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Comment on the Matrix Effect on Photochromism of Spiropyrans in Bulk Polymers

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Summary

The photochromic behaviour of spiropyran derivatives dissolved in a polymer matrix or incorporated in the backbone of bulk polymers is discussed. The deviations from first order kinetics of the thermal decolouration in glassy specimen are attributed to both influences of local free volume and of different merocyanine isomers during the decolouration reaction. The application of the free volume theory in terms of a WLF-equation is proven for the first time in these systems and conclusions are drawn on chain segmental mobility.

Introduction

The investigation of the photochromism of spiropyrans in bulk polymers has been the subject of many publications (cf.[1]). It has been stated that the deviations from solution like behaviour in the thermal bleaching reaction are related to restrictions in the rotation of the open merocyanine forms caused by the limited available free volume and the limited chain segmental mobility [2-7]. The two or three simultaneous first order processes occurring in glassy specimen have been explained by the existence of different isomers [2,5,6,8] and attempts have been made to describe these anomalies as compared to solution by e.g. a distribution of environments in the polymer matrix [3], a defect diffusion model [7] or density distribution functions [9].

In recent papers [10-13] it was shown for the first time that the photochromic behaviour of aromatic azo compounds in bulk polymers, independent of the way in which the chromophore is incorporated in the polymer matrix, can be perfectly described by using the WLF-theory; the thermal cis-trans isomerization is directly associated with the chain segmental mobility, and from the isomerization behaviour even different kinds of molecular relaxation processes of chain segments can be discriminated. This was also found to be true for the photochromic behaviour of pendent spiropyran chromophores in various poly(methacrylates) [11-13]. In order to complete this picture, the influence of a polymer matrix on the photochromism of spiropyrans which are built into the polymer backbone or simply dissolved in the polymer will be discussed in this paper, based on the findings mentioned above

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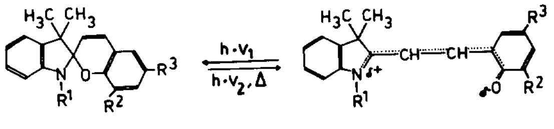
Results and discussion

The photochromic properties of spiropyrans are based on the heterolytic cleavage of the 1,2-single bond of the pyran ring, followed by a rotation of part of the molecule to achieve coplanarity:



The open merocyanine form exists in several coloured stereoisomers of different thermodynamic stability 14) which thermally fade to the colourless closed spiro structure. Especially for the bleaching process, a lot of kinetic data (first order rate constants k) exist in literature which have been used for the calculation of the a_T-figures (ratio of the relaxation time of the thermal back reaction from the open merocyanine form to the closed spiropyran at temperature T to its value at T_g) discussed in this paper; the k-values on which the a_T-values in the following Figures are based were either determined from graphs or, if possible, taken from tabulated data in the papers referred. By using a_T (the so-called "shift factor" in the literature of dynamic mechanical or dielectric relaxation processes, cf. 15)) the decolouration rate constants are reduced to

