PHOTOCHEMICAL REACTIONS IN POLYMERIC SYSTEMS

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ABSTRACT

Photochemical reactions have been examined in relation with the physical properties of the solid polymeric matrix in which they are carried out. Three main reaction types are considered:

(i) *photocrosslinking* reactions resulting from cyclodimerization of unsaturated groups and from the decomposition of photolabile groups into very reactive species, e.g. nitrenes from azides;

(ii) *photoisomerization* reactions in the case of aromatic azoderivatives, and photochromic spirobenzopyran compounds;

(iii) *photodissociation* reactions in the case of bisanthracene- and benzpinacol derivatives.

Each class of reaction is illustrated by recent data from the literature, as well as by new results obtained in our laboratory in photochemical isomerization and dissociation experiments. The reversibility of these reactions is discussed in terms of chain segment mobility and free volume distribution, and correlated diffusion effects in the case of dissociation reactions. The importance of the chemical incorporation of the photosensitive groups into the polymer is stressed by comparison with the photoresponse of corresponding model compounds dissolved in a polymeric matrix.

INTRODUCTION

Photochemical reactions in high polymers are based on a primary light energy absorption step followed by a reversible or irreversible chemical transformation. The initial photophysical act is evidently the absorption of a quantum of light, which is directly related with the electronic structure of the compound. By this absorption the molecule is brought into a singlet excited state of which the lifetime is determined by several competing phenomena, such as fluorescence back to the ground state, non-radiative decay, intersystem crossing to the triplet state, and eventually chemical reaction. Similarly the deactivation of the triplet state can proceed by phosphorescence, by non-radiative (energy transfer) processes and by chemical reactions.

Photochemically induced reactions are therefore one of the possible deactivation processes of the singlet and triplet excited states; these highly reactive intermediates are responsible for the course of the reaction, which very often differs fundamentally from thermal reactions in the ground state.
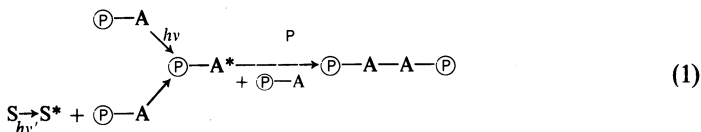
If we consider now the photochemical reaction types which occur in a macromolecular system, several classes can be distinguished of which the most important are related with photocrosslinking, photoaddition, photo-dissociation (including photodegradation), photoisomerization and photo-rearrangement reactions. It is evidently outside the scope of this lecture to present a general review of these different classes; the reader should refer to recent survey articles in this field[1, 2]. By contrast, we will concentrate our attention on the comparison between photochemical reaction in a polymer system with that of the model compound, especially when the photo-chemical transformation is carried out in a solid polymer matrix. As a general statement, it can be foreseen that, when compounds are bound to a polymeric substrate or are incorporated in a rigid medium strong restrictions are imposed to their translation and rotation possibilities. On account of differences of chain segment mobility these restrictions will be most pronounced in the rigid glassy state. In the rubbery region, above the glass transition domain, the matrix can be compared to a highly viscous medium, and the translation and rotation possibilities will strongly increase and approach progressively those observed in solution. On the basis of such considerations, a drastic change in reaction rate has to be expected in the neighbourhoud of the glass transition domain.

With these assumptions in mind, we will consider successively photo-crosslinking, photoisomerization and photodissociation phenomena on the basis of their general reaction principles, and illustrate them with recent data from the literature as well as our own experimental results.
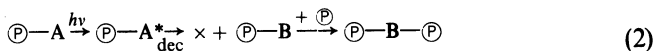
Photocrosslinking reactions

The irreversible transformation of photosensitive polymers by light-induced crosslinking reaction into insoluble materials is very likely the most important photochemical reaction from a technical point of view; thus photoresist materials are applied as thin coatings on a substrate and provide a chemically resistant coating in the light-struck regions.

These crosslinking reactions can proceed following two different reaction principles. In the first reaction scheme the polymer molecules P contain unsaturated groups A; these chromophores are activated either by direct light absorption, or by energy transfer in the presence of a photosensitizer S, and dimerize by reaction with a second chromophore A in the ground state.

$$\begin{array}{c} \text{P—A} \\ \searrow h\nu \\ \text{P—A*} \xrightarrow[+ \text{P—A}]{\text{P}} \text{P—A—A—P} \\ \nearrow \\ \text{S} \xrightarrow{h\nu'} \text{S*} + \text{P—A} \end{array} \qquad (1)$$

In a second reaction scheme the polymer molecules contain photolabile groups A, which decompose into very reactive species B that in their turn add to and/or insert on the polymeric substrate and provide insolubilization.

$$\text{P—A} \xrightarrow{h\nu} \text{P—A*} \xrightarrow[\text{dec}]{} \times + \text{P—B} \xrightarrow{+ \text{P}} \text{P—B—P} \qquad (2)$$

Cyclodimerization of polyvinylcinnamate (PVCinn) and its higher vinylogues is very likely the most thoroughly studied example of reaction mechanism (1); crosslinking results mainly from the formation of an α-truxillic type cyclobutane ring, which corresponds to one of the cyclodimers of cinnamic acid[3].


$$(3)$$
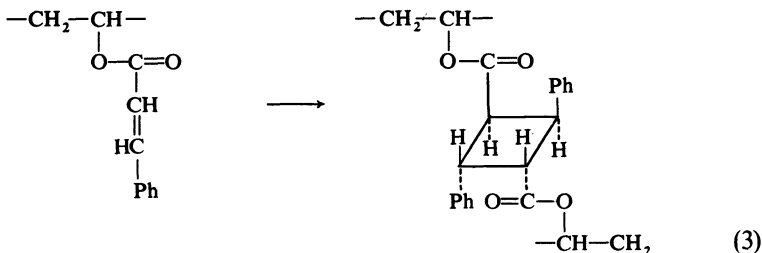
Some contribution of a vinyl type free radical polymerization cannot, however, be excluded on the basis of the formation under irradiation of two different types of radicals, by e.s.r.-measurements[4], and on the basis of triplet energy transfer experiments with pyrilium salts[5].

Since PVCinn has its maximum sensitivity between 290 and 310 nm, it is desirable to add sensitizers in order to extend the photoresponse to much higher wavelengths and to increase the relative response speed. Assigning a relative response speed of unity to pure PVCinn, it is indeed possible to obtain a speed as high as 500 by inclusion of adequate sensitizers.

