

NEW DEVELOPMENTS IN PHOTOCHROMIC POLYMERS AND RELATED PHENOMENA

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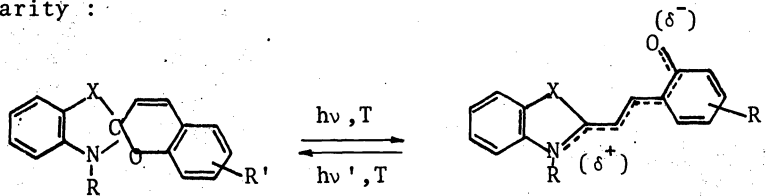
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Abstract - A short review of the properties of photochromic copolymers and copolyesters containing indolinobenzospiran groups attached as side chains or incorporated in the backbone has been given. The ring closure reaction of benzopyrans in polymer media has been analyzed from the point of view of the intra- and intermolecular interactions as well as the steric restrictions for trans-trans and trans-cis isomerization. The ring closure reaction model based on the defect diffusion controlled interaction between merocyanine forms and photochemically generated conformation defects has been proposed. The model has been examined considering the results of color fading of two indolino-benzospiropyrans dissolved in polyalkyl methacrylates and the diffusion constants and activation energy of defect diffusion have been calculated. The limitations of the proposed model and suggestions for its further development has been given.

INTRODUCTION

Although the photochromic properties of spiropyrans are known since about two decades, their study is still of increasing interest, owing to their several potential applications in image formation and dosimetry, as well as for the production of protective materials and memory devices. Many problems concerning their photocoloration and thermal fading necessitate a more detailed analysis of their reaction mechanism and reaction kinetics.

Spiropyrans are still the most important group of photochromic compounds. The basic principle of their photochromism consists in the scission of the C-O pyran bond followed by a rotation of one part of the molecule leading to coplanarity :



where $X = \text{CMe}_2, \text{S}$; $h\nu = \text{ultraviolet light}$; $h\nu' = \text{visible light}$

The open ring merocyanine is characterized by a very strong absorption in the visible range of the spectrum. It may exist in the form of several colored stereoisomers with slightly different absorption bands. In the studies of spiropyrans emphasis was given to the elucidation of the mechanism of the photochemical ring opening reaction (3-9), to the structure determination of colored stereoisomers (2,10,11) as well as to investigations of the photochemical and thermal ring closure reactions which are directly related to color fading (8,12,13,14-17).

Recently new interesting results have been obtained by the study of solid solutions of photochroms in polymers (18-19). Many of the recent efforts were devoted to the synthesis of photochromic polymers. In these materials the photochromic groups were incorporated in the backbone of the chains or attached as side groups (20,21). A very interesting phenomenon related to photochromism and chain segment mobility is the photocontractile behaviour of crosslinked photochromic polymers which has been reported recently by Smets et al. (22). Similar effects were observed by Agolini et al. (23) and Prins et al. (24).

The photocoloration of indolinobenzopyrans in liquid solution occurs very fast and results in the formation of several colored isomers depending on their chemical structure and their interactions with the solvent. In solid solutions e.g. in solid polymeric matrices the photocoloration reactions is much slower owing to the rigidity of the glassy state. This remark is also important for photochromic polymers, where a lower extent of photocoloration is related to smaller quantum yield when energy migration has to be considered.

In liquid solutions in which the specific interactions can be neglected the kinetics of decoloration is well described by 1-order equation. In solid solutions of photochroms (e.g. in polymeric matrices) the rate of color fading is much lower and occurs with a different kinetic behaviour. In the glassy state one has to take into consideration that this process is diffusion controlled; consequently a detailed discussion of the experimental results is much more difficult.

The analysis of the decoloration reaction needs also the knowledge of the mechanism of colored isomers interconversion. These processes have to be investigated in liquid solutions of low molecular weight photochromes with identical or similar structure to that of the photochromic groups of the polymer. The study of solvent effects on the merocyanine shows a strong negative solvatochromism and an ability to form complexes with many solvents. The influence of the medium on the position and shape of absorption bands of the colored isomers allows to use the photochroms as indicators of molecular interactions. From the kinetic studies of color fading conclusions about different relaxation processes in polymer matrices can be drawn when the studies are carried out in a wide temperature range above and below the glass transition temperature (T_g). As a matter of fact, the strongest progresses have been obtained mainly by the study of photochromic polymers and solid solutions during their decoloration processes. This statement does not mean that the coloration reactions in liquid and solid solutions are fully understood; till now no detailed analysis is available concerning the photocoloration mechanism in polymer matrices. Only Wilkinson and al. (3) have shown the influence of the polarity of the matrix upon the energy of the excited triplet state, which is responsible for the cis-trans isomerization.

It is the purpose of the present paper to examine the results of color fading studies in photochromic polymers and in the mixtures of photochroms with polymers as well as to discuss the solvent and diffusion effects on ring closure reactions. The understanding to what extent these effects may influence the decoloration reaction is of basic importance for further progress of the investigations on photochromism and its application.

I. PHOTOCHROMIC POLYMERS AND PHOTOCHROMIC SOLID SOLUTIONS

The increasing interest in photochromic materials has resulted in new syntheses and in the study of several photochromic polymers as well as the study of solid solutions of photochroms in polymer matrices. The chemistry and photochromic properties of these systems have been discussed by Smets in some excellent reviews (20,25,26) and in many original papers. Photochromic behavior can be shown by homopolymers and copolymers. Several polymers were obtained by copolymerization of vinyl monomers with unsaturated indolinobenzospiropyrans, azo-compounds and mercury dithizonates. Other classes of photochromic polymers are spirobenzopyran polypeptides, polyazomethines and polyamides containing azobenzene residues in the backbone. Oligomeric condensation products of a bisindolenine with two molecules of substituted salicylaldehyde or of a bisalicylaldehyde with two molecules of mono-indolenines have been prepared. Photochromic polyesters and crosslinked photochromic copolymers were also obtained. Very interesting photochromic polymers are the polythiazine redox-systems described by Kamogawa. The behavior of solid solutions of different photochroms in polymeric matrices has been investigated throughly especially in the case of indolinospirobenzopyrans (ISBP) (18,19, 27,28).