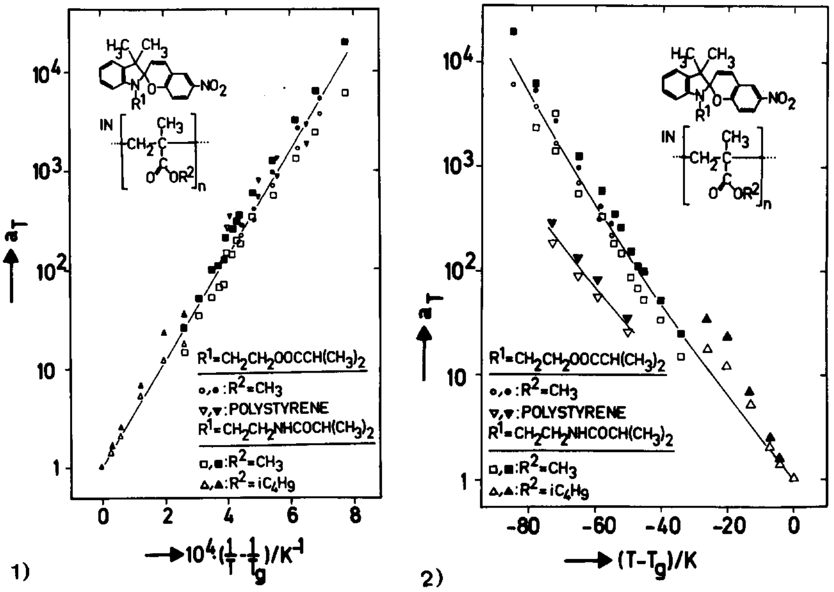
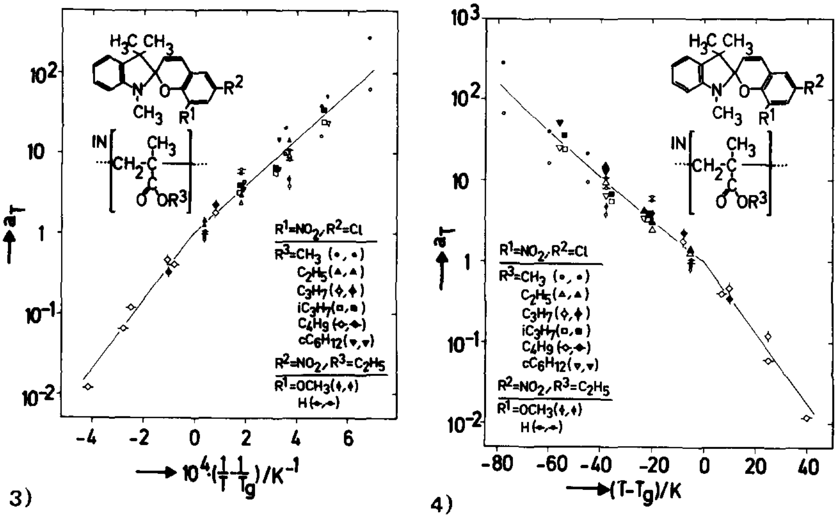
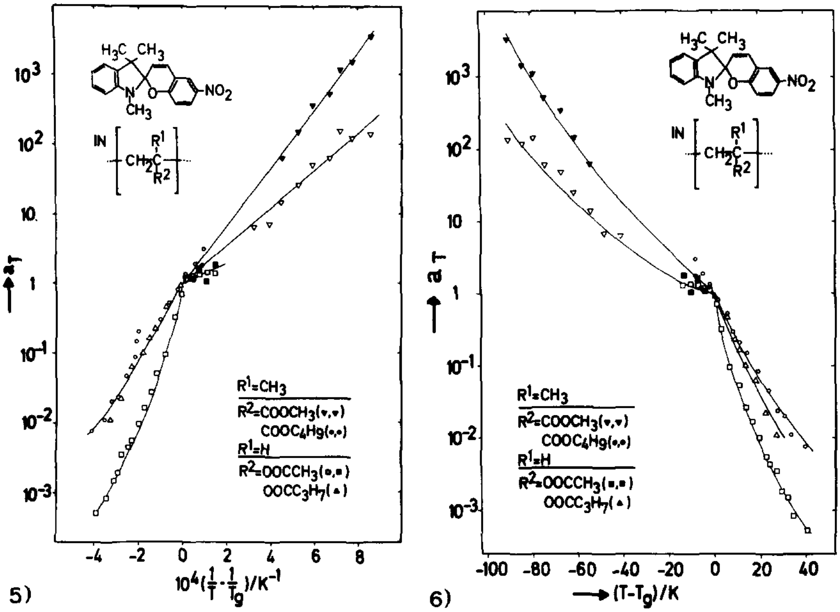


Fig. 1,2: Modified Arrhenius-plot (Fig. 1) and WLF-plot (Fig. 2) for the decolouration of spirobenzopyrans dissolved in poly(methacrylates) (2-5 wt-%); a_T calculated from the data given by Verborgt and Smets 5); open and filled symbols represent different stereoisomers of the open merocyanine form.



3) 4)

Fig. 3,4: Modified Arrhenius-plot (Fig. 3) and WLF-plot (Fig. 4) for the decolouration of spirobenzopyrans dissolved in different polymers (~1 wt-%); a_T calculated from the data given by Gardlund and Laverty [2]; open and filled symbols cf. legend Fig. 1.



5) 6)

Fig. 5,6: Modified Arrhenius-plot (Fig. 5) and WLF-plot (Fig. 6) for the decolouration of 1'-methyl-3',3'-dimethylspiro-6-nitro-[2H-1-benzopyran-2,2'-indoline] dissolved in different polymers; a_T calculated from the data given by Kryszewski et al. [4]; open and filled symbols cf. legend Fig. 1.

