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Chelating Copolymers Containing Photosensitive Functionalities. 3. Photochromism of Cross-Linked Polymers

G. Sudesh Kumar,[†] C. Savariar,[†] M. Saffran,[‡] and D. C. Neckers*[†]

Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403, and Department of Biochemistry, Medical College of Ohio, Toledo, Ohio 43699.

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ABSTRACT: A series of cross-linking agents of azobenzene with amide and sulfonamide spacer groups were prepared. Several homo- and copolymers were prepared with the azo cross-links by radical polymerization using AIBN initiator. The polymers undergo typical photochemical cis–trans isomerism to varying degrees. The thermal relaxation data indicate the importance of the structural and steric environment surrounding the cross-links. For example, a bulky phenyl substituent next to azobenzene seems to retard the photoisomerization. The nature of the polymeric matrix and the molecular weight did not affect the degree of isomerization, and the cis–trans cycle could be carried out without any fading. There was also no photoviscosity effect.

Introduction

The cis–trans isomerism of azobenzene moieties has recently been utilized as a photosensitive "switch" to regulate physical and chemical phenomena.[1-3] From the literature, it is obvious that the nature and the morphology of the polymer have an essential influence on the photo- and thermochromism of a chromophore in a given polymer matrix. The photochemical isomerism and the thermal isomerism of aromatic azo chromophores dissolved in a polymer matrix,[4,5] those wth a pendant group, or those which were part of the polymer backbone[6-11] have been investigated extensively. It was concluded that photochromic processes in bulk polymers are linked to particular motions of chain segments[12,13] and that the relaxation behavior of the photochrome depends on the free volume as described by a form of the WLF equation.[13]

The remaining question is 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 it from the main chains. Eisenbach investigated the photomechanical changes (i.e., a reversible contraction and expansion of such an oriented rubbery film upon irradiation based on change of dimensions of the cis and trans form of the azo chromopore) due to the isomerization of azo cross-links in poly(ethyl acrylate) networks and concluded that the same parameters of chain segmental mobility and of free volume as found for pendant groups, e.g., linear polyacrylates of polymethacrylates, are valid.[14]

The combination of a chelating group and a readily isomerizable group in a macromolecule whose physical and mechanical properties can be controlled by an external source presents the possibility of a structurally modifiable photosensitive ion switch. We have reported earlier the incorporation of azo aromatic groups in bipyridine- and pyridine-based macromoleular ligands and studied their complexing behavior under irradiation.[15-17] A detailed investigation of structure and morphology of a family of polymers on the behavior of photochromic cross-links and the effect of spacer arms separating it from the backbone is necessary for the construction of macromolecular ligands with photochromic cross-links. The photochemical and thermal cis–trans isomerizations of the azo aromatic cross-links in different structural and steric environments are described in this paper.

Experimental Section

4,4′-Divinylazobenzene was prepared by the same sequence of reactions that we reported earlier for the synthesis of 4,4′-divinylbenzophenone[18] (Figure 1).

Synthesis of 4,4′-Dimethylazobenzene.[19] To a solution of 109.7 g (0.8 mol) of *p*-nitrotoluene dissolved in 1 L of MeOH contained in a three-necked round-bottom flask equipped with a condenser and mechanical stirrer was added a solution of 130.0 g (3.24 mol) of NaOH dissolved in 300 mL of H_2O. The mixture was stirred and 106 g (1.64 mol) of Zn dust was added. The reaction mixture was refluxed for 11 h and filtered while still hot. Evaporation of the filtrate gave an orange product. Part of the product that remained in the filter was extracted with acetone, which on evaporation gave more of the product. The combined products were then stirred in 2% HCl, warmed, and filtered. The product was washed several times with hot water and then recrystallized from EtOH. The orange crystals of Ia were dried under vacuum: yield 50 g; mp 134 °C; NMR δ 2.32 (s, 6 H), 7.1–7.9 (2 d, 8 H).

4,4′-Bis(bromomethyl)azobenzene. A mixture of 19.5 g (92.8 mmol) of 4,4′-dimethylazobenzene, 36 g (202 mmol) of *N*-bromosuccinimide (NBS), and 0.6 g of benzoyl peroxide in 250 mL of CCl_4 was heated under reflux for 3 h, after which the yellow color of the NBS had disappeared. The mixture was cooled in ice water and filtered with suction, the filtrate was washed thoroughly with water and dried over $MgSO_4$, and the solvent was evaporated. The residue was recrystallized from CCl_4, yielding

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[†] Bowling Green State University, Center for Photochemical Sciences.