Important information on the properties of photochromic polymers and model systems were obtained by following the color fading reaction. From the log (optical density) versus time diagrams one can describe the decoloration reaction with appropriate equations. In liquid solutions the disappearance of the merocyanin (in several stereoisomers) occurs according to first-order kinetics. In solid solutions of IBSP in polymers and in solid photochromic polymers deviations from first order kinetics were found. These deviations were interpreted assuming simultaneous occurrence of several first-order reactions. These processes characterized by different rates constants were dis-

cussed assuming the existence of various colored stereoisomers (18,20) or the existence of colored forms in a different environment within the polymer matrix (27,28). Such kinetic curves are observed in the case of diffusion controlled reactions; an attempt can thus be made to analyse the color fading of IBSP in solid systems taking into consideration a model appropriate for diffusion controlled reaction.

At first, it seems necessary to present some characteristics of photochromic behaviour of vinyl copolymers with different IBSP side chains and some copolyesters. These two groups are selected for the discussion since they are the best known systems and can be compared to appropriate models e.g. solid solutions of low molecular weight photochroms dissolved in polymeric matrices.

a. Photochromic spirobenzopyran copolymers. Smets et al. (20,25,29,30) discussed the methods of synthesis of photochromic copolymers with spirobenzopyrans in the side chains. The photoreactions leading to merocyanine colored forms of IBSP side chains are similar to those of not bonded molecule. The isomerizations cis-trans in liquid solution of such copolymers is not restricted (or only slightly hindered) by bonding of IBSP to the main chain. The comparison of photochromic behaviour of model solutions and copolymer solutions shows that the rate constants of ring closure reaction (first order kinetics) as well as the position of λ_{\max} of the merocyanine are much the same. An interesting exception is the copolymer of methyl methacrylate with 1-methyl-3'-phenyl-6'-nitro-8'-methacryloxymethylene-benzothiazolino-benzopyrylspiran for which a distinct difference in the kinetics of ring closure reaction (no first order kinetics) and in the positions of λ_{\max} of open forms, as compared to model solution, has been found. The local viscosity influences the rate of color fading when a small amount of t-butanol is added to the solution. In this mixed solvent a change in coil dimensions were found. It seems that apart from viscosity changes which have been shown to influence the rate of trans-cis isomerization one should consider the strong dipole interactions of polar benzothiazolino benzopyrylspirans residues of the same macromolecule. The extent of these interactions is increased with the local concentration which also is connected with the coiling of the macromolecules. This effect may lead to the formation of aggregates which have been observed in concentrated solutions (12). The deviations from first-order kinetics may be due to intermolecular hydrogen bond too. The rate of color fading in solid photochromic copolymers below T_g is much lower than that in liquid solutions and deviations from first-order kinetics were observed. The rate of decoloration can differ considerably, depending on whether the photochrom is bonded covalently to the polymer backbone as a side group through copolymerization, or if it is dissolved in an amorphous polymeric matrix. In some cases the rate of decoloration of the copolymers is higher than in the solid model solutions and in the other it is lower (29). In the rubbery region i.e. above T_g the copolymers and model solid solutions show an increase in the rate of decoloration although the kinetics does not follow the first order scheme. This rate increase, according to Smets, is mainly related to considerable entropy increase (below T_g , ΔS is strongly negative, above T_g , ΔS is positive), however, there is an increase of activation energy. It indicates that the dramatic change in segmental mobility above T_g influences the rate decay of the colored form. A very interesting phenomenon related to photochromism is the photocontractile behaviour of crosslinked photochromic poly(ethyl acrylates) (22). On irradiation of stretched samples at constant temperature, shrinking (2-3%) takes place, while length recovery takes place in the dark, as shown in Fig. 1.

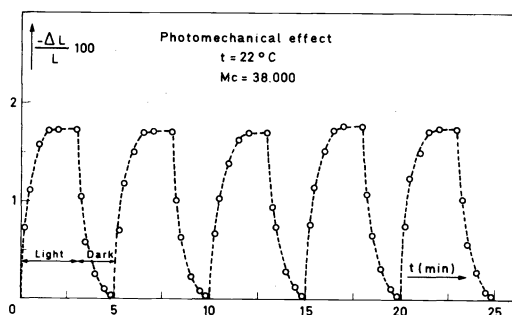
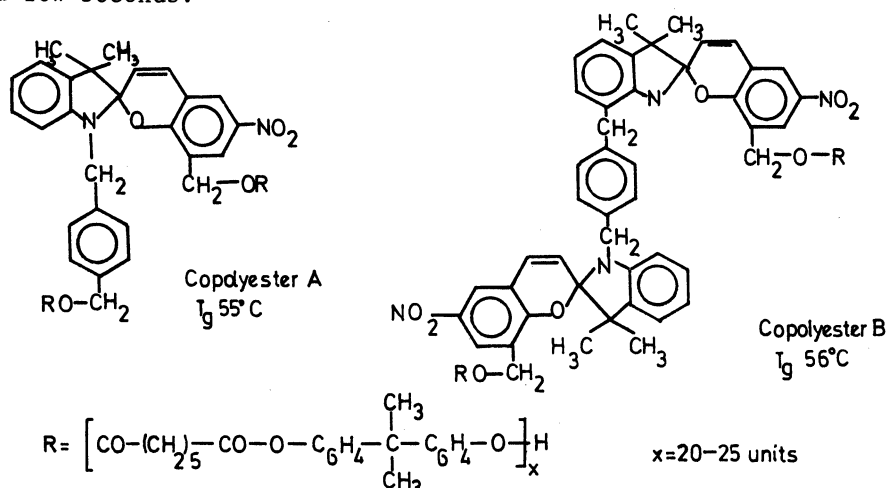