Evidently photocrosslinking by cyclodimerization is not restricted to PVCinn, and the syntheses and photochemical behaviour of polymers carrying chalcone, coumarins, fenylacrylic and stilbazol side groups have been reviewed by Delzenne[6].

Very interesting results were recently obtained with polyvinyl chalcone acrylate which contains chalcone units together with cinnamic ones as side groups.

$$(4)$$
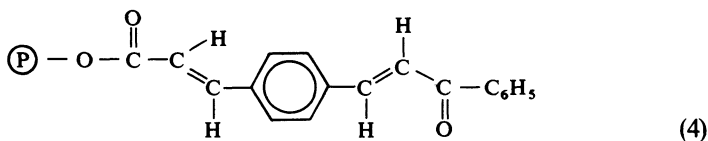
This structure permits to increase the speed to 15 000 to 20 000 compared to unity for PVCinn, and by sensitization the relative speed becomes as high as 35 000–50 000. As pointed out by Williams[5] the greater the inherent response of the polymer, the smaller the increase of response on sensitizer addition.

In these crosslinked chalcone acrylate polymers, it may be assumed that both chalcone and cinnamic groups participate in the cyclodimerization reaction. An analogous system was recently examined by Tanaka, Tsuda

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and Nakanishi[7,8] in the case of polyvinylcinnamylidene acetate and its low molecular

$$C_6H_5—CH=CH—CH=CH—CO—O—\text{(P)} \qquad (5)$$

models in which the reactivity of the double bond adjacent to the carbonyl group is larger than that of the double bond adjacent to the phenyl group. The rate of the reaction as well as the quantum yield are higher in the polymer film than in solution ($\phi = 0.48$ instead of 0.1), on account of the higher concentration of chromophores, and to a decrease of *trans* → *cis* isomerization in the solid state, which takes place easily in solution.

Moreover, they showed that polyvinylcinnamylidene acetate undergoes at least partially a reversible photodissociation upon irradiation with 254 nm light. These results are in agreement with the data of Takahashi, Hasegawa and co-workers[9] on photodegradable poly ω,ω'-alkylene diphenyltruxillamides.

The comparison of the photoresponsive behaviour of groups whether they are incorporated in the polymer backbone by polycondensation or present as pendant side groups was possible with polyesters and copolyesters of p.phenylene bisacrylate of aliphatic diols and their corresponding polyvinyl derivative.
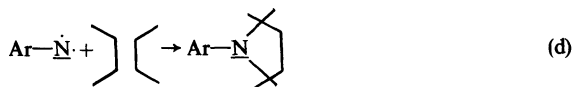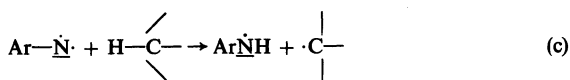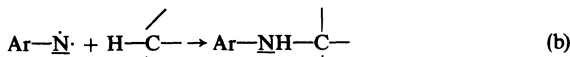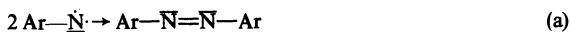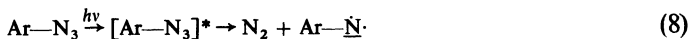

(6) $x = 7,9$

(7) R = ethyl 2-ethyl-hexy
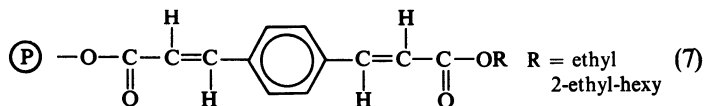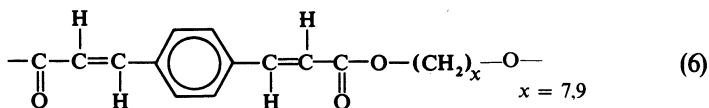
As could be expected, the polyvinyl derivative shows a much higher relative speed of photoresponse, owing to the greater mobility of the photoreactive side groups.

Crosslinking reaction mechanism 2 can be adequately illustrated with arylazide photosensitive polymers[6,10]. On light irradiation energy is absorbed by the aromatic group and transferred to the azido group, which then eliminates a nitrogen molecule and gives formation of nitrenes in singlet or in triplet state (equation 8). The nitrenes in their turn can easily dimerize (a), insert within carbon–hydrogen bonds (b), abstract hydrogen with radical formation, or add to double bonds (c, d).
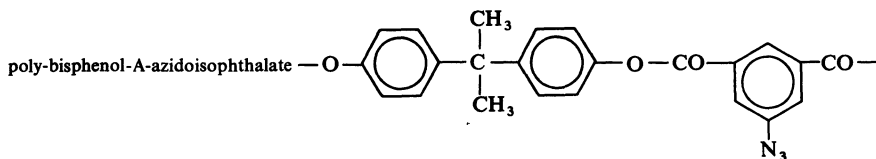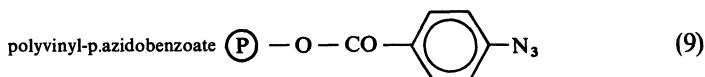
At high azide content bimolecular reaction (a) becomes prevalent, and the azo bridges are responsible for the yellowing of the film. By contrast, at low

$$Ar\!-\!N_3 \overset{h\nu}{\to} [Ar\!-\!N_3]^* \to N_2 + Ar\!-\!\underset{\cdot\cdot}{\overset{.}{N}}\cdot \qquad\qquad (8)$$

$$2\,Ar\!-\!\underset{\cdot\cdot}{\overset{.}{N}}\cdot \to Ar\!-\!\overset{\cdot\cdot}{N}\!=\!\overset{\cdot\cdot}{N}\!-\!Ar \qquad\qquad (a)$$

$$Ar\!-\!\underset{\cdot\cdot}{\overset{.}{N}}\cdot + H\!-\!\overset{\diagup}{\underset{\diagdown}{C}}\!- \to Ar\!-\!\underset{\cdot\cdot}{N}H\!-\!\overset{|}{\underset{|}{C}}\!- \qquad\qquad (b)$$

$$Ar\!-\!\underset{\cdot\cdot}{\overset{.}{N}}\cdot + H\!-\!\overset{\diagup}{\underset{\diagdown}{C}}\!- \to Ar\underset{\cdot\cdot}{N}H + \cdot\overset{|}{\underset{|}{C}}\!- \qquad\qquad (c)$$

$$Ar\!-\!\underset{\cdot\cdot}{\overset{.}{N}}\cdot + \;\rangle\!=\!\langle \to Ar\!-\!\underset{\cdot\cdot}{N}\diagdown\!\!\!\diagup \qquad\qquad (d)$$

azide concentration, primary and secondary amines are the main products of the photolysis, their distribution being strongly affected by the rigidity of the matrix as shown by Reiser, Leyshorn and Johnston[11]. In a rigid polymer, the amino radical and the substrate radical produced in reaction (c) remains together sufficiently long for electron spin inversion, and radical coupling occurs giving secondary amines and crosslinking. In less rigid or liquid systems, they diffuse apart and the amino radical abstracts a second hydrogen from another site of the macromolecule producing primary amines.

