Photochemistry of Azobenzene-Containing Polymers

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Overview

Photochemical reactions which occur in small molecules can also be induced to occur in macromolecules. Though, in macromolecular environments there are constraints which are not present on a small-molecule scale, the challenge is to apply fundamental principles to macromolecules which may coil, branch, or be chemically cross-linked increasing the order of complexity. The free volume available to a reactive site or dissolved probe controls the course of photophysical and photochemical processes, for example. Likewise, molecular mobility plays an important role in determining the course of photochemical reactions in polymers and is related to the size of the molecule, the flexibility of the polymer chain, and whether the polymer is in solution or the solid state. In order to fully understand these effects, it is useful to select one or two simple photochemical reactions which are well-known and to study them in a macromolecular environment. Such a photochemical reaction is the cis–trans isomerism of an azobenzene.

I. Photochemistry of Azobenzene: Cis–Trans Isomerism

Azobenzene and many of its derivatives are characterized by reversible transformations from the generally more stable trans form to the less stable cis form upon irradiation with UV or visible light to yield a photostationary composition that is wavelength and temperature dependent (Figure 1). Azobenzene is thus a textbook representative demonstrating the rotoresistant property of the N=N double bond,[1,2] and spectroscopists and photochemists have long been aware of the inversion–rotation mechanistic dichotomy. Many theoretical and experimental papers deal with this subject.[3-10]

The intense absorption at 320 nm due to the π–π^* transition of the trans isomer decreases during such an isomerization, while the absorption maximum due to the cis isomer at 430 nm which is due to the n–π^* transition increases. Thermal isomerism from the photogenerated cis to the trans form is also shown in Figure 1. The thermal isomerization follows first-order kinetics and the slope of a plot of log $(A_\alpha - A_t)$ against time gives the rate. Quantum yields are generally high for the isomerization of azobenzene and there are no competing reactions of significance. Therefore, the cis–trans isomerization of the azobenzene moiety represents virtually a model photochemical process in which one stereoisomer is favored thermally and the other stereoisomer is favored photochemically. The conversion of one isomer to the other is virtually quantitative. There is no known evidence of emission from the excited states of azobenzene either in the cis form or in the trans form, so the photochemical process is entirely efficient, at least to the extent that it can be experimentally traced.

Photoinduced isomerism of azobenzene also proceeds with large structural change as reflected in the dipole moment and change in geometry. The isomerization involves a decrease in the distance between the para carbon atoms in azobenzene from about 9.0 Å in the trans form to 5.5 Å in the cis form, and the local contraction may be even greater.[11] Likewise, *trans*-azobenzene has no dipole moment while the dipole moment of the nonplanar cis compound is 3.0 D.[11] These properties when manifested in polymers are useful probes of conformational dynamics of macromolecules by site-specific photolabeling, in estimating the free volume in cross-linked networks, and in designing photoreactive polymers responsive to external stimuli.

II. Macromolecular Photochemistry

Macromolecular photochemistry involving azobenzene moieties has progressed along two lines. Early[12,13] studies sought to clarify a physical problem.

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Douglas Neckers received his A.B. degree from Hope College in 1960 and his Ph.D. from the University of Kansas in 1963. Following postdoctoral work at Harvard University under Paul D. Bartlett, he held faculty appointments at Hope College and the University of New Mexico before coming to Bowling Green State University in 1974 as Professor and Chair of the Department of Chemistry. Prof. Neckers is Executive Director of the Center for Photochemical Sciences and Director of the McMaster Institute. In 1986 he was named the first Distinguished Research Professor at Bowling Green. He has authored 10 books and over 140 scientific papers and holds a number of U.S. and Canadian patents. Prof. Neckers is an internationally recognized expert in polymer-assisted photochemical processes.

What is the nature of hindered rotation in long-chain molecules? What is the distribution of free volume in the glassy state? What is the flexibility of chain molecules? Later studies concentrated on the photochromic properties of the materials. Since azo labels can be selectively attached to the side chains, main chain, cross-links, or chain ends of the polymer as photochromic "probes", selective site labeling allowed one to identify motion associated with a specific location on the polymer chain. By varying the molecular structure and the polymeric system, as well as by inhibiting the motion of the polymer matrix, it was possible to construct materials having photochromic characteristics.

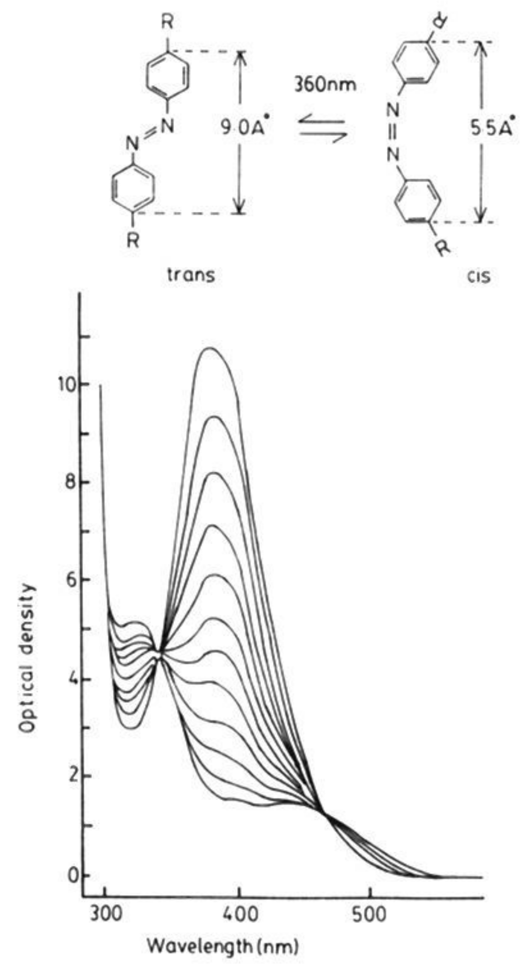


Figure 1. Absorption spectra of azobenzene in $CHCl_3$ showing thermal recovery (T = 28 °C) and geometrical changes.

