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Photoisomerization and Fluorescence of Chromophores Built into the Backbones of Flexible Polymer Chains[1]

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ABSTRACT: Three copolyamides were prepared with azobenzene residues in the chain backbone. The photoisomerization in dilute solution was found to have the same quantum efficiency for the polymers and their low molecular weight analogues. This result shows that the "crankshaft-like motion" model for conformational transitions in the backbone of polymer chains cannot apply in dilute polymer solutions. Polymer solutions in dimethyl sulfoxide (DMSO) containing a high concentration of glycol or glycerol exhibited a behavior suggesting the presence of polymers in two different states, representing probably aggregated and molecularly dispersed chain molecules. In glassy films, the quantum yield for photoisomerization was very low for azobenzene residues in polymer backbones, while this quantum yield was reduced by a relatively small factor for the polymer analogues. A polyamide with stilbene residues in the chain backbone exhibited less intense fluorescence in dilute solution than its analogue. In plasticized films, the emission intensity decreased in a similar manner for the polymer and its analogue with increasing plasticizer concentration.

In previous work in this laboratory[2] we compared the rate of hindered rotation around bonds in the backbone of flexible chain polymers and their low molecular weight analogues in dilute solution. Since a conformational transition around a single bond in the backbone of a polymer would involve rapid motion of a large part of the molecular chain through the viscous medium with a prohibitively large dissipation of energy, it had been suggested by Schatzki[3] that two conformational transitions are correlated in time in a "crankshaft-like motion" so that only a short segment of the chain has to be displaced. This concept would, however, seem to lead to an increase in the free energy of activation for the hindered rotation, so that conformational transitions around a given bond in a polymer backbone would be much slower than in a low molecular weight analogue. The experiments referred to above were, therefore, designed to find whether such effects can be observed.

Results obtained in a NMR study of the rate of hindered rotation around the amide bond in piperazine polyamides revealed no significant difference between the behavior of the polymer and its analogues.[2a] Similarly, the thermal cis–trans isomerization of azobenzene residues built into the backbone of a polyamide proceeded at rates comparable to those in analogous small molecules.[2b] (It should be noted that for the purpose of this study there is no difference in principle between cis–trans isomerization around a double bond and hindered rotations around single bonds.) These results indicated that the rotation around the amide bond (or the cis–trans isomerization of the azobenzene residue) does not necessitate a simultaneous conformational transition around another bond in the chain backbone. We assumed, therefore, that the rotation around the amide or azobenzene residue involves many small oscillations of the internal angle of rotation. The distortion of this angle and the relaxation of the distorted angle would be slowed down by incorporation into the polymeric chain by the same factor, so that no effect on the rate at which the transition state is surmounted would be observed.[4] This model predicts then that the internal viscosity of the polymeric chain should have no effect on rates of conformational transition involving high activation energies, ΔE^*, just as the viscosity of a solvent medium has no influence on the rate of bimolecular reactions characterized by high values of ΔE^*. However, just as bimolecular reactions become diffusion controlled if ΔE^* is sufficiently low, so the rate of conformational transitions should become dependent on the rate of distortion of internal angles of rotation if the energy barrier for the transition is small. Under these conditions the restraint imposed by the requirement for two correlated transitions in polymer chains should become observable.

Zimmerman et al.[5] suggested that the photoisomerization of azobenzene involves a thermal reaction between the excited trans and cis states separated by a low-energy barrier. This concept was later confirmed by Fischer and Malkin[6] in their study of the temperature dependence of the quantum yield for the trans–cis photoisomerization which yielded an estimate of 2–3 kcal/mol for the energy barrier separating the two excited states. The low value of this energy barrier would, therefore, make a study of the photoisomerization of azobenzene residues in the backbone of polymer chain molecules and their analogues eminently suitable for the characterization of the general behavior of conformational transitions involving low activation energies and this report is concerned with a study of this kind. A related problem is concerned with the dependence of such photoisomerization rates on the polymer concentration. Tabak and Morawetz[2b] had found no slowing down in the rate constant for the thermal cis–trans isomerizatio of azobenzene residues in the backbone of polyamides when the polymer concentration was increased to a point where the chain molecules were heavily intertwined. Paik and Morawetz[4] found however that the photochemical trans–cis isomerization in polymers of this type is greatly reduced in concentrated systems. Similar observations have been reported by Smets and Evens[7] on a polyester with spirobenzopyran residues built into the chain backbone. The characteristic photochromism, in which a conformational transition follows the breaking of a covalent bond, was here shown to be suppressed below the glass transition temperature of the polymer.