Typical examples of azide group containing polymers are

$$\text{polyvinyl-p.azidobenzoate } \textcircled{P} -O-CO-\hexagon-N_3 \qquad\qquad (9)$$

$$\text{poly-bisphenol-A-azidoisophthalate } -O-\hexagon-\overset{CH_3}{\underset{CH_3}{C}}-\hexagon-O-CO-\underset{N_3}{\hexagon}-CO-$$

At low azide concentration, the crosslinking reaction will indeed be enhanced by the rigidity of the polymeric system, e.g. in polyaromatic matrices.

As in the case of PVCinn and analogous polymers, photosensitization of arylazidopolymers is required for extending the sensitivity to higher wavelengths and increasing the speed of photoresponse. Though a triplet energy transfer mechanism is usually admitted, sensitization with anthracene and diphenyl oxazole derivatives also supports a singlet energy transfer mechanism of aryl azides[9].

Photoisomerization

The isomerization reactions that we will consider here are the reversible *cis* ⇌ *trans* isomerization of aromatic azo compounds, and the ring-opening/closure of spirobenzopyran derivatives. It is well known that *trans* azo

compounds are more stable than their *cis*-isomer by lack of coplanarity due to steric hindrance in the *cis*-compound. The lower resonance energy of the latter results in absorption at lower wavelengths.
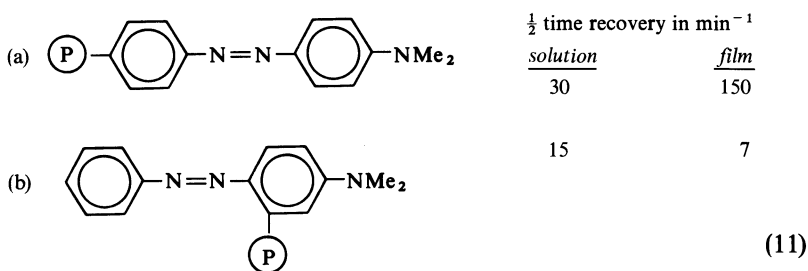
$$\text{Ar}\diagdown_{N=N}\diagup^{\text{Ar}'} \quad \rightleftharpoons \quad \text{Ar}\diagdown_{N=N}\diagdown_{\text{Ar}'} \qquad (10)$$
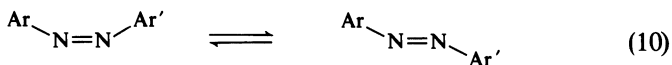
In the activated state the double bond character between the two nitrogen atoms is decreased, and only a small amount of energy is required to twist the halves of the molecule around the N—N bond so that the *cis* and *trans* isomers will rapidly interconvert. The photochemical equilibrium depends on the several rate constants involved in the photoactivation and deactivation processes; it differs considerably from the thermal *cis–trans* equilibrium, which is only determined by the difference in energy of the ground states.

It is therefore very easy to perturb the *cis* $\rightleftharpoons$ *trans* equilibrium by irradiation at an adequate wavelength, then to follow the thermal recovery reaction back to the thermal equilibrium value and to examine if the rate of thermal isomerization is influenced or not by the polymer matrix where the reaction takes place.

Such studies were done by several authors, and will be briefly summarized here. Priest and Sifain[12] examined the photochemical and thermal *cis* $\rightleftharpoons$ *trans* isomerization of 2,2′-azonaphthalene and 4-ethoxy-azobenzene in polystyrene-*n*-butylbenzene compositions.

The *cis* content on photochemical isomerization increases by lowering the T_g of the mixture. Above T_g, all thermal isomerizations obey first-order kinetics; by contrast, below T_g the initial isomerization rates were abnormally fast. Kamogawa, Kato and Sugiyama compared the recovery half-times in solution and in bulk of copolymers of vinyl-dimethylamino azobenzene and styrene (molar ratio 1/9), with those of the model compounds ($P=CH_3,H$) in solution and embedded in a polystyrene matrix[13],
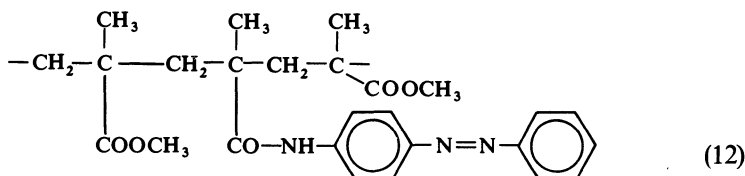
		$\frac{1}{2}$ time recovery in min^{-1}	
		solution	*film*
(a)	(P)—⟨◯⟩—N=N—⟨◯⟩—NMe$_2$	30	150
(b)	⟨◯⟩—N=N—⟨◯⟩—NMe$_2$ (P)	15	7

$$(11)$$

where P corresponds to the polymeric chain $-\text{CH}-\text{CH}_2-(\text{CH}-\text{CH}_2)_9-\cdot$ with Ph below.

They found not only a strong dependence from the site of attachment of · the polymeric chain with respect to the azo link, but for the copolymer (b) even a higher rate of recovery in the solid state than in solution. For the model

compounds also no apparent regularities could be found by comparing solution/bulk behaviour. In order to account for these results the authors suggest the existence of two opposite effects: (i) the well known aggregation of azobenzenes in solution and film, which can be prevented in a copolymer (9 ST/1 azo), where the azo groups are isolated from each other; (ii) the steric hindrance in polymeric systems. In this respect mention should, however, be made of the unsuccessful attempts of Löhr and Schulz[1] in order to detect any cooperative effect in the thermal $cis \rightleftharpoons trans$ isomerization in the case of polyamides and polyesters with azo groups in the main chain.