[‡] Medical College of Ohio.

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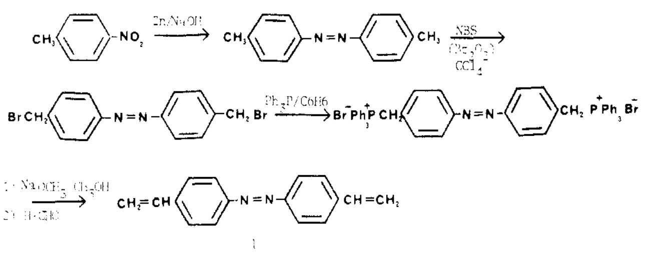


Figure 1. Synthetic scheme of 4,4′-divinylazobenzene.

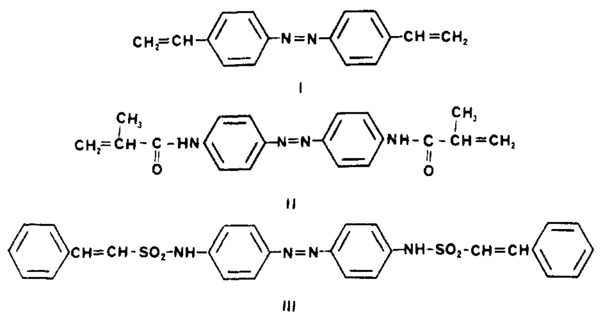
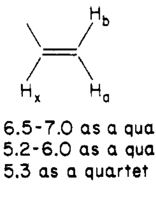


Figure 2. Structures of cross-linking agents.

11.8 g of the product; mp 145–160 °C. The solid from the first filtration was washed with water, taken up in benzene, and dried over $MgSO_4$. Evaporation of the solvent gave about 7 g; mp 140–155 °C. NMR spectra of both mixtures showed that they had nearly the same composition, consisting of approximately 80% of the desired bis(bromomethyl) compound: δ 4.5 (CH_2Br). Purification was carried out on the final product to avoid greater losses.[18]

4,4′-Bis(bromomethyl)azobenzene Bis(triphenylphosphonium) Salt. The combined products of the above reaction (20.6 g, 56 mmol of pure bis(bromomethyl) equivalents) were boiled under reflux in 400 mL of dry benzene with 31.0 g (118 mmol) of triphenylphosphine for 14 h with vigorous stirring. The thick oil, which separated quickly, turned into a solid. Filtration gave about 60 g of yellow phosphonium salt (80% yield).

4,4′-Divinylazobenzene. To a cooled solution of 8.60 g (9.64 mmol) of bisphosphonium salt in 75 mL of methanol was added 20 mL of 37% formaldehyde solution in water. NaOH solution (4 N) was added dropwise with constant stirring, and, as each drop was added, a green color developed and quickly disappeared. The addition was carried out till no more green color could be observed; on subsequent addition, the orange solid that precipitated out was filtered off, dissolved in CCl_4, and dried over $MgSO_4$. This carbon tetrachloride solution was chromatographed over silica gel. Addition of small amounts of chloroform to CCl_4 was useful as an eluent mixture, giving about 1.5 g of crude divinyl compound. The progress of the elution of the orange divinyl compound could be followed visually. Recrystallization in ethanol gave 1.2 g of divinyl compound: mp 126–128 °C (IR (KBr), characteristic $CH{=}CH_2$ absorption at 920 and 990 cm^{-1}; the NMR ($CDCl_3$) spectrum consisted of an ABX pattern strongly resembling that of styrene for vinyl protons and an AB quartet for the four aromatic protons.



H_x, δ 6.5–7.0 as a quartet
H_b, δ 5.2–6.0 as a quartet
H_a, δ 5.3 as a quartet

***N*,*N*′-Bis(β-styrylsulfonyl)-4,4′-diaminoazobenzene.** 4,4′-Diaminoazobenzene (0.05 mol) was dissolved in a mixture of 40 mL of anhydrous acetone and 6 mL of dry pyridine in a 250-mL flask and 0.10 mol of β-styrenesulfonyl chloride was added. The reaction mixture was set aside for 36 h with stirring, and almost pure compound III was filtered. The product (III) was washed with Na_2CO_3 solution and with acetone and vacuum-dried. The charactertistic IR bands assigned to sulfonamide (1350, 1230, 1140 cm^{-1}, etc and characteristic pattern between 1300 and 700 cm^{-1}) are present. The syntheses of 4,4′-bis(methacryloylamino)azobenzene[14] (II) and 4-vinyl-4′-methylbipyridine[20,21] were carried out as reported earlier (Figure 3).

