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Steric Effects in Photochromic Polysiloxanes with Spirooxazine Side Groups

Alexander Zelichenok, Frida Buchholtz, Shlomo Yitzchaik, Judith Ratner, Mark Safro, and Valeri Krongauz*

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot 76100, Israel

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ABSTRACT: Synthesis and properties of linear and cyclic polysiloxanes with photochromic spirooxazine side groups were investigated. The photochromic groups were connected to the main chains through a flexible $(CH_2)_n$ spacer. The number of photochromic groups that can be incorporated in the polymer by a polymer analogous reaction is restricted for the short spacer $(CH_2)_3$ to ~50%, while the photochromic groups with the longer spacer $(CH_2)_6$ can be added to practically each polymer unit. The rates of the thermal decoloration reactions are also determined by the spacer lengths and the spirooxazine content. At high content, a deviation from first-order kinetics was observed for the color decay. The effects are explained by the steric interactions of the bulky photochromic groups. Computer simulation of the molecular movement in the macromolecules confirmed the explanation.

Introduction

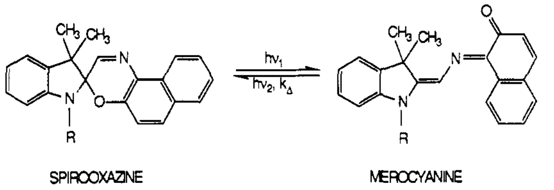
Photochromic polymers, i.e., polymers which contain photochromic groups in a macromolecule, are materials of significant scientific and technological interest.[1] Earlier, we reported on a number of side-chain photochromic polymers, in which photochromic spiropyran or spirooxazine side groups are attached to a main chain through a flexible spacer.[2–8] Such a structure allows incorporation of a very high content of a photochrome in a polymer which can reach 100%, i.e., each structural unit of the polymer contains the photochromic group. Properties of such polymers can be substantially different from the properties of the polymers containing photochromic molecules as solute. This relates not only to kinetic and spectral characteristics of the photochromic process but also to structural and thermodynamic properties of the polymers themselves.[4–7,9]

As a rule, both photochemical and thermal reactions (Scheme I) are retarded by a polymer matrix, as compared with liquid. This effect is usually attributed to the steric hindrance of the reactions by the polymeric medium.[10] It is most pronounced when the reaction is connected with a significant conformational change of the molecule. In the case of photochromic polymers additional factors, such as very close vicinity or aggregation of photochromic groups, may play a significant role.[1,11] The retardation of the chemical reactions in the polymeric media is often a substantial obstacle for applications of these materials.

We have recently found that photochromic spironaphthoxazine side groups incorporated in liquid crystalline polysiloxane macromolecules with *p*-cyanophenylbenzoate mesogenic side groups revealed a remarkably fast rate of thermal decoloration reaction at room temperature.[8] This is apparently explained by the very low glass transition temperature (T_g) for the polymers, which is below room temperature, and the lack of aggregation of the merocyanine form of the photochrome.

In the present paper, we report the kinetic studies of a variety of new photochromic amorphous polysiloxanes with spironaphthoxazine side groups. A new synthetic method was used for incorporation of the spirooxazine in the macromolecules. This allows one to skip the synthesis of the active ester side-chain polymer[6,8] by using new spirooxazine monomers with alkene substituents. The studies showed that the efficiency of the addition reaction depends on the length of the alkene group, while the rate of the thermal decoloration reaction of the resulting polymer depends on the content of the photochrome in a macromolecule.

Scheme I
Photochromic Transformation of Spironaphthoxazine



Experimental Section

Chemicals. The following chemicals were used without further purification: 2,3,3-trimethylindolenine (Aldrich), allyl iodide (BDH), 6-bromo-1-hexene (Fluka), 1-nitroso-2-naphthol, 98% (Aldrich).

Polymers poly(methylhydrosiloxane), $n = 35$ (Merck), tetra(methylhydrosiloxane), and penta(methylhydrosiloxane) (Petrarch Systems) were used for the synthesis of photochromic polymers.