A more quantitative study of the photochemical and thermal isomerization of azoaromatic residues in polymers in bulk was recently described by Paik and Morawetz[14]. Copolymers of 4-(N-methacryl) amino azobenzene with methylmethacrylate (one mole per cent) present in the bulk an isomeriza-


tion quantum efficiency which is about $\frac{1}{4}$ to $\frac{1}{5}$ of that in solution. The photo-stationary states, as well as the first-order rate constants of $cis \rightarrow trans$ isomerization were equivalent in bulk above T_g and in solution. On the contrary, below T_g the photostationary state is substantially lower, and a portion ($\frac{1}{7}$) of azo groups reacts anomalously rapidly. The authors assume a non-equilibrium distribution of the free volume in the glassy state, by which cis-isomers, trapped in a strained conformation, return more easily to the $trans$ form than those in an equilibrium environment.

In the case of glassy polymers with azoaromatic groups in the backbone, e.g. poly-bisphenol-A-isophthalate containing 1.4 per cent pp′azobenzene-dicarbonyl units the photostationary fraction of cis-isomer is very low (0.025); however, the rates of thermal isomerization are only slightly different.
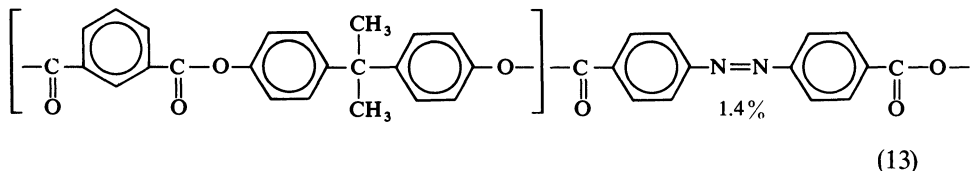
The second isomerization reaction to be considered is based on the photochromic properties of spirobenzopyran derivatives. These compounds undergo under ultra-violet irradiation a C—O— scission followed by $cis \rightleftharpoons trans$ isomerization during which deeply coloured open ring mero-cyanines are formed, e.g. in the case of 1-benzyl-3,3-dimethyl-6′-nitro-indoleninospirobenzopyran.

$$\xrightleftharpoons[\Delta t]{h\nu} \tag{14}$$
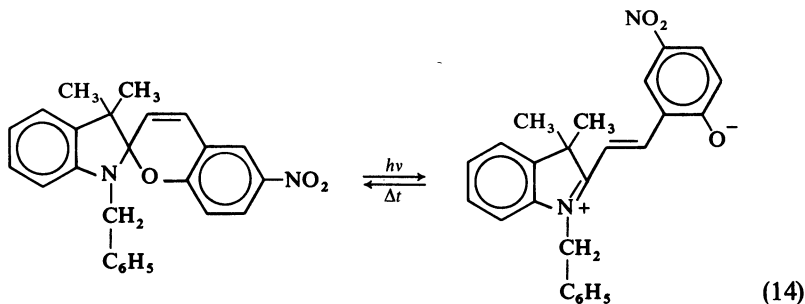
These coloured species revert to the colourless compound by a thermal process[15]; (ΔH about 1 to 3 kcal mol^{-1} in polar solvents, and 4 to 8 kcal in non-polar media)[16].

We concentrated our efforts on this class of compounds, because it rapidly became clear that the results with spiro benzo(naphtho)-pyran derivatives are much more coherent and the effects are much more pronounced than with the aromatic azocompounds.

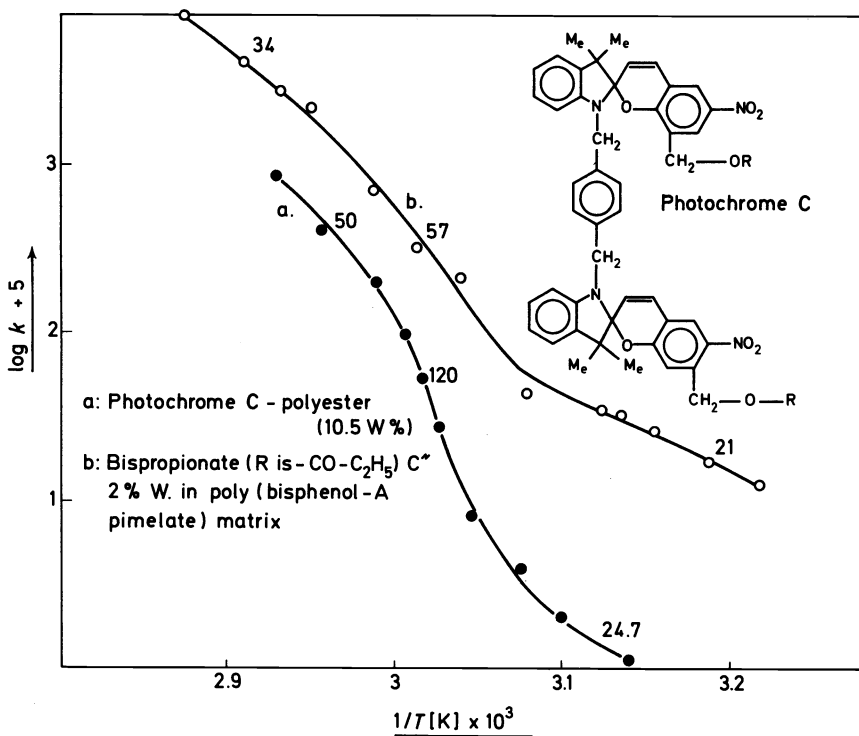The kinetics of decolouration in solution of photochromic spirobenzopyran

Figure 1. Dependence of ln k versus $1/T$ for photochrome C-polyester (curve a) and photochrome C-bispropionate embedded in poly(bisphenol-A pimelate) matrix.

copolymers, polypeptides and condensation polymers have been compared with those of the model compounds and reviewed recently[17].

In the present article only behaviour in solid matrices will be reported.

(a) The rate of decolouration depends on the chemical nature of the matrix on account of the negative solvatochromism of these derivatives, e.g. it is about ten times faster in polystyrene than in polymethylmethacrylate.

(b) The rate of fading and its overall activation energy increase markedly around the glass temperature T_g[18,19]. The effect is most pronounced for photochromes built into the polymer backbone[20] as illustrated in *Figure 1*, in which the logarithm of the rate constant of decolouration is plotted against $1/T$.