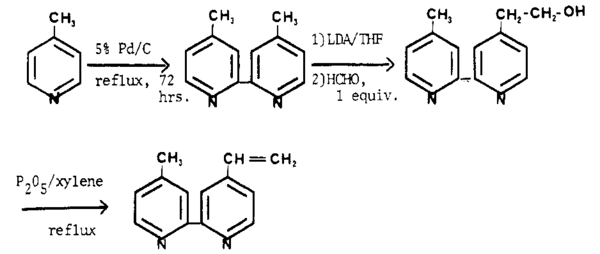


Figure 3. Synthetic scheme of 4-methyl-4′-vinylbipyridine.

Table I
Analytical Data of Cross-Linking Agents

compd	λ_{max}, nm (ϵ)	elem anal.[a]
I	355 (2.85 × 10^4)	C, 82.0 (82.0) H, 5.9 (6.0) N, 11.9 (11.8)
II	362 (3.5 × 10^4)	C, 68.7 (68.5) H, 5.7 (5.7) N, 16.0 (15.8)
III	360 (1.9 × 10^4)	C, 61.7 (61.3) H, 4.4 (4.2) N, 10.2 (10.1) S, 11.7 (11.8)

[a] Found values in parentheses.

Starting materials were obtained from Aldrich Chemical Co. and purified, when necessary, by appropriate procedures. The monomers were purified by standard techniques after removal of the inhibitor.

All polymerizations were carried out at 60 °C using AIBN initiator under vacuum. The polymerization mixture was poured into methanol to precipitate the polymers. All polymers were again dissolved in benzene and reprecipitated in methanol and vacuum-dried. All samples were pale yellow. The viscosity measurements were carried out in a constant-temperature bath using an Ubbelohde viscometer. For photoviscosity measurements, solutions were irradiated with a GTE/Sylvania 500-W, 120-V mercury lamp suspended in close proximity to the viscometer.

Irradiations were carried out with a Bausch and Lomb monochromator at 360 nm. Absorption spectra of the polymers were measured with a Cary 219 spectrophotometer. The temperature of the cell was controlled with a temperature-controlled circulating bath. The sample temperature was controlled to within ±0.05 °C. The amount of cross-linking agent was also determined by elemental analysis. Infrared spectra were obtained on a Perkin-Elmer 237 grating spectrophotometer and NMR spectra on a Varian CFT-20.

Results and Discussion

Azobenzenes undergo a reversible photochemical isomerization reaction. Depending upon the associated conjugated functional groups, the photostationary state ranges from 70% to 100% cis isomer under conditions where the trans isomer is absorbing all the light. Quantum yields for this reaction are generally high and there are no competing reactions of significance. Therefore, the cis–trans isomerization of an azobenzene moiety represents virtually a model photochemical process in which one stereoisomer is favored thermally, the other isomer is favored photochemically, and the conversion of one isomer to the other is virtually quantitative. These systems have another advantage, and that is there are no known evidences of emissions from the excited states of azobenzene in either the cis or trans form. Therefore, there are no known processes of spectroscopic inefficiency competing with photochemical isomerization.

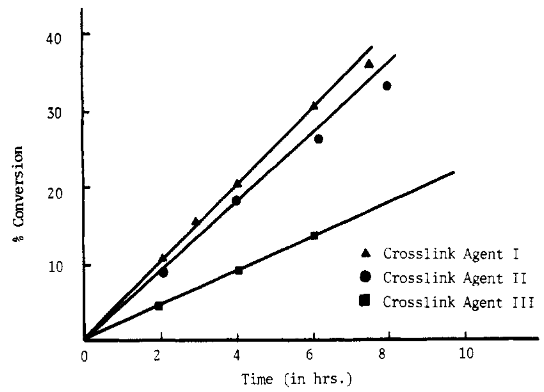


Figure 4. Polymerization of styrene with different cross-linking agents. Solvent, benzene; temperature, 60 °C; concentration of AIBN, 1×10^{-3} mol/concentration of crosslinking agent; 4×10^{-5} mol.