Fig.1. Contraction/dilatation cycles of photochromic crosslinked poly(ethyl acrylate) according to Smets. Reprinted with permission from J.Polym.Sci. Polym.Chem.Ed. 13, 2223 (1975)

This cycle may be repeated and is reproducible. This photocontractile effect depends on the stress applied to the sample, on the temperature at which the experiments are carried out, on the degree of crosslinking of the rubbery poly(ethyl acrylate), and on sites of attachment of the incorporated photochrom. The dark length recovery takes place within a time lapse of about 2 min, which corresponds to less than 5% decoloration of the photochromic material. Thus, only a small percentage of photochromic groups are efficient with respect to the photomechanical behaviour. The activation energy of photomechanical effect (about 7 kcal/mol) is much lower than that for thermal fading of the spiro-benzopyran. According to Smets, on irradiation, the spiro forms are transformed into planar merocyanines which are more mobile and favourably affect the mobility of the neighbouring chain segments. As a consequence, the entropy of the systems increases on irradiation and contraction occurs. By increasing the temperature the relative importance of the entropy contribution becomes smaller and the contraction is less pronounced. The decrease in decoloration rate on stretching the sample is attributed to the important decrease in chain mobility and demonstrates the sensitivity of IBSP-photochroms to chain orientation.

b. Photochromic copolyester. Copolymers containing the photochroms in the main chain were synthesized and examined by Smets et al. (21). Incorporation of IBSP photochroms into the polymer backbone causes, as one would expect, a strong stabilization of the merocyanine form at room temperature when T_g of the polymer ranges between 50-69°C. The photoresponse of photochromic copolyesters A is quite small at room temperature, if the duration of irradiation is limited to a few seconds.



At temperatures above T_g (60°C) the irradiation causes a fast photoresponse and the decoloration of copolyesters is very rapid following a first order relationship. Below T_g the rate is much slower and the curve of thermal fading becomes linear only after a first rapid decoloration step. The photochromic behaviour of photochrome copolyester B and of the corresponding model solution have been compared. The model shows higher rate constant than copolyester B. The temperature dependence of ring closure reaction around T_g is much higher for the photochromic copolyester. This demonstrates clearly that the photoresponse of the systems depends considerably on the incorporation of the photochrome residues in the polymeric backbone.

The results discussed above show that photochromism of IBSP in polymeric matrices may give interesting information on the mobility of polymer chain elements and mobility of photochroms. The deviations from the first-order kinetics were interpreted taking into consideration the existence of colored isomers, whose rate of interconversion (trans-trans) isomerization depends on diffusion to a higher degree than that of trans-cis isomerization (ring-closure reaction). This interpretation seems to be arbitrary, at least in some cases, because in some systems, where the presence of only one active isomer has to be accepted without doubts, similar deviations from the first order kinetics are also observed below T_g (31,32). Thus, in some papers (27,28) the discrepancies from first-order kinetics were interpreted in terms of non-homogeneous environment of the colored isomers.

The ambiguity of elucidation of these effects may cause that the rate constants of color fading have not a well defined meaning. An attempt was made, then, to apply the model of diffusion controlled reactions. In the following part the color fading of photochroms in liquid solutions will be considered. Subsequently the influence of diffusion on trans-trans and trans-cis isomerization will be analysed.

II. INTRA - AND INTERMOLECULAR INTERACTION AND DIFFUSION EFFECTS ON RING CLOSURE REACTION

Considering the rate of diffusion controlled reactions one should distinguish three cases for which the ratio of the rate of chemical reaction (v_{chem}) to the diffusion rate of reactants (v_{diff}) have different values :

- i $v_{\text{chem}} \ll v_{\text{diff}}$. chemically controlled reaction
- ii $v_{\text{chem}} \approx v_{\text{diff}}$. chemically and diffusion controlled reaction
- iii $v_{\text{chem}} \gg v_{\text{diff}}$. diffusion controlled reaction

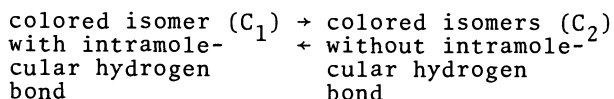
The information on the ratio of these rates is of basic importance for description of the kinetics. For case iii the parameters describing the kinetics are not connected with the chemical steps. Unlike in case i the diffusion may be neglected. The need of detailed information on all chemical transformations is particularly important for IBSP because one should expect the different influence of diffusion on different isomerization reactions.

a. Ring closure reaction of IBSP in liquid solutions. NMR (11), IR-studies (33) and a strong negative solvatochromism as well as dipole moment measurements (34) indicate that open form of IBSP has a merocyanine structure. Its rather high conformational freedom related to low activation energy of rotation about C=C bonds (10) results in creation of several colored isomers. The existence of different colored products due to photoinduced ring opening reaction has been demonstrated by spectroscopic methods in organic glasses at low temperature (8,13). In liquid solutions at room temperature the life times of metastable primary products of ring opening reaction and of phototransformation of colored isomers is very short (8,17). They can be shown only by flash photolysis. For most normal spectrophotometric studies of IBSP a small hypsochromic shift of absorption of merocyanine bands is observed, although the kinetics is described by first order equation (1).