If isomerization of the excited chromophore competes with fluorescence, increasing rigidity of the medium should enhance the fluorescence intensity. Unfortunately, azobenzene derivatives do not fluoresce and we had to use for a study of this effect a different system, i.e., a polyamide with stilbene residues in the chain backbone.

Experimental Section

Chemicals. Isophthaloyl chloride and 4,4′-sulfonedianiline were recrystallized from *n*-hexane and 95% alcohol. The dimethyl sulfoxide, dimethylacetamide, dimethylformamide, and dichloroethane used were spectrophotometric grade. Formic acid and adipoyl chloride were vacuum distilled. All the above chemicals and 1,6-hexanediamine, benzoyl chloride, and *n*-propylamine were purchased from Aldrich Chemicals. Isophoronediamine which is a mixture of two stereoisomer forms of 3-aminomethyl-3,5,5-trimethylcyclohexylamine was purchased from Veba-Chemie A.G. and was recrystallized from aqueous alcohol. 4,4′-Diaminostilbene dihydrochloride was purchased from Pfaltz and Bauer Inc. 4,4′-Azodianiline was bought from Eastman Organic Chemicals and recrystallized from H_2O. *p*-Nitrobenzoic acid and thionyl chloride were from Matheson Coleman and Bell. Spectroquality glycerol and ethylene glycol were purchased from Fisher Scientific Co.

Polymers. 4,4′-Azodibenzoic acid (synthesized from *p*-nitrobenzoic acid[8]) was converted to the acid chloride, mixed in a molar ratio of 1:24 with adipoyl chloride, and used for interfacial polycondensation with 1,6-hexanediamine[9] yielding polymer P-I. 4,4′-Azodianiline was mixed in the molar ratio 1:50 with 4,4′-sulfonedianiline and condensed in dimethylacetamide solution with an equivalent amount of isophthaloyl chloride. After 1 h at 15 °C another equivalent of the mixed diamines was added and the temperature was raised to 50 °C. Polymer P-IIs was precipitated from the solution by addition of water. Solution polycondensation of isophthalyl chloride with an isophoronediamine–azodianiline mixture (molar ratio 65:1) in the presence of excess triethylamine yielded polymer P-IIi. A similar procedure with the use of 4,4′-diaminostilbene in place of the azodianiline was used to obtain polymer P-III. The chromophore content of the polyamides (as estimated from uv spectra) was similar to that in the mixed monomers. Intrinsic viscosities (dl/g) at 25 °C were 0.234 for P-I (in 90% formic acid containing 2 M KCl) and 0.72 for P-IIs (in dimethyl sulfoxide). Reduced viscosities at $c = 0.51$ g/dl in DMSO solution were 0.22 for P-IIi, 0.23 for P-III, and 0.23 for poly(isophoronediamineisophthalamide). Characteristic absorption maxima of polymers I, IIs, IIi, and III were at 327, 383, 395, and 358 nm, respectively.

Polymer Analogues. The compounds 4,4′-(*N*,*N*′-*n*-propyl)azodibenzoylamide (A-I), 4,4′-(dibenzoyl)azodianiline (A-II), and 4,4′-bis(benzamido-*trans*-stilbene) (A-III) were used as analogues of the chromophore residues in the polymers.

Plasticized Films. Films were cast from DMSO solutions and vacuum dried for different lengths of time to obtain samples with different contents of residual DMSO plasticizer. The composition of the plasticized films was obtained from infrared spectra. For polymer P-IIs peaks at 1060 and 1110 cm^{-1} characteristic of DMSO and the sulfonedianiline residue, respectively, were employed. For polymers P-IIi and P-III peaks at 953 and 825 cm^{-1} were used for DMSO and the isophorone residues. Glass transition temperatures of the films were obtained by DTA using a Du Pont 900 thermal analyzer.

