Notes

Photochromism of Azobenzene-Containing Polymers. 4. Effect of Spacer Groups

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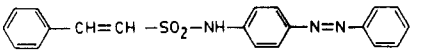
Background

Stereochemical changes induced in photochromic units incorporated in polymer chains can cause conformational variations of the polymers.[2-5] The photoisomerizations of azobenzene units in a polymer matrix, those polymers with a pendant azo groups, or those that were part of macromolecular backbone have been extensively investigated.[6-8] Isomerization rates and quantum yields for such materials are affected by restrictions in movement imposed by the molecular chains or by steric or shielding effects arising from chain cross-linking, chain coiling, etc.[2-5] In a series of papers, we have reported the photo- and thermochromism of azobenzene units lodged in the backbone and at the cross-link junctions.[9-11] A study of the dark reaction following a photochemical trans–cis isomerization of dilute solutions of polymers containing azobenzene units in the backbone and in the cross-links yielded the following results: (1) The reaction was strictly first-order. (2) There was no significant difference between the observed rate constants for cis–trans isomerization of azo polymers and analogous low molecular weight compounds. (3) The point of attachment to the polymer chain and the microenvironment surrounding the cross-links did affect the isomerization rates.

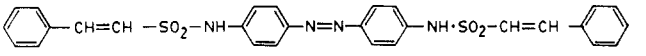
One of the unanswered mechanistic questions is how the photochromism of azo groups lodged in the side chains and cross-links would be influenced by the presence or absence of spacer groups separating the azofunctionality from the main chain. In order to understand the rates and kinetics of thermal reaction of photochromic molecules in terms of their molecular environments, we have studied the kinetics of reactions from metastable cis form to stable trans form of azobenzene units attached through rigid and flexible spacer units. The purpose of this study is to reveal fundamental matters of mechanism in photochromic reactions of azo polymers and to apply this basic knowledge to construct photochromic polymers.

Experimental Section

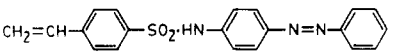
Azofunctional monomers/cross-linkers (I–IV) were synthesized according to the following procedures. *N,N'*-Bis(β-styrylsulfonyl)-4,4'-azodianiline (II) was prepared as reported earlier.[9] *N,N*-Bis(*p*-styrylsulfonyl)-4,4'-azodianiline (IV): 10.3 g of styrene-4-sulfonic acid sodium salt (Aldrich) was refluxed with 15 mL of $SOCl_2$ in DMF for 2 h. The reaction mixture was poured in ice cold water, and the viscous liquid was extracted in chloroform. Yield: 9.0 g. IR: 1360 cm^{-1}. A total of 0.99 g of *p*-phenylazoaniline was taken in 10 mL of CH_3CN with 0.75 g of K_2CO_3, and 1.11 g of *p*-styrenesulfonyl chloride in CH_3CN (10 mL) was added with stirring. After 2 h, the product was extracted with CCl_4 and



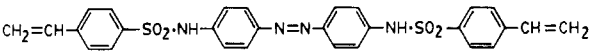
(I)



(II)



(III)



(IV)

solid was recovered. Yield: 1.6 g (80%). IR: 3400, 1625, 1340 cm^{-1}.

N-(*p*-Styrenesulfonyl)-4-aminoazobenzene (III) was prepared as above with 1.11 g of *p*-styrenesulfonyl chloride and 0.49 g of 4-aminoazobenzene. Yield: 80%. Similarly, *N*-(β-styrylsulfonyl)-4-aminoazobenzene was prepared from 0.19 g of 4-aminoazobenzene and 0.20 g of β-styrenesulfonyl chloride in acetone/pyridine mixture. Yield: 70%.

All the polymerizations were carried out at 65 °C by using AIBN under N_2 atmosphere (Table I). Irradiations were carried out with a Bausch and Lomb monochromator at an absorption maximum of each sample as given in Table I. Absorption spectra were measured in a Shimadzu UV–vis spectrophotometer in a temperature-controlled circulating bath.