Thus, for short and long time scale one observes different intermediates of merocyanine form e.g. biradicals (35) which may be detected (because of short life times) only at low temperature.

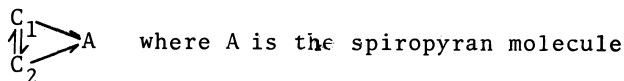
The equilibrium between the colored forms in short time periods does not correspond to that which is expected for long time periods. Thus, the conclusions drawn from flash photolysis studies may be not justified for longer time intervals.

In some papers (10,33) an intramolecular hydrogen bond of merocyanine form of IBSP was suggested. It seems that the formation of such bond may lead to the following equilibrium:



The equilibrium mentioned above may have an essential importance for the ring closure reaction due to the fact that the transformation energies of isomers without intramolecular hydrogen bond (trans-trans isomerization) and the equilibrium enthalpies are low. In order to prove the existence of intramolecular hydrogen bond the solutions of IBSP-A in CCl_4 with small amount of methanol were investigated (34), Fig.2. A small amount of MeOH (0.25%) causes a drastic hypsochromic shift of long wavelength absorption band without a change in short wavelength absorption band. This short wavelength band is shifted when the solutions contain more MeOH (0.75%)-due to solvation. It shows that an intermolecular hydrogen bond is formed between long wavelength absorbing isomer and MeOH. At 60°C the hydrogen bond is broken. The other isomer which has an absorption band at $\lambda=555$ nm does not form an hydrogen bond with MeOH because it is probably stabilized by intramolecular hydrogen bond. This intramolecular hydrogen bond causes a decrease in the transition moment. It results in an hypochromic effect connected with the formation of intermolecular hydrogen bond between isomer without intramolecular hydrogen bond and MeOH.

The equilibrium enthalpy value of trans-trans isomerization given below from spectroscopic studies for IBSP-A in CCl_4 equals to 4kcal/mol. This enthalpy may influence the C_1 and C_2 isomerization :



The equilibrium between C_1 and C_2 depends on the strength of the hydrogen bond which in turn depends on inductive and resonance effects of electronwithdrawing substituents in the chromene part of IBSP. This equilibrium depends on the solvent polarity because the colored form without intramolecular hydrogen bond has a greater dipole moment.

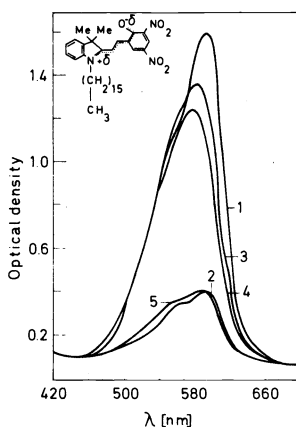


Fig.2. Absorption bands of merocyanine form of IBSP-A in CCl_4 at 20°C (1) and at 60°C (2); in $CCl_4 + 0.25\% MeOH$ (3) and in $CCl_4 + 0.75\% MeOH$ (4) at 20°C; in $CCl_4 + 0.25\% MeOH$ at 60°C (5).

The electron donor-acceptor ability of the merocyanine may lead to other specific interactions with the solvent molecules. It may result in different equilibrium condition between colored isomers. The dipole moments measured for merocyanine form of IBSP-A in toluene and dioxane are 12 D and 18 D, respectively. It shows the formation of complexes with dioxane.

The first order kinetics of color fading of IBSP in liquid solutions indicates that the state of the systems is close to the steady state. A small hypsochromic shift, sometimes to be observed in merocyanine absorption band, allows to conclude that the rate of trans-trans isomerization ($C_1 \rightleftharpoons C_2$) is not very much higher than that of trans-cis isomerization. The remarks indicate the existence of the equilibrium between hydrogen bonded and non bonded isomers which however, does not cause deviation from first order kinetics of the ring closure reaction. It means that the activation energies of trans-cis isomerization are higher than that of trans-trans isomerization.

In solid solutions one shall not expect a difference in solvent effects in comparison with the model liquid solution. Thus, the departure from first order kinetics observed in solid solutions must be due to restrictions of rotation possibilities.

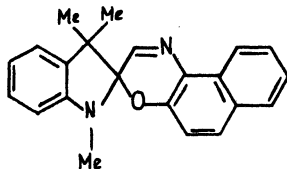
b. Diffusion limit-ed ring closure reactions of IBSP in solid solution. The diffusion effects on the decoloration rate can be discussed considering more carefully the particular steps of this reaction. Wilson and Drickamer (36) who have carried out high pressure studies of solid solutions of spiropyrans in polymers conclude that the isomerization of merocyanine form to a closed spiropyran form results in a volume increase (1-2 cm^3/mol at 50 kbar). Several isomers of merocyanine form, due to their coplanarity, exhibit much smaller differences in their volume although the estimation of their structure shows that the distance between N and O atoms for different colored isomers equals to 4.2 Å, 4.9 Å and 6 Å respectively (10). Assumption of a very strong diffusion influence upon trans-trans isomerization leads to conclusion that one should expect different products of photoreaction in the solid state and in liquid solutions. This would be due to the fact that during irradiation metastable products are formed which subsequently undergo isomerization by thermally activated reactions reaching finally thermodynamic equilibrium. The comparison of the absorption bands of the merocyanine in model liquid solutions and in solid solutions shows, however, that the final products (isomers) are identical. This result allows to accept that trans-trans isomerization is hardly diffusion limited. The rate constants of IBSP trans-trans isomerizations in solid polymeric matrices (in which the specific interactions may be neglected) estimated by us from electrochromism studies are much higher than those of ring closure reactions (37). Further arguments may be reached from the discussion

of the photomechanical effect presented by Smets et al. (22). The observed phenomena may be discussed in terms of $C_1 \rightleftharpoons C_2$ equilibrium. The C_2 isomers may be responsible for the photomechanical behaviour of these systems because of their greater conformational freedom as compared to the C_1 isomer for which the entropy values may be only slightly different from the spiropyrane form. Switching off the illumination causes the length recovery which occurs at rate depending on the rate of reaching the equilibrium $C_1 \rightleftharpoons C_2$. Low activation energies of the photomechanical effect support this interpretation.