Kinetic Studies. A Cary 14 spectrophotometer was modified so that samples were alternately irradiated with a 450-W xenon Osram lamp, with the light passing through a rotating chopper, and analyzed in two directions perpendicular to each other. Bausch and Lomb interference filters 33-78-38 and 33-78-39 (transmission maximum at 379 and 395 nm, half-width 16 and 14 nm, respectively) and a Corion interference filter (transmission maximum at 334 nm) were used to isolate the spectral band for the irradiation. Liquid samples were placed in thermostated fluorescence-type quartz cells and were stirred during irradiation. In studies of dilute polymer solutions, the polymer concentrations were chosen so as to yield an initial optical density of the azobenzene residues of about 0.5 in a 1-cm cell. This corresponded to concentrations below 0.05 g/100 ml. Film samples were placed between two quartz plates in a slit cut in a copper block at 45° to the irradiation beam. The incident light intensity I_0 was determined with a Black-Ray uv intensity meter (Ultraviolet Products, Inc., San Gabriel, Calif.). The kinetics of the photoisomerization were followed using relation 1,[10] which is applicable when the thermal isomerization is negligible compared to the photochemical process. Here D_∞ is the optical density in the photostationary state, $\delta \equiv D_\infty - D$ where D is the optical density at time t, ϕ_t the quantum efficiency for the trans–cis photoisomerization, ϵ_t is the molar extinction coefficient of the trans isomer, and y_∞ is the fraction of the chromophore in the cis form in the photostationary state.

$$I(\delta) \equiv \left[1 + \frac{D_\infty}{2} + \frac{{D_\infty}^2}{12}\right] \ln|\delta| - \left[\frac{1}{2} + \frac{D_\infty}{6}\right] \delta + \frac{\delta^2}{24} = -At + \text{const}$$

$$A = I_0\, \phi_t \epsilon_t / y_\infty \tag{1}$$

Fluorescence Measurements. A Hitachi Perkin-Elmer Model MPF-2A Fluorescence Spectrophotometer was used. Reflectance fluorescence spectra were recorded from films of polymer III with an average thickness of 0.03 mm and an optical density at the excitation wavelength (360 nm) of 0.5.

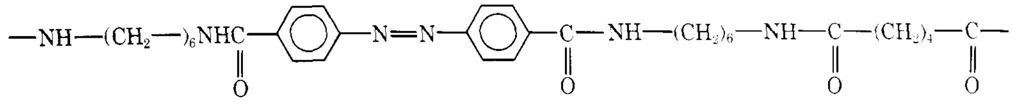
Results and Discussion

The structures of polymers and polymer analogues used in this study are represented in Chart I. We used P-I, P-IIs, P-IIi, and their analogues for studies of photochemical and thermal isomerization while P-III and A-III were used for fluorescence studies.

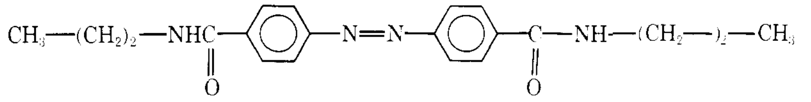
Photoisomerization in Dilute Solution. Polymer P-I and analogue A-I are only soluble in acidic media. In such solutions, the azo group may be protonated, changing the kinetics of the isomerization reaction. Our studies were carried out in formic acid solution containing 5.34 M H_2O, which has an acidity characterized by $A_0 = -1.18$.[2b] The spectrum of A-I has, in this medium, an absorption peak at 327 nm, characteristic of the unprotonated azobenzene residues, and no peak is observed at 415 nm where the protonated A-I absorbs in more strongly acidic media.

The course of photoisomerization of P-I and A-I is represented in Figure 1 as the time dependence of y, the fraction of azobenzene residues present in the cis form. It may be seen that there is no significant difference between the behavior of the polymer and its analogue. A similar identity of photoisomerization rates was observed when comparing P-IIs with the analogue A-II. These two substances contain no methylene groups so that conformational transitions in the ground state would involve higher energy barriers than in P-I and A-I. As explained in the introductory section, we expected, in view of the low activation energy separating the excited trans and cis states, that the isomerization in the backbone of the polymer chain would require two correlated conformational transitions and that it would, therefore, be substantially slower than in the analogue. The absence of such an effect shows that the "crankshaft-like motion" model is not applicable to the dynamic behavior of excited chain molecules in dilute solution. We may express our conclusion in a somewhat different way: the lifetime of the excited state of the azobenzene residue is