Synthesis (Scheme II). (a) 1-(1-Prop-2-enyl)-3,3-dimethyl-2-methyleneindoline (IV). A mixture of 2,3,3-trimethylindolenine (I) (10 mL) and allyl iodide (II) (6.07 mL, 67 mmol) was heated at 100 °C for 3.5 h. A solid was obtained. It was dissolved in a mixture of water and ethyl acetate and then basified with sodium carbonate to pH 8. The Fisher base obtained was extracted with ether three times, dried over anhydrous sodium sulfate, and passed through a 5-cm column of basic alumina. The ethereal solution was evaporated to dryness. The product was reacted without further purification. Yield: 9.5 g (76%).

(b) 1-(1-Hex-5-enyl)-3,3-dimethyl-2-methyleneindoline (V) was prepared in a similar way to IV. Yield: 68%.

(c) 1′-(1-Prop-2-enyl)-3′,3′-trimethylspiro[indoline-2,3′-[3*H*]-naphtho[2,1-*b*]-1,4-oxazine] (VI) was prepared in a way similar to that described for oxazine VII (see below). The crude material was flash chromatographed on silica gel using ethyl acetate/hexane (1:20) as eluent. Yield: 26%. Anal. Calcd for $C_{24}H_{22}N_2O$: C, 81.96; H, 6.01; N, 7.65. Found: C, 80.84; H, 6.20; N, 7.82. ^1H NMR ($CDCl_3$) δ 1.34 (s, 3 H), 1.37 (s, 3 H), 3.78 (m, 2 H), 5.16 (m, 2 H), 5.90 (m, 1 H), 6.60 (d, 1 H), 6.86–7.80 (9 H, aromatic rings), 8.55 (d, 1 H, aromatic ring).

(d) 1′-(1-Hexenyl)-3′,3′-trimethylspiro[indoline-2,3′-[3*H*]-naphtho[2,1-*b*]-1,4-oxazine] (VII). A solution of Fisher base (V) (9 g, 0.037 mol) and 1-nitroso-2-naphthol (6.4 g, 0.034 mol) in 30 mL of analytical grade methanol and was refluxed for 40

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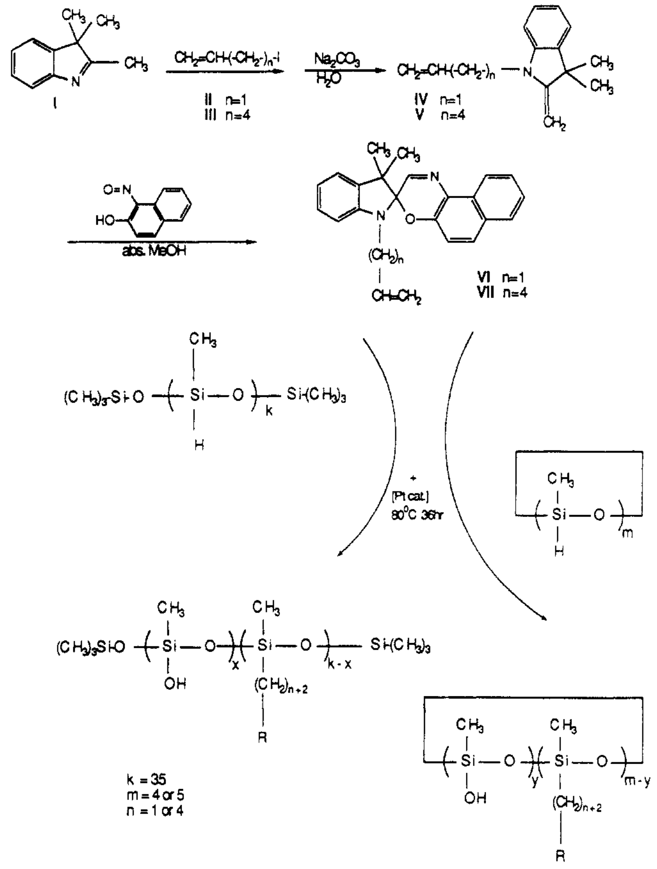
Scheme II
Synthesis of Spironaphthoxazine Monomers and Polysiloxanes Containing Spironaphthoxazine