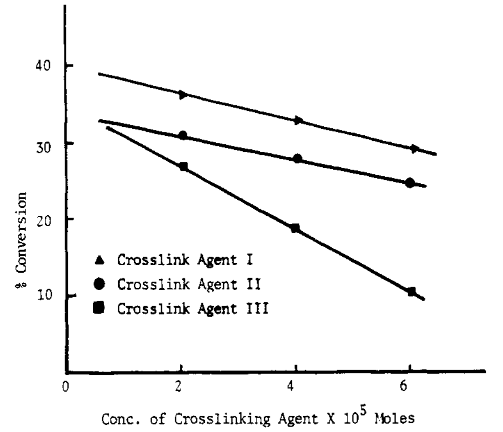


Figure 5. Polymerization behavior of styrene with different cross-linking agents. Solvent, benzene; temperature 60 °C; time, 6 h; concentration of AIBN, 1×10^{-3} mol/L. (In the case of cross-linking agent III, a small amount of Me_2SO was added to dissolve the polymer.)

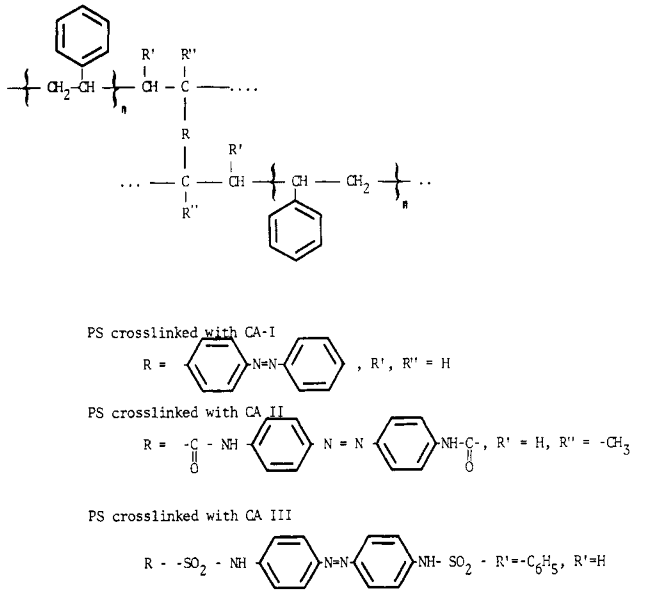


Figure 6. Portion of the structure of photochromic polystyrene network with different azo aromatic cross-links.

The data related to the characterization of polymerizable derivatives of azobenenes I, II, and III are presented in Table I.

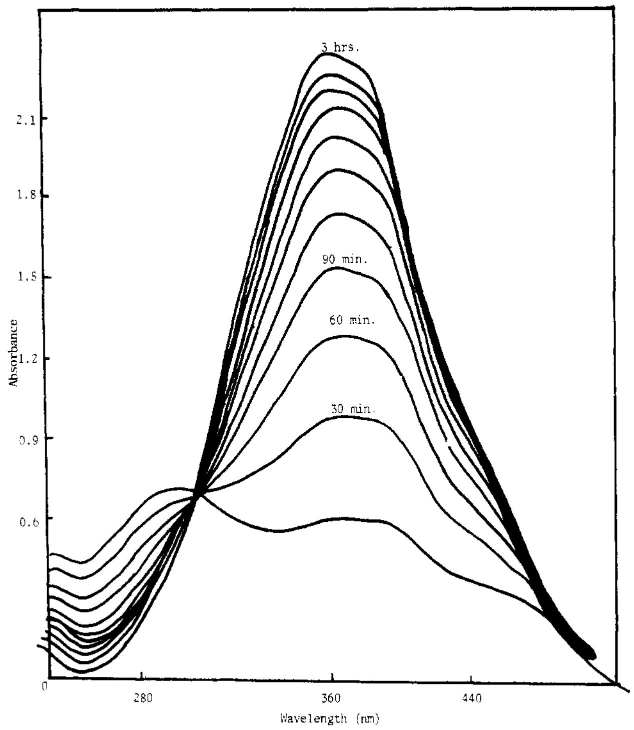


Figure 7. Absorption spectra of styrene–azo I in CH_2Cl_2 showing thermal recovery after irradiation at 360 nm. Temperature, 28 °C.