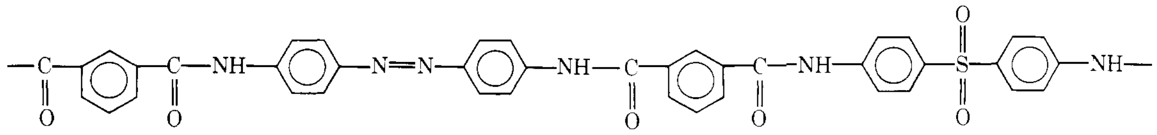
Chart I



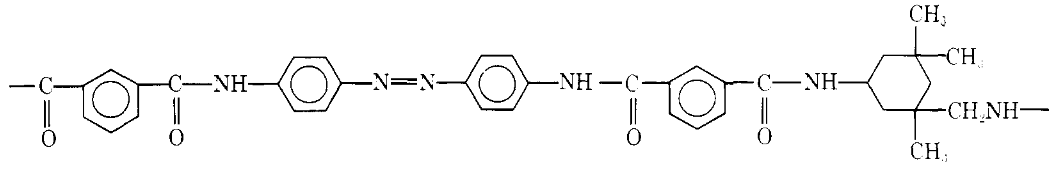
P-I



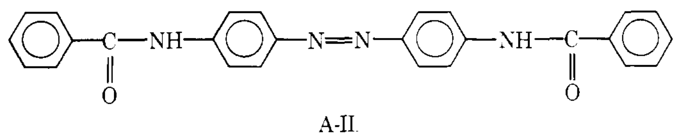
A-I



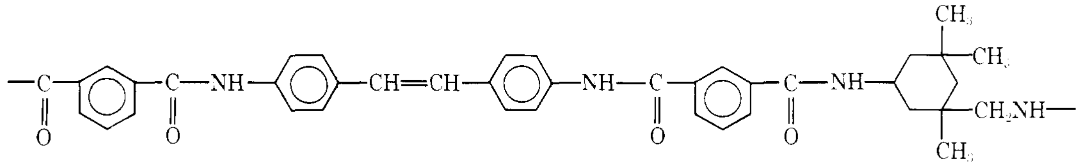
P-IIs



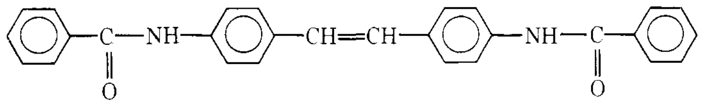
P-IIi



A-II



P-III



A-III

of the order of 10^{-9} s.[6] Unless the polymer chain can attain, during this very short time, a conformation allowing the trans–cis isomerization to take place, the excited trans residue would have to fall back to its ground state. Our results suggest that there is no detectable difference in the extent to which this condition limits the photoisomerization process in the polymer and its analogue.

Photoisomerizations of the polymer P-IIs and its analogue A-II were studied in mixed solvent media to assess the effect of a variation in solvent viscosity. Linear plots of $I(\delta)$ against time, as required by eq 1, were observed except for the polymer solutions in DMSO mixtures containing more than 65 vol % of glycerol or ethylene glycol, for which the plots were strongly curved as illustrated in Figure 2. Characterizing arbitrarily such nonlinear plots by the average value of $dI(\delta)/dt$ over the first 70% of the approach to the photostationary state, a dependence of the relative quantum yield on the composition of DMSO–glycol and DMSO–glycerol shown in Figure 3 was obtained. For the analogue, the quantum yield decreases linearly with an increasing glycerol or glycol content. With the polymer, this decrease is much more pronounced. The effect seems to be characteristic of viscous hydrogen-bonding nonsolvents since methanol (a hydrogen-bonding nonsolvent of low viscosity) and glycerol triacetate (a viscous nonsolvent lacking hydroxyl groups) had no effect on the photoisomerization of A-II and only a small effect on the photoisomerization of the polymer.

The deviation of the $I(\delta)$–t plot from linearity in the case of polymer solutions in DMSO containing a high concentration of glycol or glycerol indicates a microheterogeneity of these systems, with the chromophores in two different environments. We believe that these represent aggregated polymer chains from which the hydroxylic nonsolvent is excluded and molecularly dispersed polymer chains. The high viscosity of the system tends, apparently, to slow down the exchange of the chain molecules between these two regions and the photoisomerization is more efficient in the aggregates.