Another argument for a rather small diffusion limitation of trans-trans isomerization of colored forms is supplied by the studies of color fading of IBSP solutions in polymeric matrices above T_g . In most cases (18,27) the ring closure reaction at temperature exceeding T_g i.e. in the viscoelastic state, may be described by first order kinetics. This process is still diffusion controlled because it occurs much slower than in liquid solutions. Concerning the assumption that the trans-trans isomerization in the viscoelastic region is also diffusion controlled to a higher extent than the trans-cis isomerization, what is usually accepted in the glassy state, then deviations from first order kinetics should be observed. To elucidate the differences in mechanism of ring closure reaction above and below T_g one must accept that the process below T_g is connected with an important diffusion influence on trans-trans isomerization and that above T_g on trans-cis isomerization. Such a model is at least arbitrary.

Summarizing, we believe that the trans-trans isomerization, which needs only a small reorientation of the surrounding molecules, is rather chemically controlled although the diffusion effects may cause its rate to decrease. Thus, the rate determining process of the thermal decoloration reaction of IBSP in solid solution is the diffusion controlled trans-cis isomerization (case iii) or diffusion and chemically controlled one (case ii).

All the processes mentioned above were discussed in long time scale. For short time scale the behaviour of these systems may be different. Shahvierdov (38) has shown by flash photolysis that at low temperatures the transformations of IBSP colored isomers in solid PMMA matrices, at low temperatures, are very fast and the equilibrium is reached in a few μ s similarly to the liquid solution. On the other hand, trans-cis reactions may be fast too e.g. we have shown that ring closure reaction of the following photochrom,



in PMMA solid matrix occurs in a few seconds (39). These studies suggest that fast chemical reactions are diffusion controlled to less extent than slow chemical reactions of the same type. Thus, time dependent relaxation effects of the environment of the active photochrom must be taken into consideration.

III. DEFECT DIFFUSION MODEL

Discussing the model of diffusion controlled reactions in amorphous polymers we have to consider that the relaxation phenomena in high molecular weight materials are described in a phenomenological manner. This is due to the deficiency of detailed theories analyzing these phenomena on molecular level and to limited information on the heterogeneous physical and chemical structure (chemical defects) of glassy polymers. On the other hand, our knowledge of the interaction of the excited photochrome molecules with the polymeric matrix as well as on the reorientation of the surroundings due to thermal collisions or the energy migration are very deficient too. In that situation it would be an advance to form a model, consistent with the phenomenological description, which may elucidate, at least in an approximate way, the mechanism of observed phenomena. Analyzing the basic conceptions of the proposed model we want at first, to discuss the beginning step of the reaction in which excited spiropyran molecule transforms into merocyanine and, then, to describe the mechanism of its thermal transformation into closed ring molecule.

a. Development of defect diffusion model (DDM). Electronically excited spiropyran molecule may dissipate its energy by several physical and chemical relaxation processes. The importance of different excited electronic and vibrational levels in the ring opening reaction is still a matter of discussion (3-9,36) although many studies show that the triplet states are of the greatest significance (3-5,36). In the photoreaction no luminescence related to radiation desactivation of colored isomers was found. It indicates that electronic excited spiropyran molecule is transformed into a merocyanine

in electronic ground state, but in excited oscillation and rotation levels. The energy of such an excited merocyanine molecule may be dissipated by radiationless and chemical relaxation processes. It means that a large part of this energy which is equal to the energy difference between electronic excited state, ($\lambda_{365} \approx 78$ kcal/mol) and of the C-O bond scission, is transferred to the medium. Assuming that the energy of ring opening reaction equals to 20 kcal/mol (from IBSP thermochromism studies) one can estimate that about 58 kcal/mol is transmitted to the vicinity. This energy may lead to such a change in conformation of the neighbouring elements of the macromolecules which at room temperature is improbable to occur. This energy is transferred to the medium within the time of several vibronic relaxations. The energy of side groups which are in the vicinity of the merocyanine molecule increases very fast and reaches high values leading to some conformation changes of the main chain even in the glassy state (defect I). The generated constrained metastable conformation of polymer molecule elements, close to merocyanine form of IBSP molecule, relaxes fast. Then defect I is transformed into defect II of which the volume is mainly related with the volume difference of spiropyran and merocyanine forms. Defect II may diffuse due to a cooperative relaxation of side groups or may disappear. The last process seems to be slow because it needs displacement of backbone segments. The processes mentioned above can be represented by a scheme :



where : Δv_I - local volume change related to the generation of constrained metastable conformation of polymer chain (defect I)
 Δv_{II} - local volume change related to the volume difference of spiropyran and merocyanine form (defect II)
 $\Delta v_{eq.}$ - equilibrium free volume depending on the structure of matrix and temperature

Fast chemical reactions are not diffusion controlled (or only to very small extent) because they occur within defect I in analogy to a well known cage effect in liquid solutions. Kinetics of slower reactions may be at first chemically controlled but later on after the disappearance of defect I, it starts to be controlled by the defect II diffusion.