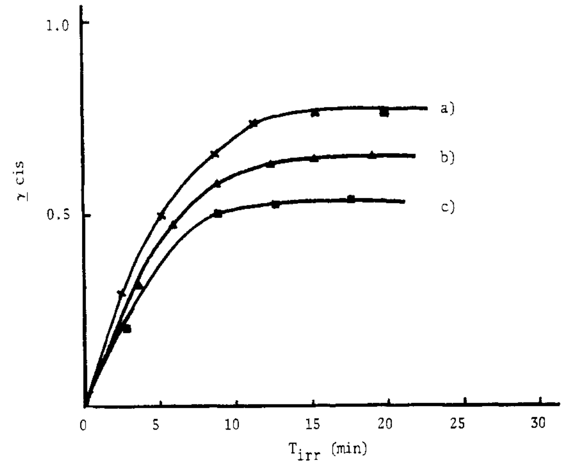


Figure 8. Photochemical cis–trans isomerization of azo groups in different cross-links at 25 °C in polystyrene. Fraction of cis isomer as a function of irradiation time (photostationary states): (a) 0.78; (b) 0.62; (c) 0.52 (λ_{max} = 360 nm). (×) Cross-linked with I, (▲) with II, and (■) with III.

The composition of the reaction mixtures for the preparation of different polymer samples is given in Table II. The polymerization behavior of these cross-linking agents with styrene is graphically depicted in Figures 4 and 5. The percent conversion when compound III is the cross-linking agent is considerably low. The incorporation of this cross-linker in the polymer is also low as determined by the concentration of the azo group. It may be attributed to the steric hindrance offered by the phenyl substituent on the adjacent carbon atom. It was also observed that with the increase in the concentration of cross-linking agents, percent conversion started decreasing. By copolymerizing other conventional monomers with these difunctional cross-linking agents, soluble polymers were prepared by stopping the polymerizations before the onset of the gel point (Table II). A representative portion of the structure of the polymers is shown in Figure 6.

As found in linear photochromic copolymers, photochemical cis–trans isomerization of the azobenzene units in the cross-linked polymers can be achieved by irradiation

Table II
Polymerization Data of Various Polymers Cross-Linked with 4,4′-Divinylazobenzene

sample	concn of DVAB × 10^5, mol	concn of AIBN × 10^4, mol	time, h	% conv	$\bar{M}_v$	E_a, kcal/mol
styrene–Azo I[a]	3.85	2.3	6	32.4	52000	24.2
styrene–Azo II	2.56	2.3	6	17.1	35481	23.5
MMA–Azo I[b]	1.28	1.37	1	18.6	18300	24.5
MMA–Azo II	2.56	1.75	2	25.1	10730	23.0
styrene–acrylic acid–Azo I[c]	2.56	2.02	2	35.0	22500	22.1
styrene–acrylic acid–Azo II	3.38	2.69	2	50.0	48600	22.2
styrene–4-bipy–Azo I[d]	2.5	2.3	12	12		23.5
styrene–4-bipy–Azo II	3.5	2.3	12	16		22.8

[a] Styrene, 5 mL. [b] MMA, 5 mL. [c] Styrene, 2.5 mL; acrylic acid, 2.5 mL. [d] Styrene, 4.5 mL; 4-bipy, 0.5g. In each case solvent was benzene (5 mL) and temperature was 60 °C.

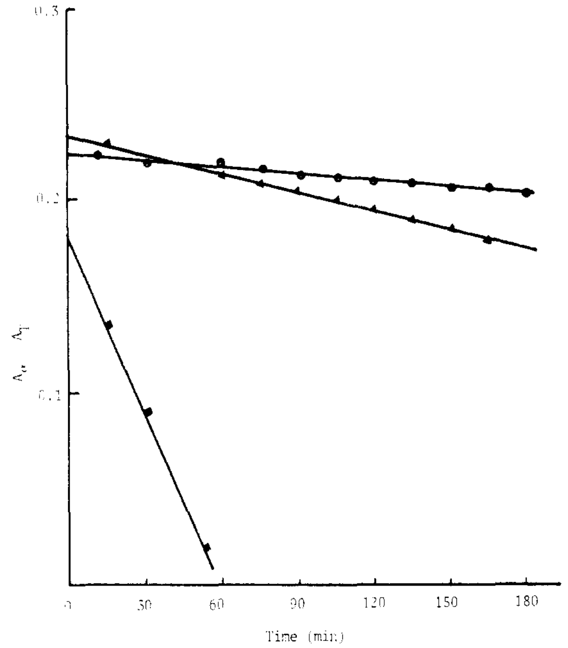


Figure 9. First-order plots for the thermal cis–trans isomerization of azo groups in different cross-links of the PMMA matrix (A_∞ and A_t are the absorbances at 360 nm at infinite time and at time t). Temperature, 30 °C, solvent, CH_2Cl_2. (▲) Cross-linked with I, (●) with II, and (■) with III.