A study of the thermal cis–trans isomerization following the photochemical process when irradiation was discontinued revealed a similar pattern as the photoisomerization data. (This study was carried out at 43 °C, since the thermal reaction was very slow at 25 °C.) Thus, the thermal reaction was slowed down by glycol, but not by methanol addition, and the deviations from first-order kinetics were observed in systems with high glycol or glycerol content. (It may be noted that similar deviations from first-order kinetics characterize the

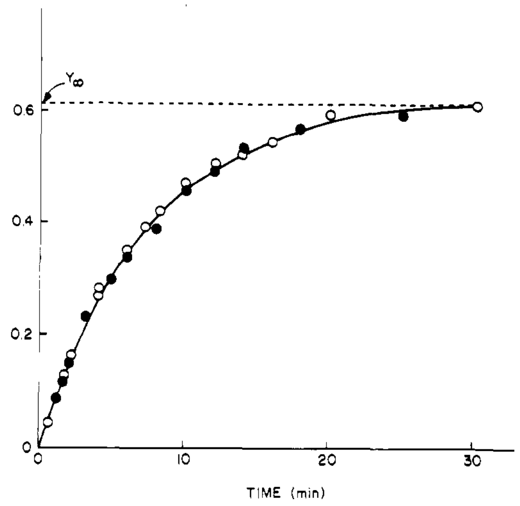


Figure 1. Course of trans–cis photoisomerization of P-I and A-I in dilute solution: (●) P-I; (○) A-I.

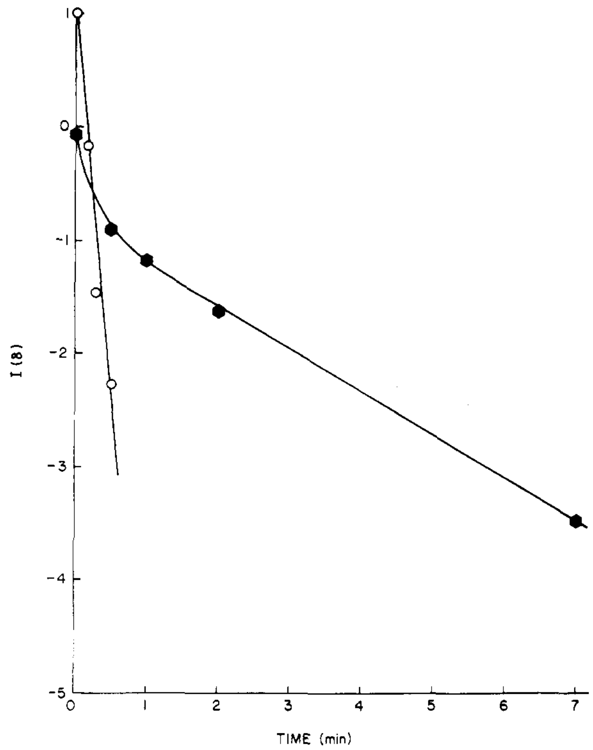


Figure 2. Course of trans–cis photoisomerization of P-IIs in DMSO (○) and in DMSO containing 65 vol % glycerol (●).

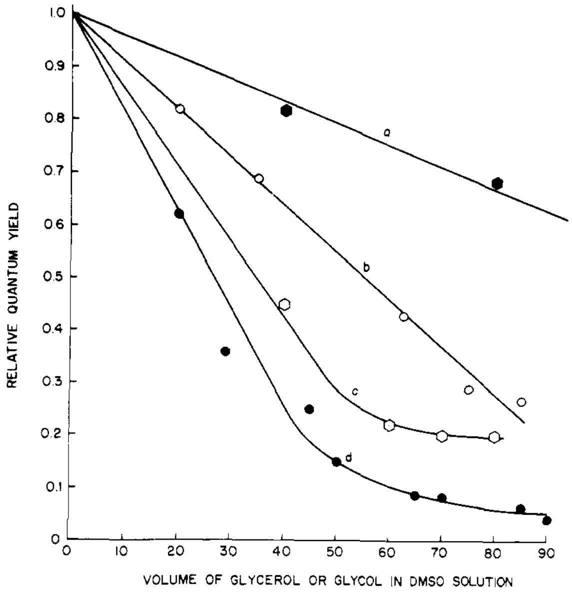


Figure 3. Relative quantum yield of photoisomerization of P-IIs and A-II in mixed solvents: (a) A-II in DMSO–glycol; (b) A-II in DMSO–glycerol; (c) P-IIs in DMSO–glycol; (d) P-IIs in DMSO–glycerol.