The introduction of defects of two kinds allows to elucidate the effects at short and long time scale as was mentioned before.

b. Intpretation of kinetics of ring closure reaction of IBSP in poly(alkyl methacrylates) using DDM. Extensive mathematical discussion of diffusion controlled chemical reactions presented by Waite (40) shows that the rate of such processes depends to a great extent upon the initial distribution of the reactants. In our case the initial distribution of distance between merocyanine molecules and defects II, which are created in their vicinity, is non uniform (the non uniform distribution of reacting pairs). Because there is no exact information on actual distribution of pairs we approximate this distribution by a gaussian distribution. Such assumption seems to be reasonable because in the case of photochemical generation of defects the system under discussion gains a definite energy.

The solution of differential equations describing the kinetics of diffusion controlled reactions requires appropriate boundary conditions to be adopted. In most processes in which diffusion rate is the controlling step of the overall rate (small diffusion rate as compared to the rate of chemical reaction) Smoluchowski's boundary conditions are accepted (41). This assumption seems to be well founded because in liquid solutions the ring closure reaction is much faster than that in polymeric matrices ($10^2 - 10^3$ times faster).

The general differential equation of diffusion controlled reactions under accepted initial and boundary conditions was solved by Waite (40). For early times such as

$$1. \quad 4D_d t \ll (\lambda r_0)^2$$

where: D_d is the diffusion coefficient of defect II

r_0 is one molecular jump of defect II

λ is a parameter describing the pairs distribution

the time dependent concentration of the colored merocyanine form C_t^M is given by the following equation :

$$2. \quad C_t^M = C_0^M - C_0^M K t^{\frac{1}{2}}$$

where: C_0^M is the concentration of merocyanine form at $t=0$

$$K=8\pi^{\frac{1}{2}}r_0 N \exp (-1/\lambda^2) D_d^{\frac{1}{2}}, N \sim 1/r_0^3; N \text{ is the normalization factor}$$

This equation may be derived from the reduced form of the general diffusion equation describing the rate of diffusion controlled reactions taking into consideration inequality 1. It follows from inequality 1 that in the case of small diffusion coefficients the linear dependence of merocyanine concentration vs $t^{\frac{1}{2}}$ may be observed even for longer time periods. It is seen from eq. 2, on the other hand, that in order to compare the rates of color fading at different initial concentration C_d^0 of merocyanine form it is necessary to normalize the kinetic plots to one chosen initial concentration.

Waite's general equation describing the diffusion controlled reaction in the case of uniform distribution of merocyanine molecules and defects related to the structure of amorphous polymer, is given by (42)

$$3. \quad dC_t^M/dt = -4\pi r_0 D_d^{\frac{1}{2}}(1+r_0/(\pi D_d^{\frac{1}{2}} t)^{\frac{1}{2}})C_d^0 C_t^M$$

where: C_t^M - is the concentration of merocyanine form at time t

C_d^0 - is the concentration of defects due to free volume distribution in an amorphous polymer

It follows from eq. 3 that when

$$4. \quad r_0/(\pi D_d^{\frac{1}{2}} t)^{\frac{1}{2}} \gg 1$$

one should expect a linear relation $\ln C_t^M$ vs $t^{\frac{1}{2}}$ in time period for which the inequality 4 holds.

The interpretation of experimental results of the studies of colour fading of two photochroms: 3'3'-dimethyl-1'-phenyl-6-nitro-IBSP-B and 3'3'-dimethyl-1'-(β hydroxyethyl)-6-nitro-IBSP-C dissolved in solid poly(methyl methacrylate) PMMA, poly(ethyl methacrylate)PEMA and poly(n-butyl methacrylate)-PnBMA was carried out using eqs.2 and 3 taking into account inequality 4. In these matrices during the course of the color fading reaction no hypsochromic band shift of the merocyanine could be detected. This eliminates some difficulties related to the necessity of consideration that trans-trans isomerization may be diffusion controlled too. The plots of normalized extinction of colored form of compound (B) in PMMA(Fig.3) show that 60-70% of merocyanine molecules undergo trans-cis isomerization according to eq. 2. An attempt to describe the observed color fading by eq.3 and in inequality 4 leads to negative results because for short time periods a distinct deviation

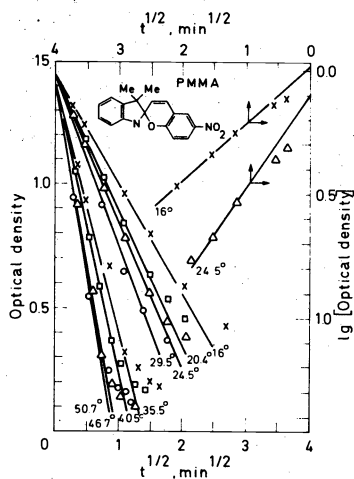


Fig.3. Thermal decay of IBSP-B colored form in PMMA at different temperatures, left-down axes -OD vs $t^{\frac{1}{2}}$, right-up axes $\lg OD$ vs $t^{\frac{1}{2}}$.

from linearity $\log C_t^M$ vs $t^{\frac{1}{2}}$ are found. This supports the assumption of non-uniform pair distribution. We have observed similar relationship for other systems. Arrhenius plot of the K constant from eq.2 for photochrom B in PnBMA is presented in Fig.4. The change in the slope at T_g is easily seen. Thus, the K-value obtained from eq.2 is a sensitive indicator of T_g . Assuming that the diffusional molecular jump of defect II equals to 5×10^{-8} cm and 1×10^{-7} cm

below and above T_g respectively and taking into consideration that $\lambda=2$ one can determine the diffusion coefficients for defect II from eq.2 ($\lambda=2$ means that the most probably distance of defect II from merocyanine molecule equals to a twofold diffusional jump distance).