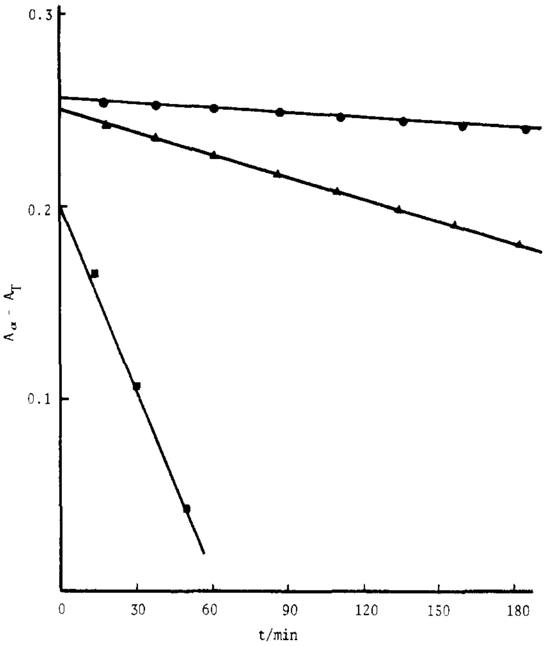


Figure 10. First-order plots for the thermal cis–trans isomerization of the azo chromophore with different spacers in cross-links of polystyrene (A_∞ and A_t are the absorbances at 350 nm (trans isomer) at infinite time and at time t). Temperature, 30 °C; solvent, CH_2Cl_2. (▲) Cross-linked with I, (●) II, and (■) with III.

in the region of 360 nm. The typical absorption spectrum of a photochromic polymer sample is shown in Figure 7 before irradiation and after reaching the photostationary state. In general, irradiation creates the cis isomer in high yield at the photostationary state except for samples cross-linked with compound III. Figure 8 shows the cis content of polystyrene samples cross-linked with these azo chromophores. In this case the isomerizable group is fixed on both ends and isomerization is possible only with a simultaneous movement of at least one of the two adjacent chain segments. The change in the geometry of the chromophore forces the polymer chains to be moved along each other as it induces a change in the polymer structure; i.e., the structural and steric environment of the cross-links might be responsible for this observation, as discussed in the next section.

Thermal isomerism from the photogenerated cis form to the trans form was followed from the absorption spectrum (Figure 7). UV spectroscopy, by which isomerization around a double bond is followed kinetically, provides an additional advantage because one can follow precisely the progress of the isomerization process to obtain a dispersion of rate constants. The isomerization follows first-order kinetics and a slope of a plot of log ($A_\infty - A_t$) against time gives the rate of the thermal isomerization. The occurrence of isosbestic point shows that this macromolecular transformation is characterized by the presence of two spectrophotometrically distinguishable species. We have also noted that this cycle was essentially completely reversible. The polymers did not show any fading, thus excluding a decrease in the concentration of the isomerizable azo groups.

It seems evident from the comparison of the first-order plots given in Figures 9 and 10 that the rate of isomerization is not affected so much by the nature of the polymer matrix, but it is affected 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.

It is of interest to note the effect of a bulky substituent on an adjacent carbon atom on the photoisomerization of azobenzene units. Even though still controversial, the trans–cis photoisomerization of azobenzene on π,π^* excitation is believed to proceed by a rotation mechanism, i.e.,

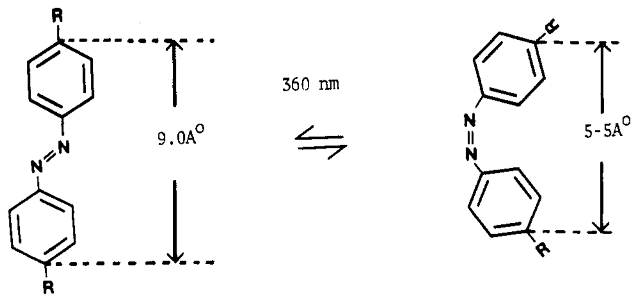


Figure 11. Change in dimensions of the aromatic azo chromophore upon irradiation.