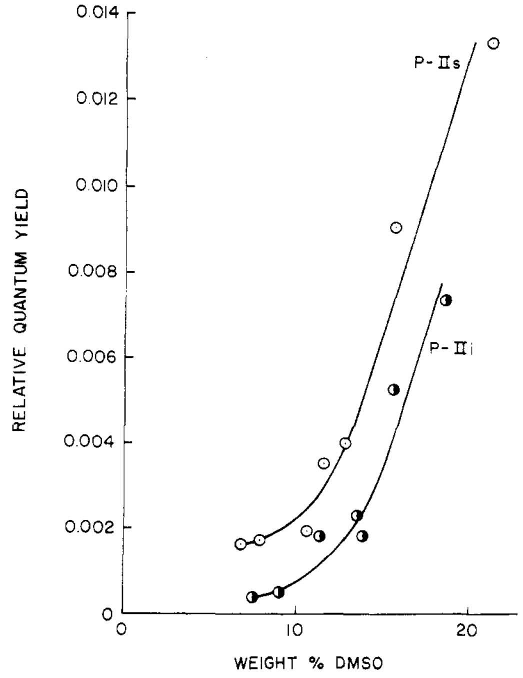


Figure 4. Photoisomerization of P-IIs and P-IIi in films plasticized with DMSO.

thermal isomerization of azobenzene residues in polymer side chains in the glassy state.[4]) When the irradiation time preceding the dark reaction was shortened so that the photostationary state was not attained, the fraction of the azobenzene residues characterized by the faster cis–trans isomerization rate was increased. Thus, it appears that the polymer aggregates which photoisomerize more rapidly isomerize also more rapidly in the reverse direction by the thermal mechanism.

The fraction y_∞ of the azobenzene residues present in the cis form in the photostationary state was found to be 0.90 for both P-IIs and the analogue A-II. Addition of glycerol reduced y_∞, which fell at a 85 vol % glycerol content to 0.46 for the analogue and to 0.28 for the polymer.

Photoisomerization in Concentrated Systems. The quantum yield of the photoisomerization of P-IIs and P-IIi in plasticized films, as compared to the quantum yields observed in dilute solution, is plotted in Figure 4 as a function of DMSO concentration. It may be seen that the relative quantum efficiency decreases rapidly with decreasing plasticizer concentration. For instance, a P-IIs film containing 10.5 wt % DMSO has a photoisomerization rate more than 500 times slower than P-IIs in dilute solution and the relative quantum yield is even lower in plasticized films of P-IIi. Over the range of plastizer concentrations for which the data in Figure 4 were obtained, the polymers were in the glassy state. (Measurement of the glass transition temperature of P-IIi as a function of DMSO concentration led to the estimate that T_g = 25 °C would correspond to 25 wt % of the plasticizer.) Although we were unable to remove all of the plasticizer from

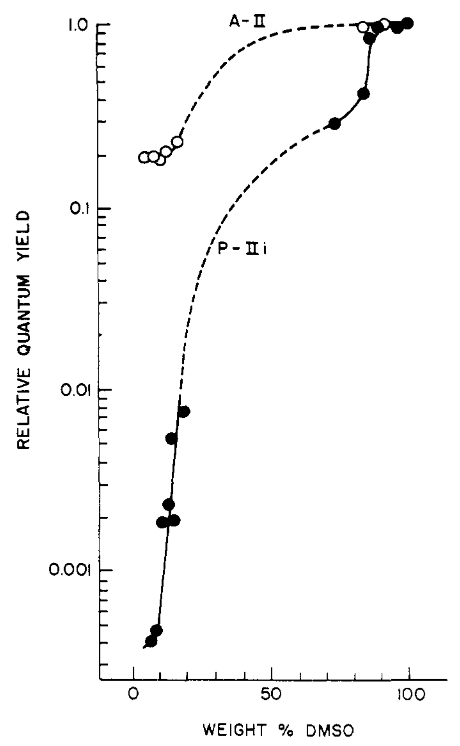


Figure 5. Relative quantum efficiency of trans–cis photoisomerization of A-II and P-IIi as a function of the composition of polymer–DMSO systems.