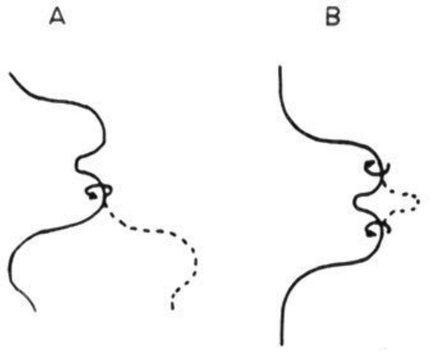


Figure 2. Schematic representation of conformational transition in a flexible chain molecule: (A) rotation around a single bond; (B) correlated rotation around two bonds.

In that the need for polymer materials is changing from structural materials to functional materials, the current trend is to employ the azobenzene moiety as a "trigger" to induce morphological changes which can be light driven. The applications are as a chemical valve or as a light-induced porous filter of differing, and easily controlled, porosity. Chemical substances which exhibit photoinduced structural changes are candidates not only to become chemical condensers for the storage of light energy but also to be used as mediators of light energy for chemical functions. The possibility thus arises that since conformations of azobenzene-containing polymers can be controlled by using photoinduced changes of the azobenzene moiety, they may provide light-controlled chemical functions. Expectedly, this would lead to the possibility of controlling the chemical functions by an "on–off light switch".

III. Dynamics through Kinetics: Azobenzene as a "Probe"

The investigation of the chemical and physical behavior of the photochromic moieties in polymeric matrices and the influence of polymers on photochromism is relatively recent. While Flory's[14] demonstration that the attachment of a functional group will, in many cases, not lead to an altered activity of a polymeric material, a number of interesting effects may be observed in special cases.[15] Differences in reaction rates of specific functions were expected and found at the ends of polymer chains, along the chain, and at irregularities within the matrices. From the literature, the nature and the morphology of a polymer chain have an essential influence on the photo- and thermochromism of a chromophore in a given polymer matrix.[12,13] The size of a chromophore, its shape, its conformation, and its point of attachment to a polymer chain also play a role in determining the effective free volume available to an isomerizable group. A comparison of results of different authors is difficult because the systems investigated and the experimental conditions employed are too idiosyncratic; besides, no meaningful theories exist as to how photochromic processes are linked to polymer properties. The regional arrangement of the polymeric environment, i.e., macroscopic and microscopic values of polarity, viscosity, T_g, and tacticity, as well as the history of the sample can affect photochemical or photophysical events. Nevertheless some trends have evolved, and we explore these trends below.

A. Backbones: "Crankshaft-like Motion"

While conformational distribution in flexible chain molecules has been the subject of intense theoretical and experimental study ever since Kuhn's pioneering work,[16] the dynamics of conformational transitions have become of interest only relatively recently. It is theorized that conformational transitions in the backbones of long polymer chains must involve two correlated hindered rotations (a so-called crankshaft-like motion) so as to avoid the need for a long chain segment to swing through the viscous solvent medium (Figure 2).[17] If this model is correct, the free energy of activation should be substantially higher for hindered rotation in polymer backbones than for a similar process in a small molecule, resulting in a large decrease in the rate of conformational transition.[17] Zimmerman et al.[4] suggested that the photoisomerization of azobenzene involves a thermal reaction between the excited trans and cis states which is separated by a low-energy barrier. This concept was later confirmed by Fischer and Malkin,[5] who showed that the temperature dependence of the quantum yield for the trans–cis photoisomerization led to an estimate of a 2–3 kcal/mol energy barrier separating the two excited states. Such a low value for the energy barrier between the trans and cis excited states of azobenzene makes the study of photoisomerization of azobenzene residues in the backbone of polymers and their analogues eminently suitable for the characterization of the general behavior of conformational transitions involving low-energy barriers.

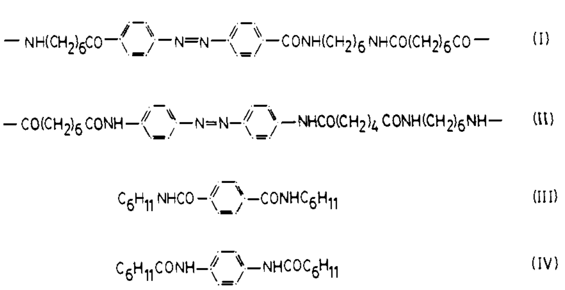


Figure 3. Polyazoaromatic amides (I, II) and model compounds (III, IV).

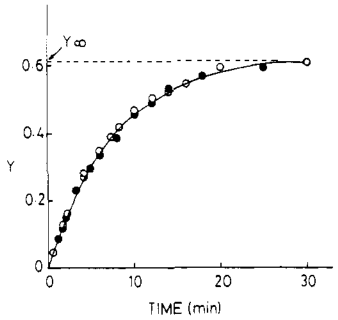


Figure 4. Course of photoisomerization of I (●) and III (○) in dilute solution. Y_∞ is the fraction of *cis*-azobenzene residues at the photostationary state.

The photoisomerization of polymeric trans azo compounds was initially studied by Morawetz and coworkers,[18-20] who first demonstrated that such provided the opportunity to observe what effect an azo linkage incorporated into the chain would have as compared to their corresponding low molecular weight analogues. Two series of modified nylon 66 polyamides were synthesized (Figure 3) by Morawetz. The isomerization about the azobenzene –N=N– bond was followed kinetically by UV spectroscopy such that any dispersion of rate constants could be characterized. Irradiation of the trans polymers I and II in formic acid solution produced photostationary states comprised of mixtures of polymers differing only in cis–trans azo linkages. Morawetz and Tabak[18] studied the dark reaction and found no difference between the rates of isomerization of azobenzene residues in the chain backbone when compared with their low molecular weight analogues. However, this data provided no conclusive evidence against the crankshaft motion, since the chain contained many bonds with much lower energy barriers. Chen and Morawetz[20] studied the rate of photoisomerization, where the energy barrier is low, and found that at high dilution the polymer and the low molecular weight analogue behaved in a similar manner (Figure 4). However, when the photoisomerization of the low molecular weight compound was followed in solutions containing added polymer, the rate of its isomerization changed very little, while the photoisomerization rate of azobenzene polymers had their rate reduced by many orders of magnitude, because of the cooperativity of conformational changes in the polymer chains. Thus the "crankshaft-like" motion has now been conclusively disproved both by computer simulation[21] and experimentally.[22]