Curve a represents the behaviour of a copolyester of bisphotochrome-C (4 mol %) (see *Figure 1*) and bisphenol-A with pimelic acid where R is

$$\left[-CO-(CH_2)_5-CO-O-C_6H_4-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-C_6H_4-O \right] -;$$
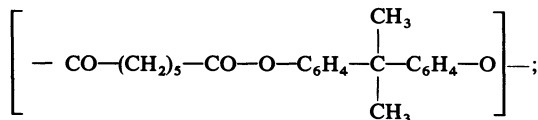
curve b corresponds to the mixture of bisphotochrome-C bispropionate embedded (2 wt %) in poly-bisphenol-A-pimelate. The figures along the curves indicate the variation of the apparent activation energies as a function of the temperature. The most striking difference between the curves lies in the much higher rate constant for the mixture than for the copolyester; furthermore, the temperature dependence around T_g is more strongly pronounced for the copolyester. This effect has been interpreted introducing a pre-exponential term into the rate constant expression, which is proportional to the reciprocal of the internal viscosity of the polymer. On the basis of the WLF equation, one can derive a final equation 16 which accords quite

$$\log (k_{T_g}/k_T) + E_a(T - T_g)/RTT_g = -17.44(T - T_g)/51.6 + T - T_g \qquad (15)$$

satisfactorily with the experimental data. k_{T_g} and k_T are the rate constants at T_g and T respectively, while E_a represents the energy of activation of ring-closure.

Very interesting is the photocontractile behaviour exhibited by some crosslinked photochromic rubbery polymers in the solid state. De Blauwe[21] prepared a rubbery polyethylacrylate ($T_g - 14°C$) crosslinked with photochrome C-bismethacrylate (R is $-CO-\underset{\underset{CH_3}{|}}{C}=CH_2$).

On irradiation of stretched samples in isothermal conditions, shrinking occurs (two per cent) while in the dark length recovery takes place; this cycle can be repeated and is reproducible. Such a photocontractile effect depends on the temperature and the stress applied to the sample as illustrated in *Figure 2*, where the relative contraction $-\Delta L/L$ is plotted against the time.
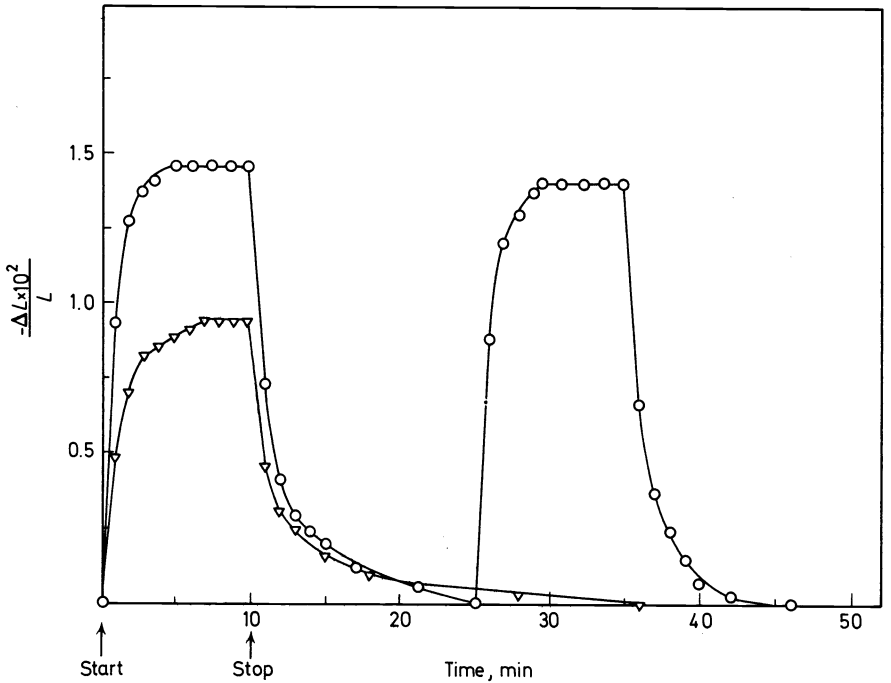
Figure 2. Photomechanical behaviour of photochromic crosslinked polyethylacrylate. Influence of the stress.

film thickness 0.48 mm load 18.5 g ▽(25°C)
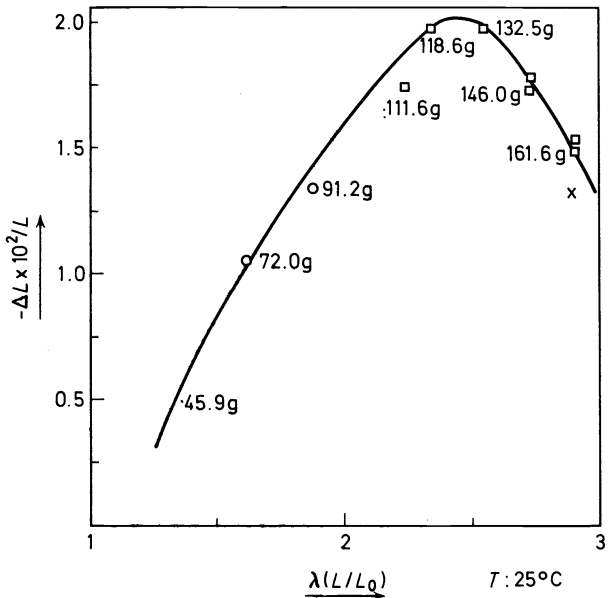film width   5.5 mm   26.8 g ○(27°C)

Figure 3. Photocontraction of photochromic crosslinked polyethylacrylate. Influence of the relative elongation film; thickness 0.69 mm ○   0.67 mm□

The photostationary contraction increases at low stresses with the relative elongation $\lambda = L/L_0$ (L_0 is the length of the unstretched samples), passes through a maximum for λ around 2–2.5, and then decreases (*Figure 3*). Simultaneously, stretching (50 per cent) of the photochromic network causes a strong decrease of the decolouration rate constant to about a third of that in the unstretched state. This photocontractile effect must be therefore related to the higher flexibility of the open-ring merocyanines compared with the stiffness of the parent ring-closed spiropyran.

Photodissociation reactions

A third class of photochemical reaction in a solid polymeric system to be considered is based on photodissociation phenomena. We will examine the photodissociation of bisanthracene derivatives and the dissociation of benzpinacol units containing polymers.

It has been known for a long time that polycyclic aromatic hydrocarbons form thermally stable photodimers[22] which can be cleaved to the original monomers by irradiation with light of suitable wavelength[23]. When the photodimer is held in a rigid matrix the 'broken' dimer can recombine efficiently in so far as both moieties are held adequately in position with respect to each other.

Chandross, Lamola and co-workers[24] used 9-substituted (CH_3—, $C_5H_{11}O$—CO—) anthracene derivatives and found a very low quantum efficiency of redimerization (~ 0.003) while that of dissociation of the dimer was 0.3.