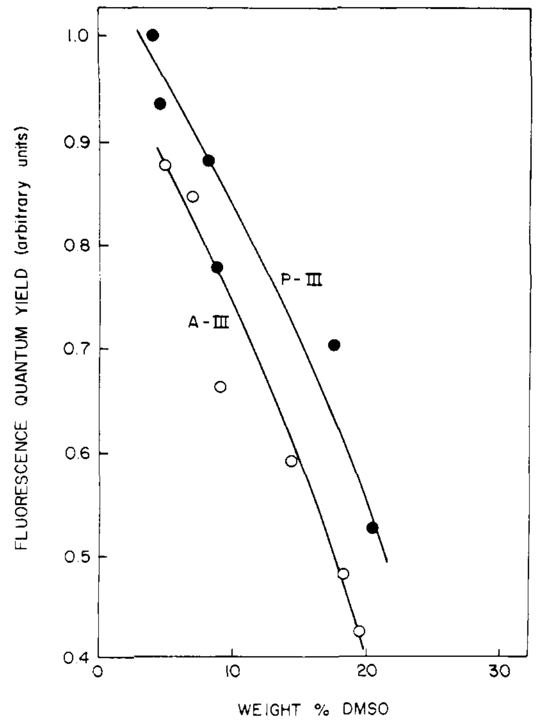


Figure 6. Relative fluorescence emission intensity from P-III films and from polymer films containing the analogue A-III.

the polymer films, the data suggest that photoisomerization in unplasticized samples would be extremely inefficient. Small concentrations of plasticizer increase by a large factor the photoisomerization rate long before the glass–rubber transition point is reached.

In Figure 5 we compare the effect of P-IIi concentration on the relative quantum efficiency of the photoisomerization of the azobenzene residue in the chain backbone with the similar process of the analogue A-II in poly(isophoronediamineisophthalamide)–DMSO systems over the entire concentration range. In the case of the chromophore in the polymer backbone, an abrupt decrease in quantum efficiency is observed at a polymer concentration of about 15%. It may be seen that the analogue photoisomerization is impeded much less in glassy polymer films than a similar process involving the chromophore in the polymer backbone. For instance, when analogue A-II was incorporated in a glassy polymer film with a DMSO concentration below 12 wt %, the quantum efficiency of the photoisomerization was only five times lower than in dilute DMSO solution and it seemed to be independent of the plasticizer content. The composition of the photostationary state is also much more sensitive to the rigidity of the system in the case of the polymer than for the analogue. Thus, y_∞ falls to 0.38 for A-II in a polymer film containing 7.5% plasticizer while it decreases to 0.05 for P-IIi containing 7.7% DMSO.

The viscosity dependence of the trans–cis photoisomerization quantum efficiency for small molecular species has been studied by Gegiou et al.[11] The effects reported by these authors are small; e.g., the quantum yield for azobenzene was at −75 °C, 60% of that observed at 25 °C, although the viscosity of the system was increased by a factor of 10^9. Paik and Morawetz[4] studied the photoisomerization of azobenzene residues attached as side chains to a methyl methacrylate copolymer and found the isomerization quantum yield to be reduced in the glassy films by only about an order of magnitude as compared to the same process in dilute solution. A previous study of a photoisomerization involving a chromophore in a polymer chain backbone was reported by Smets and Evens[7] who prepared films of a polyester with a spyrobenzopyran residue in the chain backbone and found that the photochromism was suppressed in the glassy state. Our results show then, in agreement with previous data, that incorporation of the chromophore into the chain backbone decreases by a large factor the quantum efficiency of photoisomerization in systems containing densely packed polymer chains. This is in striking contrast to the absence of such an effect in dilute solution and must, therefore, reflect the interdependence of polymer conformations in concentrated systems.

Fluorescence. Polymer P-III and analogue A-III exhibited fluorescence with a peak at 420 nm when excited at 360 nm. In the dilute DMSO solution, the fluorescence intensity was three times lower for the polymer as compared to the analogue. We have at present no explanation for this effect, which seems to deserve further study.

The fluorescence intensity of films of P-III containing varying concentrations of DMSO was compared with the dependence on plasticizer concentration of the fluorescence of A-III incorporated into poly(isophoronediamineisophthalamide) films. The results are shown on Figure 6. It may be seen that fluorescence emission is favored by a decreasing plasticizer content. However, in contrast to the results obtained with the photoisomerization, the fluorescence behavior is very similar for the polymer and the analogue. This is, perhaps, not surprising, since dense packing should not affect greatly a process in which the chain conformation remains unaltered. Unfortunately, stilbene derivatives with electron-donating substituents do not photoisomerize[12] so that we could not compare the fluorescence and photoisomerization behavior on the same system. It would be desirable to supplement the present investigation with data obtained with a polyamide containing stilbene dicarboxylic acid residues.