Kumar et al.[23,24] reported that the introduction of azobenzene groups in the main chain of polyureas does not impede photochemical isomerization in dilute solution. A series of azo polyaromatic ureas were thus synthesized incorporating pyridine moieties as polymeric ligands. The activation energies for cis–trans thermal isomerization of these polyureas suggest similar

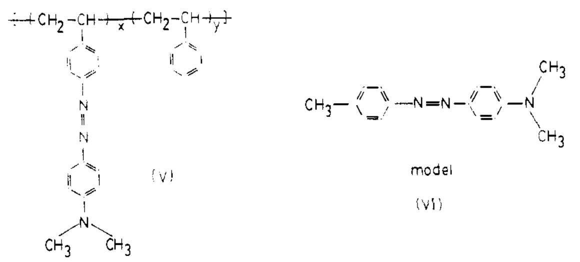


Figure 5. Structures of styrene copolymer with pendant (dimethylamino)azobenzene (V) and corresponding model compound (VI).

energy barriers to low molecular weight analogues as well as to polymers with different molecular weights and chain segments. Lamarre et al.[25] reported that, in dilute solution, the ability of the azo moiety to isomerize photochemically is not strongly influenced by the composition of the polyurethane chain, since the choice of a particular diol used for the polymer does not make much difference to the *A* values. In view of the much faster scale of photoisomerization in comparison to the motions of the polymer chain as demonstrated by Irie and Schnabel,[26] these observations are not surprising. By using flash photolysis, Irie and Schnabel reported that the cis–trans photoisomerization of the azobenzene moiety in an aromatic polyamide in solution occurs to about 90% during a 20-ns flash, with the remaining 10% complete within 100 ns after the flash. They also measured the relaxation time due to the conformational change of the total molecule in dilute solution following photoisomerization, using a time-resolved light scattering measurement. It was found to be about 1 ms—much slower than the photochemical reaction.

B. Side-Chain Effects

Copolymers containing an azo group in the side chain have been investigated by Kamogawa et al.,[27-30] who prepared several model azo compounds for comparison with the corresponding appended polymer species. The azo-bearing polymers and their models were compared in solution as well as in the film form (Figure 5). By measuring the recovery half-time periods they found that the reaction was slowest with comonomers which increase the rigidity of the chain, e.g., styrene or methyl methacrylate, as compared to methyl acrylate. As expected, recovery times were 5 times longer in polymer films than in solution. One can propose that the photoisomerization step from trans to cis induces local strain or an increased stric interference, and it is this increased local steric strain which causes the increased rate of thermal return. The effect was particularly noticeable in two cases where the azo group was appended to the polymer backbone in a manner meant to cause an unusual degree of steric interference. These investigations infer that photochemically induced strain assisted the thermal return in both systems where the azo groups are appended to the polymer chain, particularly in cases where the polymers were suspended in matrices.

Studies of polymers in bulk were pioneered by Morawetz and Paik,[19] who found that the dark reaction of azobenzenes fixed as polymer side chains had the same rate of return both in rubbery polymers and in dilute solution. In the glassy state, an anomalous fast component was observed, an effect reported previously by Priest and Sifain[31] for small azoaromatics dissolved in glassy polymers. Priest and Sifain interpreted this as evidence for the nonuniform distribution of free volume in the nonequilibrium glassy state. Important work on the volume of relaxation of glassy polymers as studied by means of the kinetics of a photochemical isomerization was reported by Sung. In the system studied a fraction of the azobenzene residues isomerizes very slowly and that fraction is a function of the distance from the glass transition temperature.[25] The magnitude of T_g depends on the way the azobenzene is attached to the polymer.[32] In a brilliant recent paper,[33] the time of dependence of T_g for azobenzenes attached to polystyrene in different ways is interpreted in terms of the changes in free volume distribution during volume relaxation.

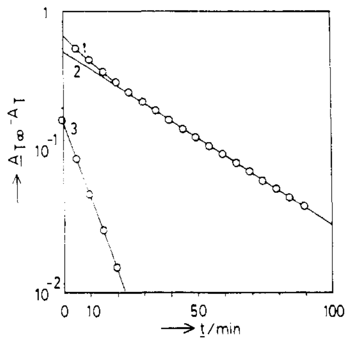


Figure 6. Resolution of the thermal cis–trans isomerization of the azo chromophore in a copolymer of ethyl methacrylate at 70 °C using two first-order reactions. A_∞ and A_t are the absorbances at λ = 353 nm at infinite time and at time *t*: (1) experimental curve; (2) normal isomerization curve; (3) fast reaction curve (Eisenbach, C. D. *Makromol. Chem.* **1978**, *179*, 2507).

More recently, a similar photochromic behavior was observed by Eisenbach[34-37] for the cis–trans isomerization of azobenzene residues attached as side groups to copolymers when examined below their glass transition temperature T_g. These copolymers were obtained by the copolymerization of the monomers 4-(methacryloylamino)azobenzene and various acrylates and methacrylates. In solution and in the rubbery state the thermal recovery follows first-order kinetics (Figure 6); however, in the glassy state some azo groups react anomalously fast, while others isomerize much slower nearly at the rate observed in solution. The decoloration curves can be resolved into two simultaneous first-order reactions. Most striking is the dependence of the rate of bleaching in the neighborhood of the T_g of the copolymer. The change of E_a and activation entropy around T_g was interpreted on the basis of physical changes of the polymeric environment, i.e., an important increase in the chain segment mobility and consequently of the free volume above T_g.

The temperature dependence of melt viscosity at temperatures considerably above T_g approximates an exponential function of the Arrhenius type. However, near T_g the viscosity–temperature relationship for many polymers is in better agreement with the Williams–Landel–Terry (WLF) treatment.[38] These authors showed that with a proper choice of reference temperature, T_g, the ratio of the viscosity to the viscosity at the reference temperature could be expressed by a single universal equation—the WLF equation.