by twisting around the central –N=N– bond. Since the end-to-end distance in *trans*-azobenzene is known to be 9.0 Å,[22] rotation of half of azobenzene requires a sphere of 4.5-Å diameter. Therefore, a sphere of 4.5 Å may be the minumum (Figure 9), possibly more because of rigid and coplanar spacers, free volume required for the isomerization, if photoisomerization takes place by a rotation mechanism. The steric hindrance from the phenyl group on an adjacent carbon atom may apparently be the reason for low cis isomer content in samples cross-linked with compound III. It should also be noted that the presence of a rigid amide spacer may influence the equilibrium at the photostationary state and reduce the rate of isomerization to some extent.

Table II depicts the series of polymers investigated to study the effect of the polymer matrix on the rate of thermal isomerization of azobenzene cross-links with no spacer groups. Both hydrophilic and hydrophobic segments and also rigid segments such as bipyridine units do not seem to significantly affect the activation energies of the isomerization process. In the same group of polymers, we failed to detect any molecular weight–activation energy relationship. The absence of any major effect of polymer matrix and differing rate constants wth different spacer groups seem to emphasize the importance of a spacer group separating the azobenzene moiety from the polymer backbone. Since the mobility of a macromolecule in solution depends on the interaction of the polymer with the solvent, the rate of a photochromic transition is influenced by the parameter χ of this interaction. The higher value of χ for polystyrene than for poly(methyl methacrylate) in benzene was suggested to be responsible for the lower cis–trans isomerization rate constant of vinyl(dimethylamino)azobenzene in copolymers with styrene than those with MMA.[23] The decrease in the rate constant with increase in the content of vinyl(dimethylamino)azobenzene in the copolymer was also explained by an increase in χ. Similar solvent–polymer interaction parameters might account for the observed activation energy values.

As can be seen from Figure 11 the isomerization involves a decrease in the distance between the para carbon atoms in azobenzene derivatives from about 9.0 to 5.5 Å[22] and the local contraction may be even larger because of rigid amide or sulfonamide groups. If the chromophore is part of a polymer network and the network is stretched, the chromophores are preferentially oriented parallel to the stretching axis (Figure 7). Upon irradiation of such an oriented sample in the maximum trans-absorption range (λ = 360 nm), the change in the conformation of the azo chromophore should cause a change in the conformation of an adjacent chain segment, which is considered to be the main effect responsible for the photomechanical effect.[24] From the organic point of view, a reversible contraction/dilation phenomenon should be observed mainly in a photochromic network below its T_g, i.e., the rubbery state where segmental mobility is important. On the other hand, it is well-known that isomerization occurs in the rubbery state almost at the same rate as in solution.[9]

Smets and co-workers[25] worked with stretched poly(ethyl acrylate) rubbers cross-linked with 5 wt % bis((methacryloyloxy)methyl)spirobenzopyran) photochrome. On irradiation 2–3% contraction was observed. Analogous experiments were more recently described by Eisenbach[14] on stretched PEA rubber cross-linked with 4,4′-dimethacryloylazobenzene; however, still smaller contractions were observed. Besides, these photomechanical effects were also observed in photochromic polyamides without cross-linking agent. Such a contraction, which should be reflected as photoviscosity effect in solution, is absent. In none of the cases were we able to observe the photoviscosity effect. The question to which extent the photomechanical effect is caused by the conformational change of the chromophore or by local heat effects due to conversion of the energy stored by the photochrome was not answered definitively in earlier reports. In the absence of such thermal effects, probably the absence of the photoviscosity effect in solution is not unexpected considering the low concentrations of cross-links. Attempts are under way to study mechanical effects in films and the effect of the incorporation of more cross-links.

Conclusions

Derivatives of azobenzene with amide and sulfonamide spacers undergo polymerization when used as cross-linking agents. At the photostationary state, polymers with amide and sulfonamide groups had lower amounts of cis content. The rate of thermal reversal also seems to depend on the structural and steric environment surrounding the cross-links. There was no correlation between the polymer matrix and molecular weight and rate of thermal isomerization.