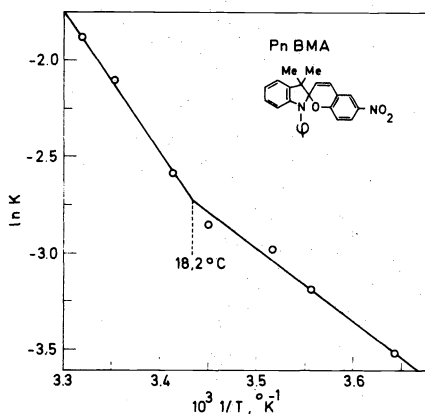


Fig.4. Arrhenius diagram of the K constant (eq.2) for IBSP-B in PnBMA.

The results of these calculations are given in the following table.

Table. K values (eq.2) and defect II diffusion parameters (activation energies and diffusion constants) of the investigated systems.

Polymers	IBSP-B			IBSP-C		
	$10^2 \cdot K^{15^\circ\text{C}}$ [s ^{-1/2}]	$10^{20} \cdot D^{15^\circ\text{C}}$ [cm ² /s]	E [Kcal/mol]	$10^2 \cdot K^{15^\circ\text{C}}$ [s ^{-1/2}]	$10^{20} \cdot D^{15^\circ\text{C}}$ [cm ² /s]	E [Kcal/mol]
PMMA	3.4	2.4	16.6	1.6	0.53	18.0
PEMA	4.2	3.7	19.6	1.9	0.72	15.8
PnBMA	T < T _g	5.8	14.8	2.5	1.3	13.3
		10.0*		20.7*	4.0*	
	T > T _g	17.2**	28.0	6.3**	8.1**	23.7

* - extrapolation at 28°C, ** - at 28°C

It follows from these data that for both compounds, when the length of the side group at the polymer chain increases the K-values and diffusion coefficients of defects II increase. Below T_g it is accompanied by a decrease of diffusion activation energies of defect II. It is interesting to note that these activation energies are comparable with activation energies of β relaxation found in the polymeric matrices (an exception being photochrome B in PEMA).

The transition from the glassy state to the rubbery state is followed by a distinct increase in diffusion coefficients of defects II and their activation energies.

The elucidation of the differences of diffusion coefficients of defect II found for photochromes B and C, which have very similar molecular volumes, may be considered on terms of their different dipole interactions with the matrices. These interactions are of particular importance at the moment of molecular jump i.e. when the defect II is generated in the vicinity of the merocyanine molecule. Strong electrostatic interactions of a very polar merocyanine molecule with polar side groups of methacrylic polymers cause a distinct decrease in the value of the diffusion coefficient. These interactions are less effective at longer distances. Smaller values of diffusion coefficients of defect II observed for photochrom C suggest that the latter is more polar than photochrome B which

may be related to the presence of hydroxyl group in the IBSP-C.

Good agreement between experimental results and the proposed model shows that the decoloration reaction of photochroms is mainly controlled by the diffusion of defects II. Diffusion of these defects below T_g is related to the relaxation of side chains (β) whereas above T_g , it is related to the relaxation of side chains and main chain segments (β and α). This diffusion controls the transformation of 60-70% of merocyanine molecules. For all investigated systems at long time periods the color fading reaction is described by quasilinear relation $\log C_t^M$ vs t . In this case the decrease in concentration of non transformed merocyanine molecules is controlled by the diffusion of defects which are related to free volume.

The analysis of the last process is very complicated because one does not know the concentration of defects related to free volume distribution. On the other hand, one should take into consideration the distribution of the sizes of free volume defects. This distribution leads evidently to distribution of relaxation times. Consequently, it may lead to a continuous distribution of rate constants which has been suggested by North (28) in his interpretation of decoloration reaction of some IBSP dissolved in solid polymers, investigated for long time periods. As the temperature increases above T_g the relaxation frequency of polymer segments increases in so far as defect II vanishes at higher rate. Thus, the color disappearance is controlled by rotational diffusion of chain segments. The rotational motion of polymer segments leads to the averaging of sizes of free volume elements and causes its homogeneous distribution. As follows from eq.3, linear dependences $\log C_t^M$ vs $t^{1/2}$ and $\log C_t^M$ vs t should be observed for short and long times respectively. The first relationship is observed for short time, thus in normal spectrophotometric measurements; it may be inappreciable, due to rather large diffusion coefficients above T_g .

It is interesting to note that a linear function $\log C_t^M$ vs t is observed in solid solutions of IBSP only at temperatures exceeding by some degrees the T_g value. It shows that the disappearance of defect II is not a very fast process slightly above T_g .

CONCLUSIONS

1. Analysis of experimental results of kinetics of ring closure reactions of two IBSP dissolved in poly(alkyl methacrylates) was carried out using the proposed defect diffusion model. A good agreement between the theoretical predictions and experimentally observed color decay was reached. It may be concluded that even in the viscoelastic state of the matrix defects II control the decoloration rate. This process occurs mainly as a result of cooperated β relaxation with a small share of α -relaxation. The proposed model describes well the disappearance of 60-70% of merocyanine molecules. The remaining part of these species undergoes a ring closure reaction controlled by diffusion of free volume defects.

Further development of this model may consist in consideration of radiation boundary conditions and electrostatic interactions. More detailed informations on the state of reorientation of matrix molecules during the photoreaction and on fast relaxation of defects are needed. They can be obtained from the studies of the fluorescence depolarization of excited merocyanine form. The investigations of these effects are now carried out in our laboratory.