Eisenbach[34-37] also showed the general validity of the WLF equation in the interpretation of the photo-

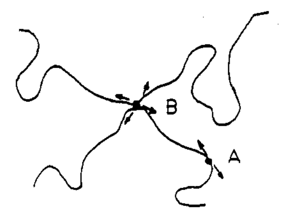


Figure 7. Schematic representation of the restrictions acting on a polymer segment in a chain (A) and near cross-link functions (B).

chromism of azobenzenes and spiropyrans linked to amorphous bulk copolymers. Eisenbach used the WLF equation directly:

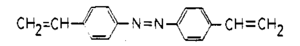
$$\log a_t = -C_1(T - T_g)/(C_2 + T - T_g)$$

where a_t is the ratio of the relaxation time at T to that at T_g ($a_t = KT_g/KT$). On the basis of this equation, he determined graphically the C_1 and C_2 for several photochromic systems. The corresponding numerical values were nearly constant for a group of polymers, e.g., for photochromophores either dissolved in different polyacrylates and polymethacrylates or attached to the latter as side groups. They differ, however, considerably below and above the T_g of the polymer system. It should be noted that these experimental C_1 and C_2 values differ markedly from the universal WLF constants. It is likely that the photochromic behavior is mainly controlled by the free volume distribution around the photochrome, which is different from its usual random distribution.

C. Cross-Links

The local orientation of rubber-like materials is of considerable interest for the understanding of the overall mechanical behavior of these materials. The experimental results are mainly interpreted by inferring that there is a greater degree of orientation of the chain segments near cross-link junctions. This concept can be rationalized by taking into account that near a cross-link junction the restrictions acting on a chain segment mainly arise from branches while only two chain branches act on segments in the chain (Figure 7). Conformational restrictions, as a consequence, should be a function of the crosslink density. A crucial test of this concept involves direct measurement of the restrictions. One possible method to make such direct measurements is to introduce conformational changes by a chemical reaction and to detect the response of the elastomeric network to this disturbance.

Kumar et al.[39] investigated the question of how the photochromism of azo groups lodged in the cross-links would be influenced by the nature of the polymer matrix and by the presence or absence of spacer groups separating them from the main chain. As found in linear or branched polymers, photochemical trans–cis isomerization of the azobenzene units in the cross-linked polymers results from irradiating at 360 nm. A series of cross-linking agents containing azobenzene units with amide and sulfonamide spacer groups were prepared (Figure 8). UV irradiation creates the cis isomer in high yields in every case except VIII. A bulky substituent next to the azobenzene functionality seems to retard the photoisomerization process in the case of VIII.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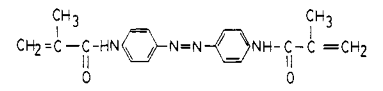
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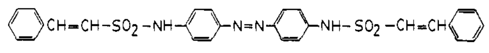
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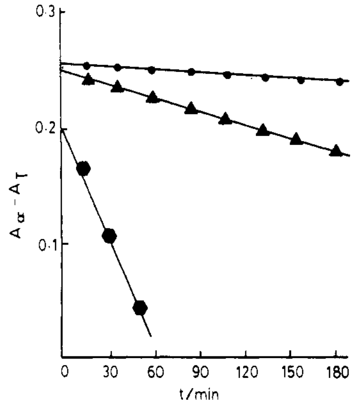
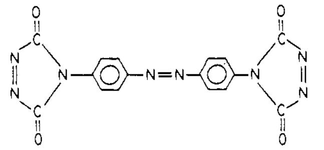


Figure 8. First-order plots for the thermal cis–trans isomerization of the azo chromophore with different spacers in cross-links of polystyrene (A_∞ and A_t are absorbances at 350 nm at infinite time and time t) (temperature, 30 °C; solvent, CH_2Cl_2): (●) cross-linked with VI; (▲) cross-linked with VII; (●) cross-linked with VIII.

When the first-order plot thermal isomerization rates are compared (Figure 8), it is evident that the back reaction is not affected so much by the nature of the polymer matrix, but by the way the chromophore is fixed. The rate of thermal recovery is fastest in the case of the sulfonamide spacer group having an adjacent phenyl group, thus pointing out the importance of the structural and steric environment surrounding the cross-links.

Stadler et al.[40,41] prepared swollen gels of polyisobutylene cross-linked with compound IX.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The butyl rubber gels are highly swollen and thus the isomerization behavior should be similar to that of dissolved polymer. The reaction rate constant for thermal reorganization was observed to depend on the cross-link density. From measurements at various temperatures it is deduced that the activation enthalpy remains unaltered. The observed temperature dependence of the reaction rate constant is the result of the dependence of the activation entropy on cross-link density. The dependence of the isomerization rate on the cross-link density can be interpreted in terms of the classical theory of rubber elasticity (Figure 9). Isomerization causes a decrease in the conformational entropy of the chains. The corresponding elastic retractive forces induce a faster cis–trans isomerization. These results seem to be in contrast to those of Eisenbach,[35] who deduced from kinetic measurements that cross-linking itself, and also the degree of cross-linking, retard the thermal isomerization process. A more detailed analysis of the data however shows that this dependence reflects the different T_g's of the systems

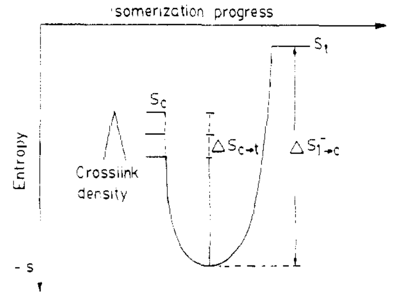


Figure 9. Schematic representation of the entropy changes for the isomerization process in the networks (Sadler et al. *Polymer* 1986, *27*, 1254).

investigated, so that the observed rate constants depend primarily on the viscous properties of the surrounding polymer matrix. They can be interpreted in terms of the effective free volume concept, where generally the differences in the activation enthalpy are considered. In these studies, the effect of the surrounding matrix diminishes because the T_g of the gels is far below the temperature of the measurement. Owing to the high mobility of the swollen state, the chains immediately reach their conformation corresponding to the thermal equilibrium. As a consequence, the activation enthalpies are constant, which is not the case for polyacrylate networks.