T_g, and the time-temperature superposition principle allows one to compare data obtained in different polymers in a common framework.

The data calculated for the decolouration of a variety of spiropyrans dissolved in different polymer matrices are depicted in Fig. 1-6 in form of reduced Arrhenius-plots (Fig. 1,3,5) and WLF-plots (Fig. 2,4,6). The relationship between a_T and $T-T_g$ clearly proves the validity of the free volume theory for these systems, as has already been shown for pendent spiropyrans [11,13].

First it has to be emphasized that the fading rates for differently substituted spiropyrans in a given family of polymers can be represented by single graphs (Fig. 1-4) but different graphs are obtained for a given spiropyran when the chemical structure of the polymer matrix is significantly changed (Fig. 2,5,6). This is certainly caused by both the effects of different solvatochromism and chain segmental mobility in differently structured polymers.

Secondly it has to be stated that the a_T-figures for the two or sometimes three simultaneous first order processes occurring in glassy polymers (open and filled symbols, Fig. 1-6) generally fall on the same line (except for poly(methylmethacrylate) matrix, s.b.). The apparent energy of activation for both first order processes is the same and figures as low as 57 kJ/mol (Fig. 3) or even 26 kJ/mol (poly(vinylacetate), Fig. 5) are found, figures which are much smaller than the energy of activation in solution of 100-120 kJ/mol. The corresponding entropies of activation are markedly negative because of the cooperativity of the displacement of chain segments and the ring closure reaction, a process which is unfavoured from the entropic point of view (cf.[10]). The lower apparent energies of activation in the glassy polymers are in the same range as the activation energies for molecular relaxation processes of the main chain [15,16] and this is a clear evidence for the predominant influence of main chain motions on the thermal bleaching reaction [+].

The explanation for the occurrence of at least two simultaneous first order processes in glassy polymers even after prolonged irradiation times is still controversial (cf.[1]). Since the final products after irradiation are the same in solution and in bulk polymers [7], but generally only one first order process is found in solution as in rubbery specimen, the appearance of deviations from single first order kinetics is most probably due to differences in the restrictions of the mobility of the intermediate species formed during the bleaching reaction by the polymer matrix rather than due to the relative amount of stereoisomers present in the photostationary state, which only might be the case after very short irradiation times when the photostationary state is not yet reached [7,8]. This explanation assumes 1) the existence of different merocyanine isomers as intermediates in the formation of the closed spiro form; 2) it considers the assumption that different density functions of free volume [9] are responsible for the kinetics of the bleaching

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[+] For poly(methylmethacrylate) matrix a shift in the Arrhenius-plot, i.e. a sudden increase of the rate constant k, has been observed at T_β, when the ester side group starts to rotate, but the apparent energy of activation of the bleaching reaction does not change at this temperature [4,5]. Above T_β local main chain motions are facilitated and this leads to an increase in the fading rate.

reaction. It is also in agreement with the explanation for the deviations from single first order kinetics in the case of aromatic azo chromophores 10-13) by a rotational and translational relaxation process which are attributed to different distributions of free volume around the chromophores. For the aromatic azo compounds only one cis-isomer is present and the cis-trans isomerization proceeds without great steric requirements in a plane; however, in case of the spiropyrans, a rotation of part of the molecule is involved in the bleaching reaction which has severe steric requirements. For this reason a translational motion of chain segments alone was found not to be sufficient to create enough free volume for the ring closure reaction of pendent spiropyrans 11,13). However, when the spiropyran is simply dissolved in the polymer and thus its mobility is less restricted, both rotational ($E_A \sim 60$ kJ/mol) and translational ($E_A \sim 25$ kJ/mol) chain segmental relaxation processes may be of importance as is suggested by the experimentally found apparent energies of activation ($E_A = 57$ and 26 kJ/mol, s. above) +).

At temperatures above T_g, relatively fast fluctuations of the free volume average the restrictions for the rotation of the different merocyanine stereoisomers; therefore, only a single first order process is found which represents an average relaxation time of the bleaching reaction as in solution. The apparent energy of activation for this first order process above T_g is temperature dependent and increases with decreasing temperature toward T_g, reaching figures up to about 300 kJ/mol (poly(vinylacetate), Fig.5). This temperature dependency is well in agreement with the WLF-theory and indicates the increasing restrictions in chain segmental mobility, which is equivalent to a decrease of the fluctuations of the free volume. Both factors impede the bleaching reaction in the dynamic state above T_g.

