester and for homo- and copolyester of bisphenol-A. In the solid state, in polystyrene and polycarbonate matrices, of which the glass transition temperatures are below the temperatures of measurement, the racemization is independent of the nature of the matrix. For the amorphous oligomer ($T_g > 200^\circ\text{C}$) the rate is about twenty times slower than for the mixtures; the influence of the glass transition on such phenomena is thus again taken in evidence. For both mixtures **c**, **d** and for the oligomer the racemization ($\log [\alpha]_o/[\alpha]$) proceeds

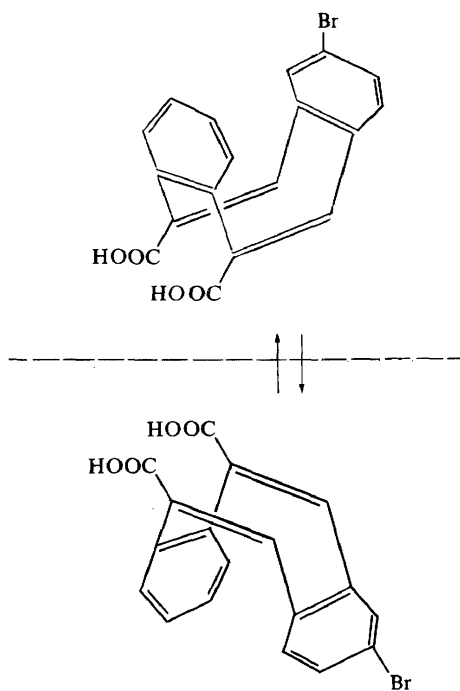


Figure 14. Racemization of 2-bromo-dibenzo (a.e.) cyclo octatetraene-6.11-dicarboxylic acid

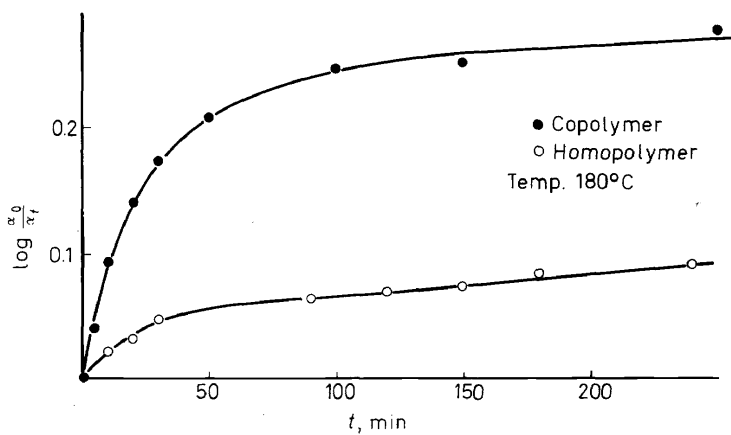


Figure 15. Rate of racemization of BCT-polymers

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Table 6. Racemization of 2-bromodibenzo-(a.e.)-cyclooctatetraene-6,11-dicarboxylic esters (BCT)

	in dioxane solution			in solid state (film)		
	diphenyl	homo* polyester	CO† polyester	Pstyr‡ matrix	Polycarbonate§ matrix	oligomer amorphous
$k_{150} \times 10^4 \text{ sec}^{-1}$	7.6	6.3	5.4	5.6	3.5	0.15
E_{act} kcal/mole	28.8	27	27.8	33.3	33.6	52.1
log A	11.7	10.7	11	13.9	13.9	22
ΔS^\ddagger	-7.2	-11.9	-10.5	+2.5	2.5	+39.9
ΔF^\ddagger	31	31	31.2	31.4	31.7	33.8

* Polycondensate of bisphenol-A with BCT-diacid chloride; molecular weight $M_n = 8300$ with Mechrolab vapour-pressure osmometry.

† Copolycondensate of bisphenol-A with BCT-diacid chloride (15 per cent) and COCl_2 ; molecular weight $M_n = 8160$ with Mechrolab vapour-pressure osmometry.

‡ 15 per cent weight model in polystyrene (T_g : 82° to 105°C).

§ 15 per cent weight model in polybisphenol-A carbonate. T_{trans} : 101° to 113°; 116° to 126° after racemization.

|| $-\text{[CO-BCT-CO-O-C}_6\text{H}_4\text{-C(Me)(Et)-C}_6\text{H}_4\text{-O]}_4\text{-[CO-O-C}_6\text{H}_4\text{-C(Me)(Et)-C}_6\text{H}_4\text{-O]}_3\text{-}$ composition; \bar{M}_n : 3500.

as expected for a first order reaction, linearly with time, and was observed up to 70 per cent conversion. By contrast, for the homopolyester **a** and copolyester **b** the racemization (Figure 15) curves level off rapidly and become very slow at conversions of 11 and 30 per cent respectively as was the case in Schulz's experiments.

CONCLUSION

Polymeric photochromic systems compared to low molecular weight homologous types show kinetic differences in their photochromic properties. These differences are especially noticeable in the solid state, and depend strongly on the glass transition temperature of the polymer. On the other hand, photochromic groups make it possible to determine secondary transition temperatures of the polymeric matrices, in which they are incorporated.

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