Sung et al.[42,43] reported a technique for characterizing epoxy cure by an azo chromophore labeling technique. A small amount of *p,p'*-diaminoazobenzene (DAA) was used as a reactive label in a model epoxy consisting of diglycidyl ether of bisphenol A (DDGBA) and diaminodiphenyl sulfone (DDS). The reactivities of DDS and DDA are similar and hence allow one to follow the cure process by the spectral changes of DAA occurring above 400 nm. As the epoxy is cured, the maximum of the $\pi-\pi^*$ transition corresponding to the azo bond of DAA shows red shifts allowing the spectral discrimination for four major cure products, namely, cross-links, branch points, linear chains, and chain ends. Deconvolution of the UV–vis spectra based on the band assignments of the model compounds representing cure products provides a quantitative estimate of the four cure products as a function of temperature or cure time. DAA-labeled epoxy (DGEBA-DDS) also exhibits very sensitive changes in fluorescence intensity corresponding to the emission by the DAA label as a function of cure extent.

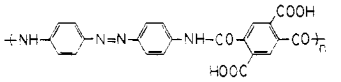
IV. Photoresponsive Polymers: Azobenzene as a "Trigger"

A photoresponsive synthetic polymer is a speciality polymer having photoreceptor chromophores which can transfer light energy into a change in the conformation of the polymer.[44] The light is stored at once in a chemical structure change of the chromophore and then transferred into the polymer chain, causing reversible conformational changes. The conformational change is expected to produce a concomitant change in physical and chemical properties of the polymer solutions and solids. The basic idea for controlling properties of polymers by photoirradiation is to use photoresponsive trigger molecules. Several examples of photostimulated physical property changes of photoresponsive polymers having azobenzene residues are described. Some of the physical and chemical properties which are reversibly controlled include (a) viscosity, (b) conductivity, (c) pH, (d) solubility, (e) wettability, and (f) mechanical properties.

A. Photoviscosity Effects

The viscosity of a polymer system is a rather direct reflection of the polymer conformation. The constitution of azoaromatic polymers containing azobenzene units in the backbone suggests that these polymers would behave like semiflexible rods in solution. The extended rodlike shape of the semiflexible chain is expected to shrink rapidly to a compact conformation when the configuration of the constituent azobenzene units changes from the trans to the cis form. This results in the change in viscosity of the polymer solutions and it is termed the photoviscosity effect.[45]

Irie et al.[46,47] synthesized the following polyamides in an attempt to control solution viscosity of polymers X–XIV. The intrinsic viscosity of polymer X in *N,N*-dimethylacetamide decreased from 1.22 to 0.5 on UV irradiation (410 > λ > 350 nm) and returned to the initial value in 30 h in the dark at 20 °C. The slow recovery of the viscosity in the dark was accelerated by visible light irradiation (λ > 470 nm). With alternating irradiation using UV and visible light, the viscosity reversibly changed by as much as 60%. The similarity of the response of viscosity and the trans form content to photochemical irradiation suggests that the photodecrease and photoincrease of the viscosity directly correlate with the isomerization of the azobenzene residues in the backbone. When the azobenzene units are connected by rigid phenyl groups, the resulting viscosity change should be large, while viscosity changes become small when the connecting groups are flexible such as in long methylene groups. Irie et al.[46] demonstrated the latter by showing the absence of a photoviscosity effect when the methylene chain is long enough to act as a strain absorber.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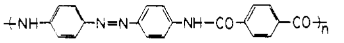
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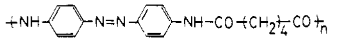
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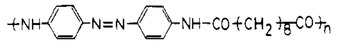
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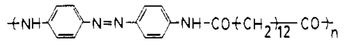

(XIV)

Similar experiments were carried out by Blair et al.[48] using polyamides having azobenzene residues in the backbone of polymers. These workers observed no decrease in viscosity under UV action although a small decrease was detected in the reduced viscosities at high concentrations. The absence of a photodecrease in viscosity in these systems is likely due to the inclusion of flexible piperazine segments in the polymer chains.

Kumar et al.[23,24] reported the photochemical viscosity decrease for a new class of azoaromatic polyureas. Since there is no effect of concentration on the viscosity of the sample, this photodecrease has to arise from a conformational change of the polymer chain and not from interchain interactions. The relationship of the

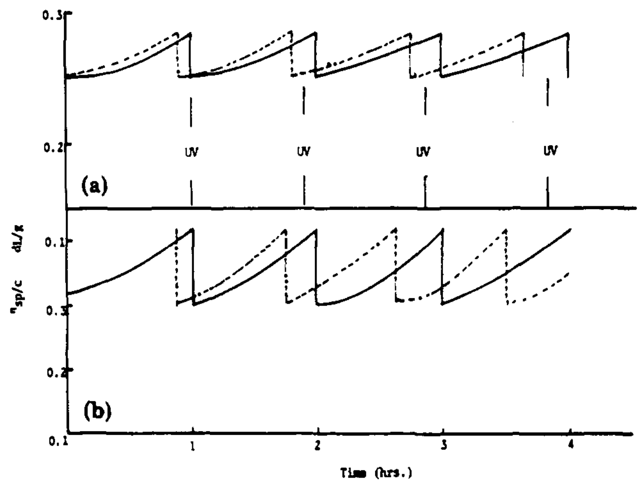


Figure 10. (a) Changes of the trans form of azobenzene residues in polyureas derived from diaminopyridine, MDI, and diaminoazobenzene (PU-MDU-DAP). (b) Viscosities of same polymer solution upon alternate irradiation at 35 °C. (—) In the dark; (···) in visible light (Kumar et al. *Macromolecules*, 1984, *17*, 1912).

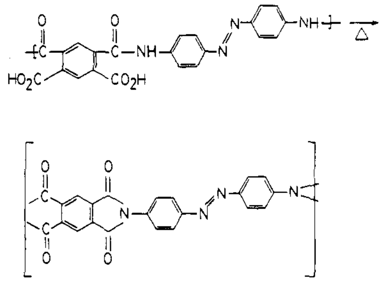
thermal recovery of the original viscosity to the recovery of absorption intensity is compared in Figure 10. These two plots effectively superimpose, indicating that the contraction of the macromolecular volume is indeed induced by the isomerization of the azobenzene residues and that slow thermal recovery expands the chain conformation.