9-R-anthracene

anthracene photodimer

(16)

acridizinium tosylate

acridizinium photodimer
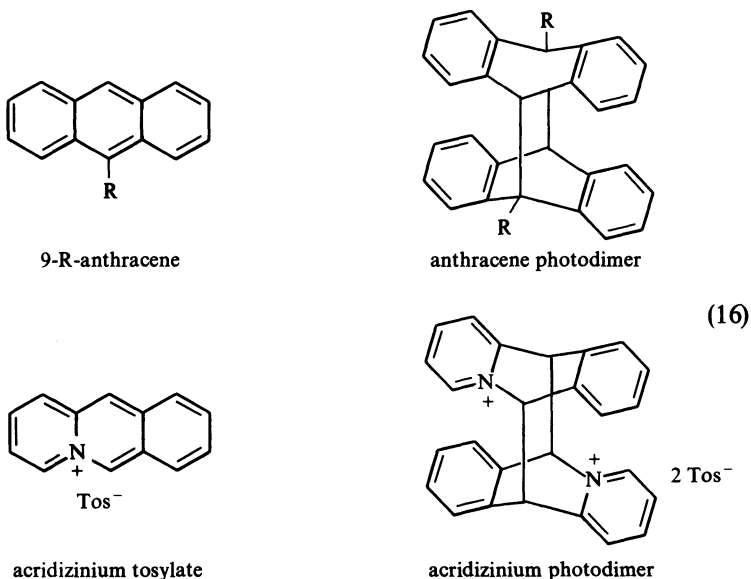
However, with acridizinium tosylate dissolved in a methylmethacrylate–acrylic acid (less than ten per cent) copolymer, much higher dimer remaking

efficiencies (25–50 per cent) were obtained. The redimerization efficiency increases somewhat by crosslinking of the matrix, and decreases with raising the temperature, as would be expected from a less rigid medium.

Analogous experiments were carried out in our laboratory by Makimoto[25] using anthracene-2-carboxylic esters (n-butyl : BAC and n-hexyl : HAC) and confirm the results of Chandross and Lamola. Some additional data only will be given in illustration. At the photostationary state (under 300 nm irradiation) about two thirds of dimer are broken to monomeric species; when after dissociation the system is exposed under 360 nm irradiation, redimerization takes place, and this cycle dissociation–redimerization can be repeated. *Figure 4* shows clearly that the decrease of optical density of broken dimer (monomer) has at least two phases, an initial one corresponding to monomers held in proper alignment and a second one where the recombination efficiency is very low. Even after prolonged irradiation 10–15 per cent broken dimer does not recombine, and this amount increases by repeating the cycle.
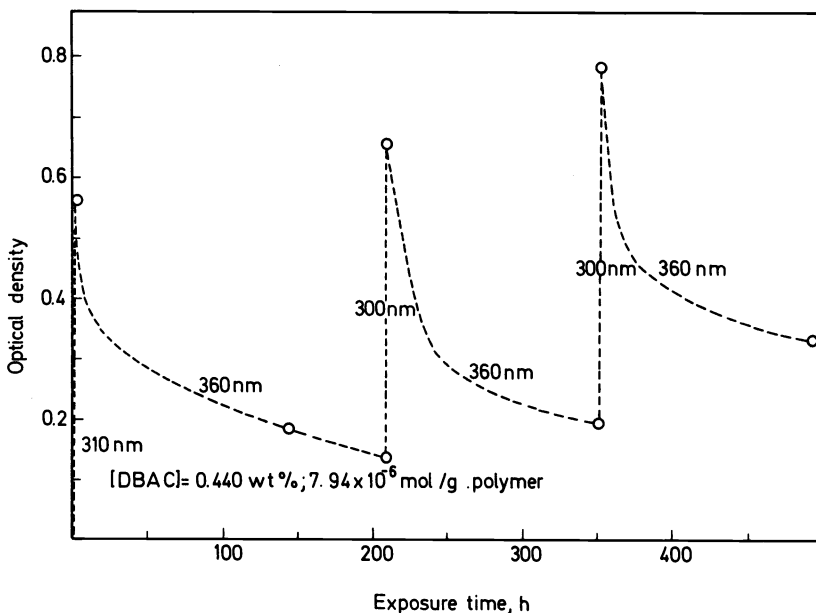

Figure 4. Photodissociation of anthracene 2-butylcarboxylate dimer (DBAC) and redimerization.

The effect of the T_g of the matrices can be seen from the comparison of polybutylmethacrylate (PBMA) and polymethylmethacrylate (PMMA) (*Figure 5*). The PBMA matrix has a much lower efficiency, the first initial rapid portion of the redimerization being ill-defined, i.e. very few or no high efficiency sites exist in PBMA matrix, even markedly below its T_g.
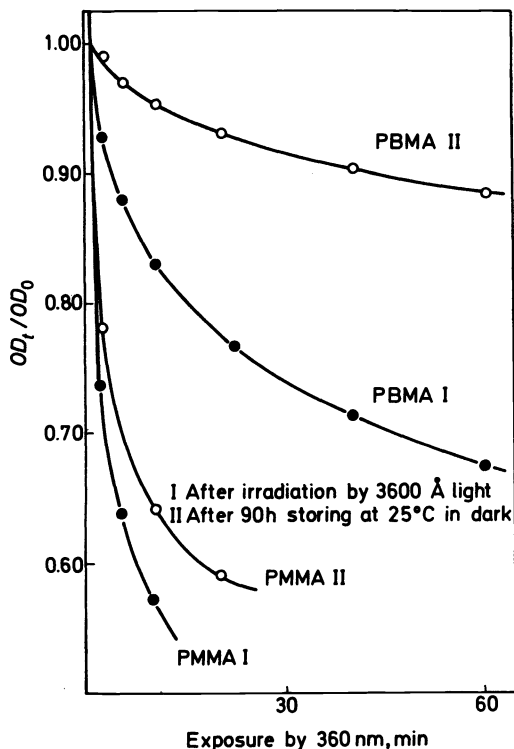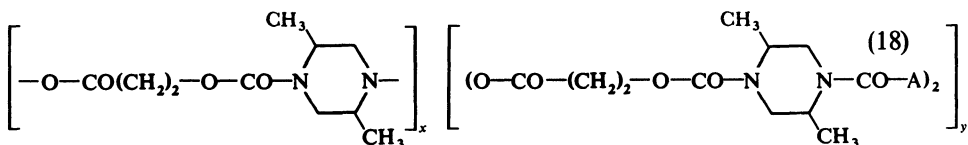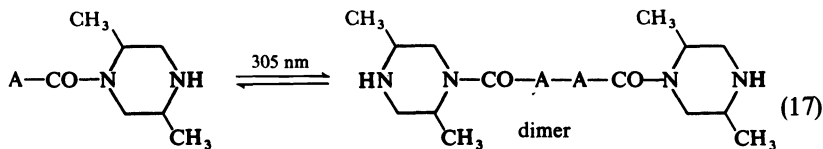
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Figure 5. Redimerization of broken DBAC in polymethylmethacrylate (PMMA) and in poly-*n*-butylmethacrylate (PBMA) matrices. Influence of T_g and of storage.