min. The solvent was evaporated and the crude material flash chromatographed on silica using hexane as eluent. Yield: 3.5 g (24%). Anal. Calcd for $C_{27}H_{28}N_2O$: C, 81.78; H, 7.12; N, 7.06. Found: C, 81.46; H, 7.13; N, 7.03. ^1H NMR ($CDCl_3$) δ 1.33 (s, 3 H), 1.34 (s, 3 H), 1.58 (m, 4 H), 2.00 (m, 2 H), 3.18 (t, 2 H), 4.90 (m, 2 H), 5.78 (m, 1 H), 6.60 (d, 1 H), 6.85–7.80 (m, 9 H, aromatic rings), 8.55 (d, 1 H, aromatic ring).

Synthesis of the Photochromic Polymers. Polysiloxanes with the spirooxazine side groups were synthesized by polymer analogous reaction in one step. Spirooxazine monomers containing olefins (VI, VII) were added to an Si–H-containing polymer according to Scheme II and as described in refs 12 and 13. The polymers were isolated and purified by repeated precipitation with methanol and freeze-dried with benzene. The yield of the polymers ranged from 50% for some of the cyclic polymers to 90% for the linear ones. The content of the photochromic groups in the polymers was evaluated by elemental analysis (according to the nitrogen content) or by UV spectroscopy as described in ref 5.

Film Preparation. Polymer films of about 1-μm thickness were prepared by dip-coating of a 20% polymer solution in THF on a glass slide.

Characterization of the Polymers. Glass transition temperatures of the polymers were measured by differential scanning calorimetry (DSC). The DSC measurements were performed with a Mettler TA3000 instrument. Optical absorption measurements were performed on a Varian 2200 spectrophotometer with a heating–cooling attachment. For some polysiloxane films the spectra were taken at low temperatures. Flash photolysis was conducted as described in ref 14, using a thin (~1 μm) polysiloxane film placed at 45° toward the flash lamp. IR spectroscopy was conducted in an FTIR Nicolet 50 spectrometer on thin films supported on NaCl plates.

Results and Discussion

Addition of Spirooxazine to Polysiloxane. The progress of the addition reaction depicted in Scheme II was monitored by measuring the ratio of the peaks Si–H (2164 cm^{-1}) to Si–CH_3 (1272 cm^{-1}), which diminished in the course of the reaction. Calibration of the IR spectra against UV spectra of the polymers enabled us to observe the kinetics of the addition reaction (Figure 1). The reaction rate was approximately the same for spirooxazines, with either propene or hexene substituents in the 1′-position, when the starting ratio between spirooxazine and polymer was low (up to 25 mol % spirooxazine, relative to the Si–H bonds). At high ratios of the photochromes (up to 100 mol %), reaction with the propene-substituted spirooxazine slowed down earlier than the reaction with the hexene-substituted photochrome. Apparently, addition of the bulky spirooxazine groups, separated from the main chain only by short $(CH_2)_3$ spacers, caused steric hindrance to further incorporation of these groups in the polymer, while the photochrome with the long spacer did not produce this effect. This difference between the two spirooxazines was not observed when the photochrome content in the polymer was low (curve 1, Figure 1), which confirms the steric character of the effect.

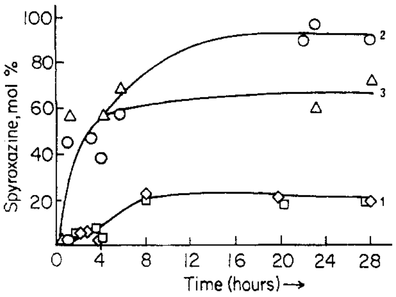


Figure 1. Content of spirooxazine incorporated in the linear polysiloxane as a function of the reaction time: 1, photochromes VI (◇) and VII (□) (see Scheme I), starting photochrome/Si–H ratio in the feed 25 mol %; 2, spirooxazine VI (△), starting ratio 100%, 3, spirooxazine VII (○), starting ratio 100%.