Results and Discussion

Functional groups bound to polymers might be expected to be sterically hindered, but this is probably only the case when functional groups are very close to the polymer backbone. As the functional groups are separated from the backbone by spacer groups, steric effects would be expected to disappear rapidly.[12] Most polymer-supported reactants are prepared from polystyrene, and the phenyl ring will act as a rigid spacer group. Under conditions where the polymer backbone and the functional group interact favorably, functional groups bound to para positions in polystyrene would not be expected to behave any different sterically from their low molecular weight analogues.[13] Our earlier paper reported the effect of amide and sulfonamide spacers at the cross-link junctions on the thermal recovery process.[9] In order to establish guiding principles for the molecular design of photochromic polymers based on the azo chromophore, we have designed two sets of monomers and cross-linking agents. Polymers I and II were prepared by using $-SO_2NH-$ as the spacer group linking the chains and the azobenzene moiety. Polymers III and IV were prepared where the azobenzene moiety is separated from the polymer backbone by a rigid $-C_6H_4SO_2NH-$ group.

A typical absorption spectrum of polystyrene with an azo pendant group attached through a sulfonamide spacer group shows a strong absorption maxima in the range of 340–360 nm. Irradiation in the region of the main

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Table I
Polymerization Data Involving Azofunctional Monomers/Cross-Linkers[a]

sample	azo monomer	monomer	time, h	mol wt ($\bar{M}_w$)	λ_{max}, nm
PS-I	I	styrene (0.54)	5	46 000	355
PS-II	II	styrene (0.54)	5	75 000	360
PS-III	III	styrene (0.54)	5	42 000	350
PS-IV	IV	styrene (0.54)	5	90 000	362
PS-HEMA I	I	styrene (0.27) HEMA (0.27)	6	150 000	350
PS-HEMA II	II	HEMA (0.27)	5	175 000	360
PS-HEMA III	III	HEMA (0.27)	6	225 000	352
PS-HEMA IV	IV	HEMA (0.27)	6	335 000	360

[a] Concentrations: I and III, 1.8×10^{-3} mol; II and IV, 1.3×10^{-3} mol. Solvent/chloroform, 150 mL; temp, 60 °C: AIBN, 6×10^{-4} mol.

Table II
Photochemical Cis–Trans Isomerization of Azofunctional Polymers (I–IV) at 30 °C in Chloroform

sample	UV irradiation time, min	y_{cis}
PS-I	20	0.76
PS-II	30	0.71
PS-III	30	0.52
PS-IV	60	0.56
PS-HEMA I	30	0.60
PS-HEMA II	30	0.68
PS-HEMA III	25	0.57
PS-HEMA IV	45	0.42

absorption band of the trans form in each case creates cis isomer in good yields. Generally, in the case of monosubstituted azobenzene derivatives, the n–π absorption was more intense at 460 nm and increased with irradiation while 4,4′-substituted azobenzene polymers (cross-linked polymers) exhibited weak absorption above 400 nm. In each case, the occurrence of an isosbestic point shows that this macromolecular transformation is characterized by the presence of two spectrophotometrically distinguishable species. The data related to the synthesis and characterization of azofunctional polymers is given in Table I and the composition of the photostationary state in Table II. The polymerizations involving the cross-linkers were stopped well before the gel point to obtain soluble samples as reported earlier.[9]

The size of the chromophore and conformation and its point of attachment to a polymer chain play a role in determining the composition of the photostationary state.[14-17] The differences in the photostationary composition (Table II) can be rationalized considering that near a cross-link junction the restrictions acting on a chain segment mainly arise from four chain branches, while two chain branches act on a pendant group. It was inferred by the fast isomerization of the pendant azo groups that neighboring phenyl groups do not impede isomerization. However, polymer IV took much longer to reach its photostationary state (50% cis). We believe that the reduced mobility of these cross-links with rigid spacer groups arises from insufficient free volume to allow the isomerization at a molecular level.

The thermal recovery[18] data indicates the importance of the structural and steric environment surrounding the azo labels. Figures 1 and 2 present the thermal cis–trans isomerization at 30 °C in dilute solutions of polystyrene and poly](Sty–HEMA) samples incorporating azo monomers/cross-linkers I–IV It seems evident from the first-order plots that the rate is affected by the nature of the spacer group as well as by the nature of polymer chain. In general, polymers with pendant azo groups seem