Lovrien and Waddington,[49] in pioneering work, designed two systems for controlling polymer conformation by light. In the first a polyelectrolyte bears covalently bound side chains capable of undergoing photochromic trans–cis isomerization. The net charge on the polyelectrolyte tends to extend the polymer via electrostatic forces, and the trans forms of the side chains generate nonpolar interaction forces that tend to contract the polymer. Illumination generates cis forms, changing these hydrophobic interactions somewhat and causing the polymer to reach new equilibrium by expansion of the coil. Photoresponsive materials of this first type were prepared by copolymerizing acrylic or methacrylic acid with 4-acrylamidoazobenzene or its 2,2-dimethoxy derivative. Viscosity increases were expected and were found in these systems upon irradiation.

B. Photomechanical Effects

To what extent conformational changes of the chromophores and connected chain segments of a photochromic polymer may induce changes of dimensions of bulk polymers and thus generate reversible photomechanical effects is an area of great interest. From the organic point of view, a reversible dilation/contraction phenomenon should be observed in photochromic networks above T_g, i.e., in the rubbery state where segment mobility is important. Considering that the isomerization occurs in the rubbery state at a rate similar to that in solution, it should be expected that the use of isomerization reactions for photocontractile behavior should be optimal with easily deformable networks.

Photoisomerizable groups incorporated into a polymer framework have been shown to cause reversible contraction or expansion of polymer samples upon irradiation. Agolini and Gay[50] prepared a polyimide containing azoaromatic groups in the backbone as shown in XV. The final imide polymer was obtained

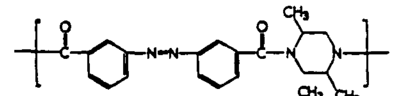


XV

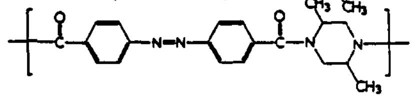
in a semicrystalline film containing the azo group predominantly in the trans form. These films contracted on heating and irradiation, due, in part, to the isomerization from the trans to the cis form in the amorphous regions of the film. However, the rates of contraction and dilation were not controlled linearly by the rate of isomerization. Stress was produced slowly when a sample held at a constant length was irradiated. In the dark at lower temperatures the films returned to the unstressed form.

Similarly, reversible contraction/dilation experiments under constant load were recently performed by Eisenbach[51] on stretched poly(EA) networks, cross-linked with 4,4-bis(dimethacryloylamino)azobenzene. Upon irradiation trans–cis isomerization caused conformational changes of adjacent network segments, which are considered to be responsible for the photomechanical effect, though the observed contraction amounted to only about 0.15–0.25%.

Blair, Pogue, and Riordan[48] described photoresponsive effects in photochromic polyamides in which every monomer unit contains an azo group. The systems investigated were the 3,3-azodibenzoyl-*trans*-3,5-dimethylpiperazine and its 4,4 isomer (XVI, XVII). On



XVI



XVII

irradiation the measured stress increases, indicating a contraction of the sample up to a photostationary state; in the dark the stress decreases again. The cycle can be repeated many times. Here again the relaxation time in the dark is much more rapid than the normal cis–trans isomerization in solution and should be due to the isomerization of a small fraction of azo residues on the local strained nonequilibrium sites in the polymer matrix.

Blair et al.[48] have also carried out Langmuir film balance measurements on monolayers of the photochromic polyamides mentioned above. Changing from dark to light, reduction in area per monomer unit was observed. This was interpreted as resulting from azo trans to cis isomerization. The differences between the pressure–area curves of the meta and para polyamides were interpreted on the assumption that the para compound is linear while the meta compound is helical.

Besides the photomechanical effects observed on rubbery networks and swollen gels, photocontractility of the photochromic systems in the solid state without the chemical cross-linking agent has been described. In some cases possibly partial crystallinity and eventually hydrogen bonding ensure physical cross-linking and consequently a network structure. In most simple cases, the photosensitive compounds were dissolved in a polymeric matrix, and the effects are based on the interactions between the dye and the polymer substrate molecule.

C. Reversible Solubility

When photoisomerizable chromophores are incorporated into the backbone of a polymer chain or as pendant groups, photoisomerization of the chromophores will affect the physical properties of the polymers and the polymer solutions, especially if the isomerization involves a change of polarity. Changes of dipole moments of pendant groups upon photoirradiation alter the balance of interchain interaction, resulting in expansion/contraction of the polymer chain. Irie et al.[52] reported the reversible solubility change of polystyrene (PS) in cyclohexane. PS with a small amount of azobenzene pendant groups (5 mol % of monomer unit) became insoluble in cyclohexane upon irradiation with UV light, while low molecular weight azobenzene itself did not show any solubility change upon photoirradiation. On visible irradiation, the polymer again became soluble. The dynamics of the formation of the precipitation in cyclohexane was studied by a laser photolysis measurement combined with a light scattering detection method. The precipitation of the polymer upon irradiation with UV light was followed by measuring transmittance at 650 nm, where azobenzene has no absorption. In cyclohexane, intermolecular interaction between polystyrene and the solvents is in balance with the intra- and interpolymer interactions. The dipole moment increase of the pendant groups by UV irradiation is considered to alter the balance of polymer–solvent and polymer–polymer interactions. The introduction of the nonpolar trans form azobenzene into polystyrene pendant groups scarcely affects the polymer–solvent interaction in cyclohexane while the polar cis form tends to decrease the polymer–solvent interaction. Therefore, upon UV irradiation, the polymer–solvent interaction decreases until the polymer precipitates. The amount of precipitation sharply increased when the azobenzene content exceeded 5 mol % of monomer units. Isomerization of a few mole percent of azobenzene units in the polymer chain is thus enough to cause a solubility change of the polymer. Recently, Irie et al.[53] also reported a reversible change of the phase separation temperature of aqueous polymer solutions by photoirradiation. Photocontrol of the phase separation temperature of aqueous solutions of poly(*N*-isopropylacrylamide) by introducing azobenzene moieties into the pendant groups was achieved by copolymerization of *N*-isopropylacrylamide with *N*-(4-(phenylazo)phenyl)acrylamide.