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2. Laser Flash Photolysis Studies on Homo- and Copolymers of Phenyl Vinyl Ketone in Solution

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ABSTRACT: The quenching of triplet excited phenyl vinyl ketone (PVK) base units either by naphthalene or by naphthalene incorporated as comonomer into poly(methyl methacrylate) (PMMA) was investigated. The quenching constant k_Q is about two times lower for homo PPVK than for a micromolecular model compound. For a copolymer of MMA and PVK k_Q was found to be about three times smaller than for homoPPVK which is explained in terms of energy migration along the chain being impossible in the case of the copolymer. Triplet excited PVK units are quenched with naphthalene incorporated in a polymer with k_Q only about two to three times smaller than for naphthalene. These results are believed to be indicative of the fact that PMMA molecules in benzene solution are capable of interpenetrating rather easily. Triplet lifetimes of excited 2,4-dibenzoylpentane and 1,3-dibenzoylpropane are about 70 ns in the absence of oxygen. Oxygen quenches triplet excited ketone groups with the following rate constants in units of M^{-1} s^{-1}: 2.4×10^9 (acetophenone), 2.0×10^9 (2,4-dibenzoylpentane), 1.5×10^9 (co-oligomer of MMA–PVK containing 9 mol % PVK), 5.4×10^8 (copolymer of MMA–PVK containing 2.8 mol % PVK). The difference between the values for low and high molecular weight compounds is explained in terms of differences of diffusion constants based on the assumption that oxygen quenching is occurring as an encounter controlled reaction.

Our laser photolysis studies on polymeric systems have been aimed at elucidating the kinetics of chemical reactions involving macromolecules in solution. Of special interest have been studies concerning (a) reactions between macromolecules possessing only a small number of reactive sites per chain, and (b) reactions of macromolecules possessing a small number of reactive sites with micromolecules (molecules of low molecular weight). Some results along these lines have been reported in part 1.[1] That work pertained to intra- and intermolecular self-quenching as well as triplet–triplet annihilation.

In this paper we wish to report (i) on triplet quenching by micromolecular naphthalene or by naphthalene incorporated as pendant group of a comonomer into PMMA, and (ii) some investigations concerning the interaction of molecular oxygen with triplet PVK units.

Besides various copolymers, micromolecular model compounds and an oligomer sample containing PVK were also investigated.

Experimental Section

A ruby laser (Korad Model K1QS2) was used as photolyzing light source (λ 347.1 nm, half-width of the flashes ca. 25 ns). Further details concerning this and also the actinometry employed have been reported earlier.[1,2]

The syntheses of polymers and copolymers as well as the preparation of samples have been described in part 1.[1] A list of samples used in this work is presented in Table I.

1,3-Dibenzoylpropane and 2,4-dibenzoylpentane were kindly provided by Drs. Hrdlovič and Lukač.

Results and Discussion

(a) Triplet Quenching by Naphthalene. Rate constants for the reaction

$$^3\text{ketone}^* + {}^1\text{Q} \xrightarrow{k_Q} {}^1\text{ketone} + {}^3\text{Q}^* \qquad (1)$$

were determined as described earlier[2] by monitoring the sensitized naphthalene triplet–triplet absorption at λ 413 nm immediately after the flash (ground state naphthalene neither absorbs light of this wavelength nor the photolyzing light at λ 347.1 nm). Straight lines were obtained in all cases when the reciprocal optical density OD^{-1} at 413 nm vs. the reciprocal naphthalene concentration $[Q]^{-1}$ was plotted. Thus, by applying the relationship

$$OD^{-1} = OD_L^{-1} + \Sigma k_1/OD_L k_Q[Q] \qquad (2)$$

the rate constant k_Q was evaluated from the slope of the straight lines. OD_L denotes the optical density obtained by extrapolating OD^{-1} to $[Q]^{-1} = 0$ and Σk_1 the first-order rate constant of triplet decay in the absence of naphthalene. Values of Σk_1 have been reported in part 1.

Results are shown in Table II. Because of the rather broad error limit the determinations were repeated several times. The k_Q values given in the table are averages from at least five or six separate runs. It turns out that k_Q for the model compound 2,4-dibenzoylpentane is about twice as high as for homoPPVK. A similar difference was found by comparing respective k_Q values obtained with butyrophenone and homoPPVK.[2] k_Q values differing by a factor of about 2 are expected for encounter controlled reactions considering the difference of diffusion constants of micro- and macromolecular compounds.[4]

In the case of CP-MMA-PVK-2.8 k_Q is markedly lower than for homoPPVK. A similar situation was encountered with CP-St-PVK-10.8 and CP-VAc-PVK-1.2. This effect may at least in part be due to the fact that energy migra-