Similar loss of high efficiency sites is observed by annealing the films of PMMA at increasing temperatures well below T_g or during storage in the dark in the glassy state.

The influence of the incorporation of anthracene dimers in the polymeric backbone has also been examined (*Figure 6*). Therefore 2-(2'5'-dimethylpiperazine carboxyl)anthracene (17) was dimerized, and incorporated as a dimer into the polyurethane chain by copolycondensation together with dimethyl piperazine and ethyleneglycolbischloroformate (18),

$$A{-}CO{-}N\underset{CH_3}{\overset{CH_3}{\diamond}}NH \;\overset{305\,nm}{\rightleftharpoons}\; HN\underset{CH_3}{\overset{CH_3}{\diamond}}N{-}CO{-}A{-}A{-}CO{-}N\underset{CH_3}{\overset{CH_3}{\diamond}}NH \qquad (17)$$

$$\left[-O{-}CO(CH_2)_2{-}O{-}CO{-}N\underset{CH_3}{\overset{CH_3}{\diamond}}N{-}\right]_x \left[(O{-}CO{-}(CH_2)_2{-}O{-}CO{-}N\underset{CH_3}{\overset{CH_3}{\diamond}}N{-}CO{-}A)_2\right]_y \qquad (18)$$
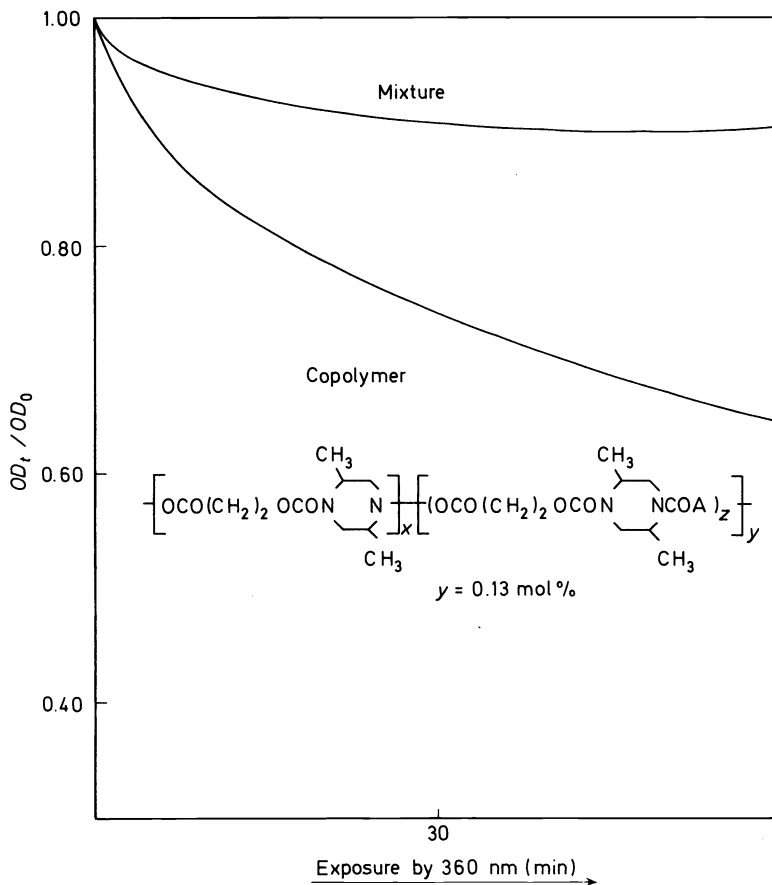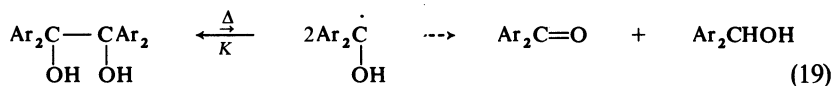
521

where A designates anthracene.

Figure 6. Redimerization of broken bisanthracenepolyurethane copolymer and 2(2'5'-dim-ethylpiperazinecarboxyl) anthracenes in polyurethane matrix.

As expected, the redimerization efficiency is higher than in the case of physical mixtures, although much lower than in a PMMA matrix owing to the low T_g of the matrix (31°C).

A second example of photodissociation phenomena in high polymers is based on the homolytic dissociation of benzpinacols into two ketyl radicals[26, 27]. In solution an equilibrium exists between these two species; further disproportionation depends on the temperature at which the dissociation is carried out.

$$Ar_2C\!\!-\!\!CAr_2 \underset{K}{\overset{\Delta}{\rightleftarrows}} 2Ar_2\dot{C} \dashrightarrow Ar_2C\!\!=\!\!O + Ar_2CHOH$$
$$\quad\; |\quad | \qquad\qquad\qquad |$$
$$\;\; OH\;\; OH \qquad\qquad\quad OH \qquad\qquad\qquad\qquad\qquad (19)$$

In the solid state, at temperatures not exceeding T_g, the disproportionation reaction is negligble, very likely because the radicals are unable to diffuse out of the cage where they are produced.

Tran Van[28] prepared polybenzpinacols by photoreductive polyrecombination of bisaromatic ketones in the presence of secondary alcohols (isopropanol, benzhydrol) following the general equation

$$\text{(20)}$$
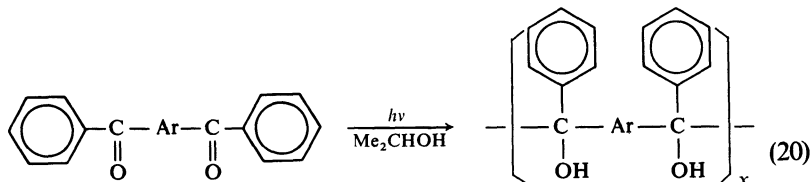
Similar polybenzpinacols were also described by Higgins and coworkers[29-31].