D. Reversible Surface Free Energy: An Interfacial Approach

The surface free energy of a solid is an important feature of printing, dyeing, and adhesion.[54] If surface free energy, which is an inherent value of the material, can be controlled by external physical signals such as light, wide application for the preparation of new materials is expected. Ishihara et al.[55–57] have synthesized photoresponsive polymers that contain photochromic azobenzene groups in their side chains. In one such example, the contact angle formed by water on the surface of the film prepared from *p*-(phenylazo)acrylanilide–2-hydroxyethyl methacrylate copolymer is changed by the photoisomerization of the azobenzene moiety. Additionally, photoinduced changes in the surface free energy of the azoaromatic polymer, prepared by the introduction of the azobenzene groups into the side chains of hydrophilic poly(HEMA) was demonstrated.

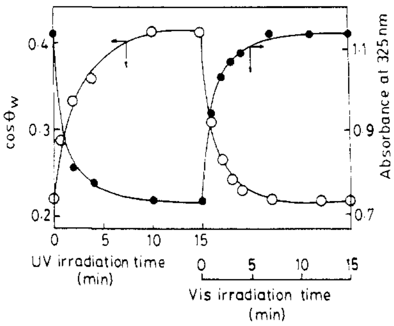


Figure 11. Photoinduced change in wettability and absorbance of azoaromatic polymer films. θ_w is the contact angle by water. (●) UV light (350 nm); (○) visible light (<470 nm). Photointensity, 14.5 mW/cm^2; composition of azobenzene moiety, 0.387.

Figure 11 shows the change in the wettability of the polymer surface by water as it relates to the absorbance at 325 nm, which corresponds to a peak for the *trans*-azobenzene moiety when a film of the azoaromatic polymer above was irradiated. When irradiation is carried out, the absorbance of the trans form decreased with irradiation time and the photoequilibrium was obtained within 15 min. The absorbance change was accompanied by an increase in the wettability of the surface of the polymer film. If irradiation by visible light follows, the absorbance of the trans form returned to its original level and the wettability decreased once again. The results indicate that the wettability of the polymer surface can be regulated by the photoisomerization of the azobenzene moiety. Irie et al.[58] also reported that the contact angle of water on butyl methacrylate–2-(hydroxyphenyl)-4-(vinylphenyl)benzyl alcohol copolymer surfaces increased greatly upon UV irradiation and reversed in the dark.

It was demonstrated that a reduction in the hydrophobic interaction brought on by photoisomerization greatly contributes to the desorption of azo dyes from the adsorbent.[55] Water-soluble polymeric azo dyes were prepared, and the photoinduced adsorption/desorption behavior of the surfactant was examined.

Ishihara et al.[59] also reported the regulation of the hydrophobic chromatography for proteins by light. Polymeric hydrophilic adsorbents containing an azobenzene moiety as a ligand were prepared, and the photoinduced adsorption/desorption behavior of proteins was investigated. The separation of protein mixtures was also investigated by using a gradient column which consisted of two polymeric hydrophilic adsorbents having different hydrophobicities.

E. Photochromic Polypeptides: Helix Reversal

Visual purple (rhodopsin) is composed of a polyene aldehyde (retinal) and a protein (opsin). When rhodopsin absorbs light, its retinal component undergoes

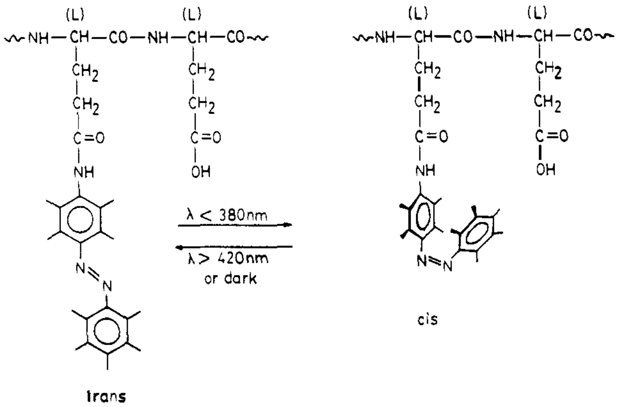


Figure 12. Cis–trans isomerism of azo chromophore bound to poly(L-glutamic acid).

photoisomerization accompanied by a change in conformation of opsin.[60] This light-induced conformational change is a trigger which excites the nerve cells of the rods of the retina. Recent progress in polypeptide chemistry has prompted several workers to construct systems analogous to that in the visual excitation which permits light-induced conformational changes of polypeptides.

The idea of studying conformational changes induced by light on modified polypeptides was originally due to Goodman et al.[61,62] Photoinduced conformational changes of polypeptides, however, were first observed by Ueno et al.[63–69] with azobenzene-containing polyaspartates in solution (Figure 12). They found that photoresponsive polyaspartates can undergo a photoinduced conversion of secondary structure in solution. These workers also reported that the backbone conformation of azobenzene-containing polyaspartates, which undergo a photoinduced conformational transition in solution, could not be changed by irradiation in the solid membranes.[70] Ciardelli et al.[71] studied water-soluble azo-modified PGAs in an aqueous solution and reported photoinduced α-helix-coil and β-structure-coil transitions that depend on the azo group content and pH value of the aqueous solution at which irradiation is carried out. The CD spectra of an azo-modified PGA solid membrane containing 14 mol % of azo groups, which are adapted in the dark or irradiated in water (pH 6.2), revealed that the UV irradiation does not induce any changes of the backbone conformation of the membrane. Later work was concerned with photoisomerization of the azo moieties in polymers of phenylalanine, aspartic acid, and L-lysine.[72–74]

F. Reversible pH Change

Light-induced pH change is of particular interest in connection with the function of bacteriorhodopsin. Bacteriorhodopsin, found in the purple membrane of Halobacteria, uses light energy to translocate protons across the membrane. The cell uses the energy stored in the electrochemical gradient for ATP synthesis.[75]

Photocontrol of the conformation of poly(methacrylic acid) in solution at degrees of ionization of 0.2 (pH 4.5–5.5), at which the polyelectrolyte molecule uncoils, is possible with the use of cationic ligands based on (*p*-phenylazophenyl)trimethylammonium iodide or the copolymers of such a cationic ligand.[76] Solutions of poly(methacrylic acid) with cationic ligands exhibit a decrease of 0.2 in the pK on trans–cis photoisomerization, caused by a change in the degree of coiling of the polyelectrolyte molecules. The photochromic copolymers also display an induced photochemical jump in pK when the azo groups pass into the cis form. Since pK = pH + log $\{(1-\alpha)/\alpha\}$, the degree of ionization of poly(methacrylic acid) modified by photochromic groups, and hence the conformation of the polyelectrolyte, should be controlled photochemically in buffer solutions.