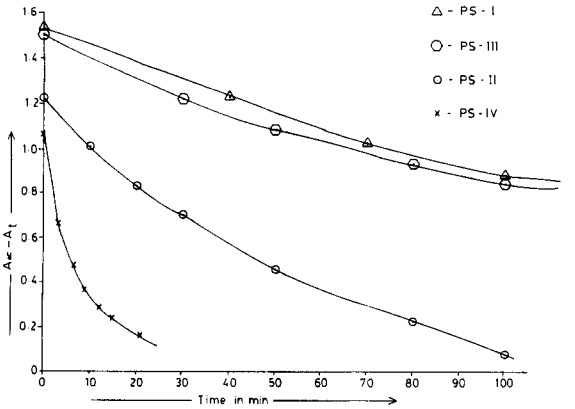

Figure 1. Thermal recovery data of polystyrene samples containing azobenzene units in the side chains and cross-links. Solvent, $CHCl_3$; temp, 30 °C.

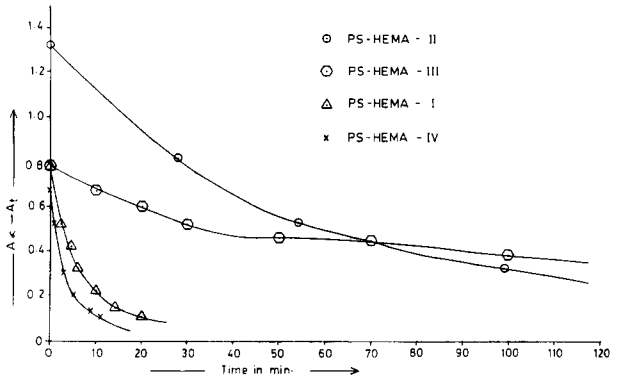

Figure 2. Thermal recovery data of poly(Sty–HEMA) copolymer samples containing azobenzene units in the side chains and cross-links. Solvent, $CHCl_3$; temp, 30 °C.

to isomerize at comparable rates in polystyrene while the azo cross-links isomerize much faster. The rate of thermal recovery is fastest in the case of azo cross-links with phenylsulfonamide spacer groups. Taking polystyrene as the standard, a relative scale of reactivities may be discussed. In PS samples, PS–I ($k_I = 8.0 \times 10^{-3}$) and PS–II ($k_{II} = 8.2 \times 10^{-3}$) both the pendant groups seem to isomerize at about the same rate, indicating the absence of any spacer group effect. However, both the cross-linked PS samples PS–III ($k_{III} = 2.0 \times 10^{-2}$) and PS–IV ($k_{IV} = 6.4 \times 10^{-2}$) undergo faster thermal reversal. The fastest recovery of PS–IV may be due to steric restrictions imposed on the photochrome by the rigid spacer groups.

The behavior of PS–HEMA I demonstrates the influence of polymer structure on the thermal reversal. The comonomer effect is manifested even in the side chains. It may point out some hydrogen bonding between the trans form and the hydroxy ethyl ester pendant on the monomer. No such effect is observed with PS–HEMA III, where the photochrome is far away from the vicinity of the polymer chain. This implies a possible influence of the polymer structure and the point of attachment of the chromophore to the polymer. We attribute the differences observed in our studies to the effects of restrictions on the mobility of the photochrome itself and/or to the effect of the length and rigidity/flexibility of the spacer group linking the photochrome to the polymer chain. The thermal isomerization studies supplement the photoisomerization studies.

From the above findings it is quite evident that photochemical and thermal cis–trans isomerization data are sensitive to the location of the photochrome along the polymer chain and nature of the polymer backbone and the spacer group. This is due to the requirement of

segmental movements of the polymer chains and rearrangements in the conformations of the polymer chains neighboring the chromophore, which are necessary for the isomerization to occur.

Even though it is still controversial, the photoisomerization is expected to proceed by a rotation mechanism, i.e., by twisting around the central -N=N- bond.[9] If free volume is greater than a critical size, the thermal reaction will proceed at a regular rate in solution, but for smaller free volume, the cis isomer will be forced in strained cis conformations from which it can return more easily to the trans form than the relaxed cis form. Alternatively, the occurrence of two different relaxational mechanisms may be responsible for the anomalously fast reactions of cis isomers. The anomolously fast isomerizations, for which a small activation energy is found, are attributed to a translational relaxation mechanism, where the "normal" isomerization is associated with rotational relaxation, a process that generally requires higher activation energy.

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(18) It was not possible to compare activation energy values (E_a) because of faster isomerization at higher temperatures in several cases such as PS-IV and PS-HEMA I, etc.