The dissociation–recombination phenomena reported here correspond to the polybenzpinacol obtained by reduction of p,p'-dibenzoyl-2,2-diphenylpropane.

$$\text{(21)}$$
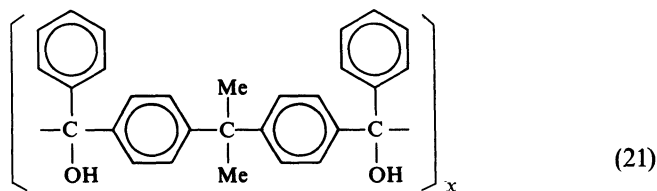
Films were irradiated with short wavelength ultra-violet light (254 nm) to such an extent that a radical concentration of about 1.4×10^{14} radicals was obtained. By keeping the samples at a constant temperature (80–120°C) (in the e.s.r. cavity) one observes initially a fast decay of radical, followed by a slow process. Ultimately an equilibrium concentration C_{eq} is attained which is equal to that obtained by thermal treatment at the same temperature.

Figure 7 represents the second-order plots of the reciprocal radical concentration versus the time at several temperatures between 80° and 118°C. A large deviation from linearity occurs at the beginning of the reaction and corresponds mainly to the rapid decay reaction.

Extrapolation of the linear portion of the diagram at time zero, permits an evaluation of concentration of the slowly decaying radicals, and consequently of the concentration of radicals involved in the initial rapid phase. It was easily shown that the fast decay reaction follows first-order kinetics.

Figure 8 gives the Arrhenius plots of the logarithms of the first and second order rate constants versus reciprocal temperatures.

For the slow decay process a discontinuity arises around the T_g of the polybenzpinacol, and E_a increases from 17.6 to 32.6 kcal owing to additional

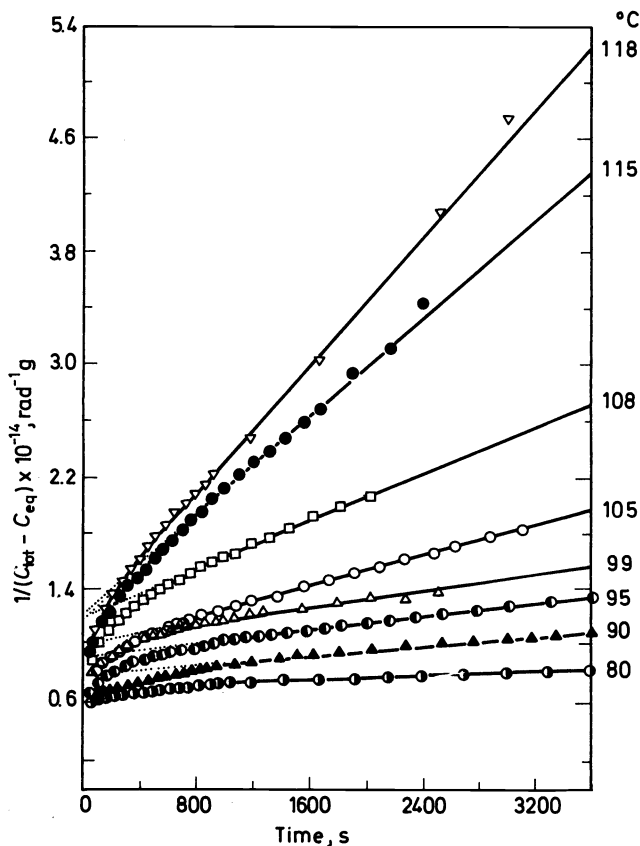*Figure 7.* Second-order plots of radical decay in u.v.-irradiated polypinacol film.

diffusion and segmental mobility effects. The fast decay reaction shows no dependence on T_g; its small activation energy ($\sim$ 4 kcal) corresponds to the recombination step of radicals distributed in pairs in the polymer cage. It may be worthwhile to point out that the thermal cleavage of pinacol film follows as expected a first-order reaction mechanism, except in the first stage where the scission proceeds much more rapidly owing to a non-equilibrium distribution of free volume inside the polymer; it can be avoided by annealing the film.

CONCLUSION

The efficiency and rate of photochemical reaction carried out in solid polymers are strongly dependent on the physical properties of the polymer matrices. The isomerization reaction which involves an important change of
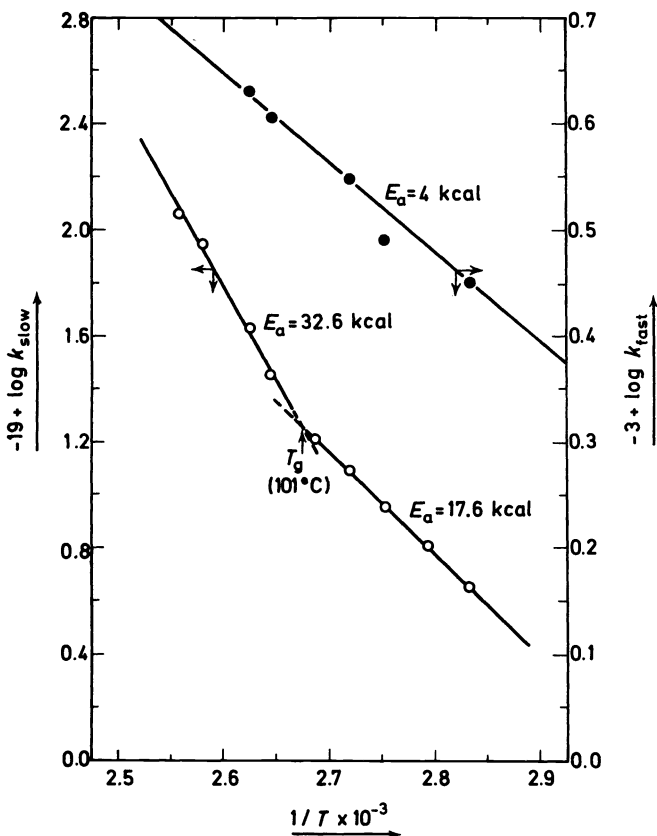
Figure 8. Arrhenius plots for the slow (O) and fast (●) decay reactions in
u.v.-irradiated polypinacol film.

conformation of the photosensitive group as well as photodissociation and
photorecombination reactions which are limited by diffusion phenomena
are particularly sensitive to changes of chain segment mobility and depend
therefore strongly on the glass transition temperature and the rigidity of
the polymer. Moreover, it has been shown that these effects are most pro-
nounced when the photosensitive groups are incorporated chemically in
the polymeric chain.

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