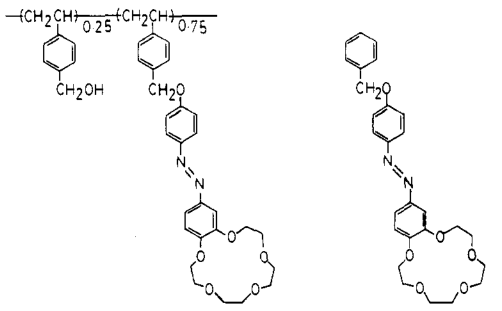


Figure 13. Photoresponsive crown ethers.

Irie et al.[52] reported that the electrical conductivity of *N,N*-dimethylacetamide solution containing polymer X exhibited a response on alternate irradiation of UV and visible light. The response of the conductivity correlated well with the isomerization of the azobenzene residues in the backbone. The correlation suggests that dissociation equilibrium of amide-substituted terephthalic acid residues in the polymer backbone is influenced by conformational change of the polymer chain. Dissociation of the acid is stimulated in the compact or shrunken conformation, while the extended conformation depressed the dissociation.

G. Photoresponsive Metal Ion Chelation

Host molecules have drawn considerable attention as simplified enzyme model systems. It is well-known that specificity is based on the spatial "fitness" between host and guest molecules. It is, therefore, expected that if the conformation of a host molecule is somewhat distorted by a change in the photoinduced "trigger", it would lead to a change in the binding ability. If this really occurs, one can control the functions of the host molecule by light. With these objects in view, Shinkai et al.[77–80] combined crown ethers as a functional group with azobenzene as a photoantenna and have attempted the photocontrol of the crown ether functions. They reported that these photoresponsive phenomena are applicable to the photocontrol of the binding properties of crown ethers on a polymer (Figure 13). It has previously been established that cis crown ethers and polymeric crown ethers favorably bind alkali metal ions with large ion radii through the formation of intramolecular 1:2 metal/crown sandwich complexes. Shinkai et al. synthesized a polystyrene derivative bearing the pendant 4-azo(benzo-15-crown-5) and its monomeric model and estimated the photoresponsive affinity toward alkali metal ions. (Figure 13.) The study demonstrated that the ion binding ability of the crown ether immobilized in the polymer changes in response to the changes in the conformation and the side-chain configuration.

Kumar et al.[23,24] prepared a series of azoaromatic polyureas with incorporated pyridine and bipyridines as polymeric ligands. The activation energies for cis–

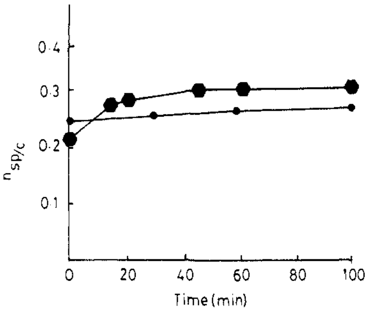


Figure 14. Changes in viscosity of PU-MDI-DAP solution with progressive complexation (●) and in the dark (⬢) when the solution is preirradiated. Concentration of polymer is 0.8123 g/dL. Concentration of $Co(OAc)_2$ is 1 × 10^{-4} mol.

trans thermal isomerization of these polyureas suggest similar energy barriers to low molecular weight analogues. An increase in E_a values was observed upon complexation with cobalt and nickel. The viscosity of a solution of the polymer also increases after complexation. Preirradiated polymer solutions showed a greater increase in viscosity and slightly larger incorporation of metal ion compared to its behavior in the dark. This observation is attributed to conformational rearrangement of the macromolecular ligand prior to complexation (Figure 14).

H. Membrane Permeability

Much effort has been directed to the characterization of the photoresponsive properties of derivative membranes entrapping photochromic compounds such as azobenzene and spiropyran derivatives. Anzai et al.[81,82] used the cis–trans isomerization of azobenzene-modified crown ethers to regulate the membrane potential across a poly(vinyl chloride) membrane. Photoinduced trans–cis isomerization of azobenzene derivatives has also been widely used to photocontrol metal ion permeabilities through PVC membranes,[83,84] liquid crystalline membranes,[85] and liposome[86] and bilayer membranes.[87] More recently, it has been shown that the membrane potentials and permeabilities of polymer membranes containing photochromic compounds in the polymer chains could be regulated by light irradiation.

Morgan et al.[88] synthesized a phospholipid molecule bearing an azobenzene linkage within one acyl chain. The lipid has been incorporated into vesicles of dipalmitoylphosphatidylcholine, (DPPC), and the effects of photoisomerization on the vesicles' permeability and phase behavior have been studied by light scattering and fluorescence spectroscopy. The phase transition temperature of DPPC is reduced, and the transition is broadened by the trans azo lipid. After photolysis the transition temperature is further reduced and nonequilibrium effects are evident. Vesicles containing the azo lipid can sustain a pH gradient before photolysis but pH slowly equilibrates following irradiation. Results indicate that photoisomerization causes no loss of bilayer integrity.

V. Conclusion

Photoresponsive polymers described in this article represent a new field of speciality polymers. As requently happens, a field that is essentially derivative develops a raison d'etre of its own. Thus, the photomechanical and photoviscosity effects and pH control systems are important by themselves and have possible commercial applications. Although they have not yet achieved practicality, it is possible for them to find applications in constructing photoactive devices in several fields in the near future, such as printing, photocopying, photolithography, photosensors, and so on.

An example of such an application which has attracted current attention is that of speciality organic materials which can store memories in the molecular levels. If one could successfully design a molecule which shows a reversible response in its physical properties to semiconductor infrared lasers, we would find many applications in electronics as information memory devices.

Another possibility is to use the photomechanical effect. Recently, much interest has been directed to shape memory metals, which memorize the shape and restore the shape after heated to the critical temperature. One might use photoresponsive polymers in similar fields as shape memory metals, such as in photomechanical engines or photoswitches.

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