The dramatic change of the apparent energy of activation when going through T_g is particularly evident in systems where the spiropyran chromophore is built into the polymer backbone, as has been shown by Smets and coworkers 6) (s. exp. points in Fig. 7). These authors have tried to interpret these results by assuming a pre-exponential term in the Arrhenius-equation (Eq. (1); k_T, k_{T_g}: rate constants at temperature T and T_g; E_A = energy of activation of the photochromic isomerization)

$$\log \frac{k_{T_g}}{k_T} = - \frac{17{,}44\ (T-T_g)}{51{,}6 + T-T_g} - \frac{E_A (T-T_g)}{R\ T\ T_g} \qquad (1)$$

+) In poly(methylmethacrylate) matrix, however, two more or less pronounced different energies of activation ($E_A = 50$ and 75 kJ/mol) are found for the two simultaneous first order processes in the glass (Fig. 5) only when the spiropyran has no bulky substituents (cf. Fig. 1). In this particular case the steric requirements for the bleaching reaction are not as pronounced as for spiropyrans with larger substituents (Fig. 1) and the two different activated processes may indicate a stronger contribution of different local segmental motions in this particular case.

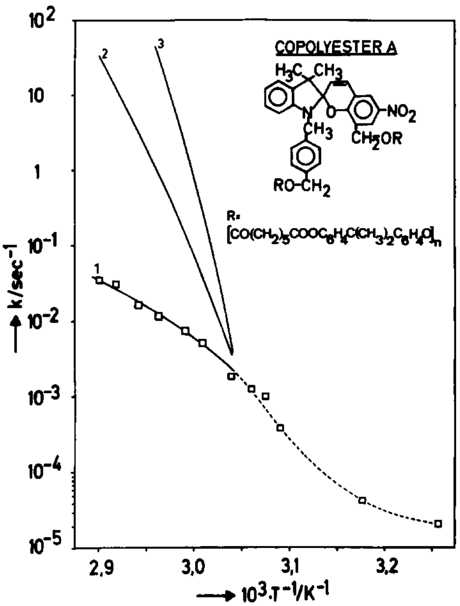


Fig. 7: Arrhenius-plot of the decolouration rate constants k_T[6] of spirobenzopyran derivative in copolyester A (10 wt-%); curve 1: curve through original experimental figures; solid line: calculated portion by using Eq. (3); curve 2: calculated by using Eq. (2); curve 3: calculated by using Eq. (1)

which would include the change of viscosity of the polymer in the transition state from the glassy to the rubbery state. However, as can be seen from curve 3, Fig. 7, Eq. (1) does not describe the experimentally found temperature dependency of the rate constants of the photochromic isomerization in such copolyesters as claimed by these authors. Additionally, the original WLF-equation (Eq. (2)) with the normally assumed figures for C_1 = 17,44 and C_2 = 51,6[17]

$$\log \frac{k_{T_g}}{k_T} = - \frac{17{,}44\,(T-T_g)}{51{,}6 + T-T_g} \qquad (2)$$

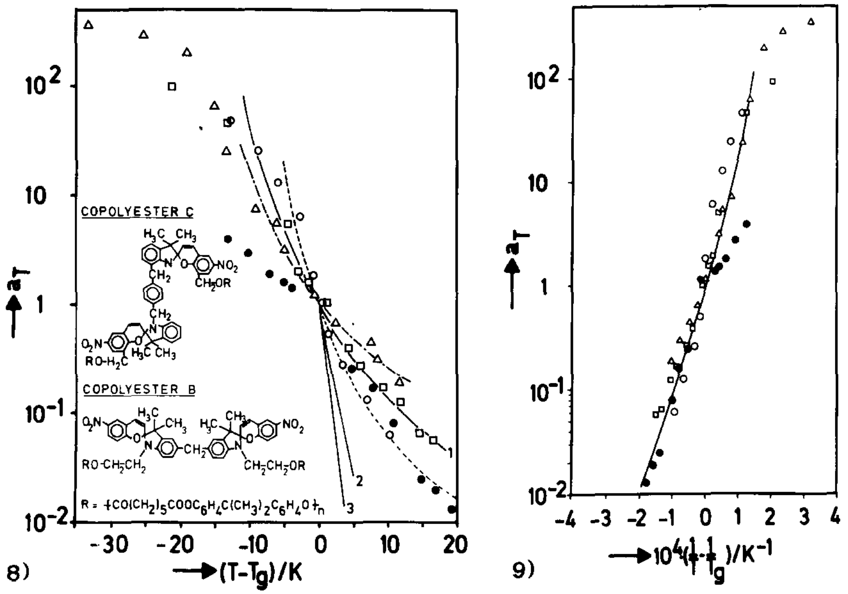
does not explain the results as can be seen from the corresponding calculated curve 2, Fig. 7. In contrast to this, a WLF-equation with quite different C_1 and C_2 parameters, Eq. (3) (cf. curve 1, Fig. 8), which are obtained by plotting $(T-T_g)/\log a_T$ versus $(T-T_g)$,