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Three Plasmids Constructed for the Production of Monodisperse Semistiff DNA Samples

Roger J. Lewis, Janet H. Huang,[†] and R. Pecora[*]

Department of Chemistry, Stanford University, Stanford, California 94305.
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ABSTRACT: We have constructed three plasmids, pLH2311, pLH1010, and pLH762/367, that can be used to produce large amounts of monodisperse DNA fragments by cleavage with the readily available restriction enzymes Pvu II and Hae III. pLH2311 produces a single fragment 2311 base pairs (bp) in length (1.5×10^6 dalton molecular weight) when cut by Pvu II. pLH1010 contains two copies of a fragment 1010 bp in length (6.7×10^5 dalton molecular weight). After cutting by Pvu II these fragments may be easily separated from the other fragments by gel electrophoresis. pLH762/367 contains three copies of a fragment 762 bp in length (5.0×10^5 dalton molecular weight) and six copies of fragments 367 bp or 368 bp in length (2.4×10^5 dalton molecular weight). The first fragments are recovered by Pvu II digestion and the latter by additional digestion of the 762-bp fragment with the enzyme Hae III. Details of the construction of these plasmids and of their use to produce monodisperse semistiff polymer samples are discussed.

Introduction

The polymer chemist who wishes to study the structure and dynamics of wormlike or semistiff molecules is faced with a perplexing situation. The mathematical complexity of the complete problem, including hydrodynamic interactions, the counterion field, etc., is presently insoluble and thus approximations of unknown accuracy are required in order to make any progress whatsoever.[1-4] There now exist a number of theories whose predictions must be tested before it will be known which of the various mathematical approaches is the most valid. For a few specific examples, see ref 3–5. This experimental verification is made significantly more difficult by the polydisperse nature of available polymer systems.[6-8] For example, if a theoretical prediction and experiment disagree, we must determine the source of difference: were the mathematical approximations in the theory invalid or was the sample too polydisperse?

Plasmids, circular pieces of DNA, produce fragments of specific lengths when cut by suitable restriction enzymes[9,10] and the precise lengths of these fragments can be determined from the nucleotide sequence of the DNA and the recognition sequence of the restriction enzyme. A number of reports have appeared in the literature in recent years in which monodisperse restriction fragments of DNA have been used as model polymer systems.[11-14] In order to apply many physical–chemical techniques, such as classical and dynamic light scattering, hundreds of micrograms of polymer are required. In order to produce that quantity of a monodisperse fragment we would need to purify 10 mg of plasmid DNA, cut the DNA with 20000–50000 units of the appropriate restriction enzyme(s), separate the resulting DNA fragments by gel electrophoresis, and then repurify the fragment of interest. If the fragment of interest is 350 bp in length and the original plasmid is 7000 bp in length, then one could obtain less than 500 μg of monodisperse DNA from 10 mg of starting material. We would obtain a low final yield because the fragment of interest represents only 5%, by weight, of the DNA originally produced. Furthermore, the effort and cost of this procedure are substantial when one considers the techniques and equipment necessary to grow 20-L cultures and the current price of restriction enzymes. This approach is therefore impractical for most laboratories. To overcome these difficulties, we have inserted multiple copies of small DNA fragments into plasmids, thus increasing the percentage of the original plasmid that is ultimately useful. In this way, the final yield is increased and the production of monodisperse DNA fragments becomes feasible for a much wider variety of investigators.

In the present work, we have applied the tools of genetic engineering to produce relatively large amounts of monodisperse semistiff polymers in a variety of molecular weights. Our hope is that the plasmids that we have constructed, and specifically the DNA samples that can be easily made from them, will allow investigators to more easily and accurately test models of macromolecular dynamics and structure.

Discussion

In designing plasmid DNAs for the production of monodisperse fragments for physical–chemical study, we followed a number of guidelines. First of all, we used only DNAs for which the complete nucleotide sequence was known. This allows the calculation of molecular weight and contour length for each fragment produced.[15] Secondly, we used only DNAs that were unrestricted by the current NIH recombinant DNA guidelines.[16] A third consideration in plasmid design involved the ends of the fragments that would be produced by cleavage with restriction enzymes.

Restriction enzymes can leave two types of ends when they cut DNA.[9,10] The so-called "sticky ends" have short single-stranded regions because the enzyme involved

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[†] Present address: School of Medicine, University of California at San Diego, La Jolla, CA 92093