2. Defect diffusion model discussed above may be applied to photochromic polymers with photochroms in side chains because their mobility does not differ very much from that of nonbound dissolved photochroms. When photochrom is built into the backbone chain ring closure reaction needs a greater reorganization of surroundings and may occur due to diffusion of a larger free volume defect than defect II. Taking into consideration homogeneous distribution of structural defects and their small diffusion coefficients one should expect a linear relation of $\log C_t^M$ vs $t^{1/2}$ below T_g , and a linear relation $\log C_t^M$ vs t above T_g due to increase of diffusion constants related to segment rotation.

3. When there is an evidence that the trans-trans isomerization is diffusion controlled to a high extent (two step diffusion controlled process) the interpretation of the kinetics of decoloration is much complicated. The difficulties are mostly related to the lack of knowledge of the exact concentrations of colored isomers and to the deficiency of ring closure reaction mechanism.

In the studies of diffusion controlled processes for which the initial distribution of pair (eg. merocyanine molecule and defect II) is nonhomogeneous, flash photolysis seems to be mostly appropriate. The generation of merocyanine forms by long irradiation causes that the initial distribution of pair changes

during the illumination. This in turn causes that one observes a relation between time of irradiation and rate of color fading at equal initial concentrations of photochroms.

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REFERENCES

1. Y.Hirshberg and E.Fischer, J.Chem.Soc., 4522 (1952).
2. Y.Hirshberg and E.Fischer, ibid. 297 (1954).
3. D.Reeves and F.Wilkinson, Faraday Trans.II, 69, 1381 (1973).
4. N.W.Tyer, Jr. and R.S.Becker, J.Amer.Chem.Soc., 91, 1295 (1970).
5. M.Kryszewski, B.Nadolski and D.Grochowska-Łapienis - Paper presented at the 2nd Conference of Luminescence, Torun, Poland (1974).
6. G.I.Lashkov, V.L.Ermolaev and A.V.Shablya, Optika Spekr., 21, 305 (1965).
7. C.Audic and R.Gautron, Bull.Soc.Chim.France, 2075 (1968).
8. T.Bercovici, R.Heiligman-Rim and E.Fischer, Mol.Photochem., 1, 23 (1969).
9. H.Bach and J.G.Calvert, J.Amer.Chem.Soc., 92, 2608 (1970)
10. O.Chaude', These,'Etude Spectrophotometrique de'isomerization de Divers Spiranes Thermochromes,' Revue d'Optique (1954).
11. A.Samat, G.Martin and R.Guglielmetti, C.R.Acad.Sc.Paris,t.279,Ser.C,573(1974)
12. J.B.Flannery, Jr., J.Amer.Chem.Soc. 90, 5660 (1968).
13. R.Heiligman-Rim, Y.Hirshberg and E.Fischer, J.Phys.Chem., 66,2465 and 2470 (1962).
14. C.Balny, P.Douzou, T.Bercovici and E.Fischer, Mol.Photochem., 1, 225 (1969).
15. G.L.Lashkov and A.V.Shablya, Optika Spekr., 19, 821 (1965).
16. A.V.Shablya, K.B.Demidov, and Yu.N.Polyakov, Optika Spekr., 19, 738 (1965).
17. W.A.Murin, W.F.Madzikov and W.A.Baraczewski, Opika Spekr., 6, 1174 (1974).
18. Z.G.Gardlund, J.Polym.Sci., B7, 719 (1969).
19. Z.G.Gardlund and J.J.Laverty, J.Polym.Sci., A11, 2423 (1973).
20. G.Smets, IUPAC International Symposium on Macromolecular Chemistry, Budapest 1969 (pp.65-87).
21. G.Smets and G.Evens, Pure Appl.Chem.Macromol.Chem., 8, 357 (1973).
22. G.Smets and F.De Blauwe, Pure Appl.Chem., 39, 225 (1974).
23. F.Agolini and F.P.Gray, Macromolecules, 3,349 (1970).
24. G.Van der Veen and W.Prins, 23rd IUPAC Congress Boston 1971, Macromolecular preprints I,p.70.
25. G.Smets, Pure Appl.Chem., 30, 1 (1972).
26. G.Smets, J.Polym.Sci.Polym.Chem.Ed., 13, 2223 (1975).
27. M.Kryszewski, D.Grochowska-Łapienis and B.Nadolski, J.Polym.Sci.Polym.Chem.Ed., 11, 2423 (1973).
28. N.C.Lawrie and A.M.North, European Polymer J., 9 345 (1973).
29. J.Verborgt and G.Smets, J.Polym.Sci.Polym.Chem.Ed., 12, 2511 (1974).
30. P.H.Vanderwijer and G.Smets, J.Polym.Sci.Part C, 22, 231 (1968).
31. M.Kryszewski, B.Nadolski and A.Fabrycy, Roczniki Chemii, 49, 2077 (1975).
32. C.S.Paik and H.Morawetz, Macromolecules, 5, 171 (1972).
33. C.Schiele and G.Arnold, Tetrahedron Letters, 13, 1191 (1967).
34. D.Grochowska-Łapienis, M.Kryszewski, B.Nadolski unpublished works.
35. K.G.Dzhaparidze, Izv.Akad.Nauk Gruz.SSR, Ser.khim, 1(2), 162 (1975).
36. D.G.Wilson and H.G.Drickamer, J.Chem.Phys., 63, 3649 (1975).
37. M.Kryszewski and B.Nadolski, J.Polym.Sci.Polym.Chem.Ed., 13, 345 (1975).
38. V.Shahvierdov, Izv.Akad.Nauk SSSR, ser.fiz. XXXII, 1564 (1968).
39. M.Kryszewski, B.Nadolski unpublished works.
40. T.R.Waite, Phys.Rev., 107, 471 (1957).
41. M.V.Smoluchowski, Z.phys.chem., 92, 192 (1917).
42. T.R.Waite, Phys.Rev., 107, 463 (1957).