$$\log a_T = - \frac{3{,}6\,(T-T_g)}{31{,}6 + T-T_g} \qquad (3)$$

gives an excellent fitting of the exp. data; this is clearly demonstrated by the full line in curve 1, Fig. 7, which represents the curve calculated by using Eq. (3).

From these findings it is obvious that only a WLF-equation with C_1 and C_2 parameters which have to be determined experimentally, is able to describe the photochromic isomerization in such a bulk copolyester. To illustrate this point, the curves calculated from Eq. (1) and (2) are depicted in Fig. 8 (curve 3 and 2), too.

Depending on the organic structure of the spiropyran and on its localization with respect to the polyester backbone, different



8) 9)

Fig. 8,9: WLF-plot (Fig. 8) and modified Arrhenius-plot (Fig. 9) for the decolouration reaction of spirobenzopyrans incorporated or dissolved in poly(bisphenol-A-pimelate); a_T calculated from the data given by Smets and Evans [6]. (□) = copolyester A (cf. Fig. 7); (▲) = copolyester B; (o) = copolyester C; (●) = dissolved spirobenzopyran (R = COC_2H_5); curve 1: calculated from Eq. (3); curve 2: calculated from Eq. (2); curve 3: calculated from Eq. (1); (-··-), (---): calculated from single WLF-equations (C_1 = 2,2 and C_2 = 27,3 (▲); C_1 = 3,4 and C_2 = 18,0 (o,●).

curves, each with their own C_1 and C_2 parameter, are obtained. The deviations of these constants among each other for different systems (cf. legend Fig. 8) and also from those in the original WLF-equation (s. e.g. Eq. (2) and (3)) are reasonable, since the parameters in the original WLF-equation are based on a uniform random distribution of the free volume in a bulk polymer. Whereas, in the systems discussed here, an unequal distribution of the free volume due to local dislocations of chain segments in the neighborhood of the chromophore has to be assumed. This will be discussed in a future publication [18].

An interesting feature of these photochromic polycondensates is that a curve calculated from a single WLF-equation fits the experimental points of the thermal decolouration of a given photochromic polyester from the rubbery state down to about 10 K below T_g, where then strong deviations from the experimental figures occur (Fig. 8, curve 1 and dashed lines). This is also evident from the reduced Arrhenius-plot (Fig. 9), where a continious increase in the apparent energy of activation is observed down to about 15 K below T_g (E_A up to 350 kJ/mol) which then drastically decreases. This means that even below T_g the bleaching reaction is controlled to a certain extent by the same relaxation mechanisms of chain segments as in the rubbery state. This is not the case for spiropyrans simply dissolved in the polyester matrix which only show coinciding decolouration behaviour with the photochromic copolyester in the rubbery state (s. copolyester A and corresponding model compound dissolved in poly(bisphenol-A-pimelate)). In the photochromic copolyester, an adjacent chain segment has to be displaced during the formation of the closed spiro form; evidently, the fixation of the photochrome in the polymer backbone increases the local mobility of preferentially adjacent chain segments, as compared to systems where the photochrome is simply dissolved in the matrix.

Conclusion

From the data presented above it can be stated that for all types of photochromic spiropyran polymer systems the free volume theory can be applied. In comparison to the photochromic behaviour of aromatic azo compounds, the photochromism of spiropyrans is more complex due to larger steric requirements, the possibility of different stereoisomers of the open merocyanine form, and a very pronounced solvatochromism. However, in bulk polymers, in principle, the same influences of segmental mobility and free volume have been shown to also be responsible for the course of the photochromic reaction of spiropyrans.

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