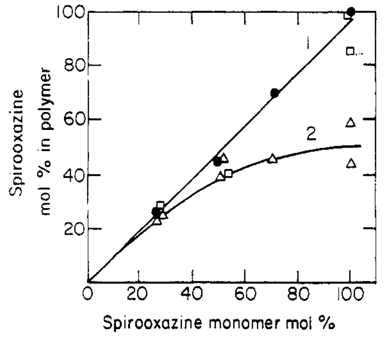


Figure 2. Content of spirooxazine in the polysiloxanes as a function of the spirooxazine monomer/Si–H bond ratio in the feed: 1, spirooxazine VII incorporated in the linear polymer (●) and in the cyclic polymer, m = 4 (□); 2, spirooxazine VI incorporated in the linear polymer (△).

Figure 2 shows the content of spirooxazine in the linear polymer synthesized by reactions depicted in Scheme I, as a function of the photochrome concentration in the feed. Curve 1 relates to the photochromic groups with the long spacer $(CH_2)_6$, and curve 2 relates to the short spacer $(CH_2)_3$. According to the figure, up to 100 mol % of the photochrome with the long spacer can be incorporated in the polymer as against only ~50–60 mol % of the photochrome with the short spacer.

An even more dramatic difference was observed with the cyclic polysiloxanes $(HCH_3SiO)_4$ and $(HCH_3SiO)_5$: up to 100 mol % of the photochrome with the long spacer was incorporated into both cyclic polysiloxanes, while only traces of the product of both cyclic polysiloxanes with spirooxazine VI were precipitated by methanol (unsubstituted polysiloxane cycles are soluble in methanol). This

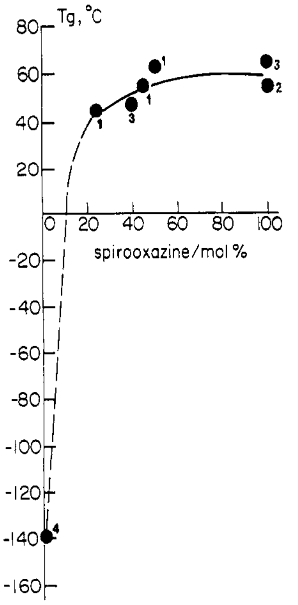


Figure 3. Dependence of T_g on the spirooxazine content in the polymers: circles 1 and 2, linear polymer substituted, respectively, by spirooxazines VI and VII; circle 3, cyclic polymer with spirooxazine VII; circle 4, the unsubstituted linear polysiloxane.

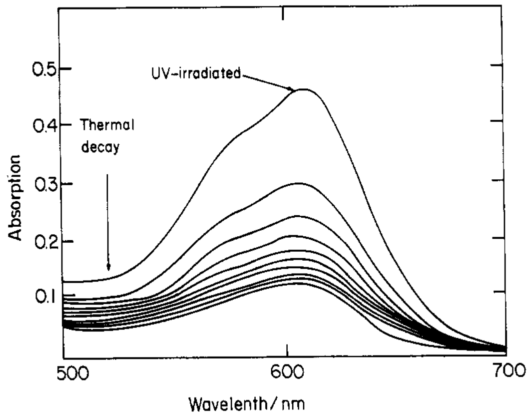


Figure 4. Change of the spectra of a photoactivated photochromic linear polysiloxane film (spirooxazine VI, 70 mol %) during the thermal color decay. The time interval between the upper spectrum and the second spectrum was 2 min. Further spectra were recorded after 10-min intervals.

means that incorporation of even one photochrome group with the short spacer in the cycles encounters some steric obstacles.

In any case, we can conclude that for the photochrome with the short spacer the steric factor controls the addition reaction.

Phase Behavior. Addition of both the spirooxazine side groups to the polysiloxanes leads to a drastic increase of the glass transition temperature (T_g) of both polymers (Figure 3). Though the data of the measurements are scattered, they indicate that T_g is roughly the same for polymers with spirooxazine content above 25 mol % and lies in the range 45–65 °C. Apparently, the side photochromic groups rather than the spacers or the polysiloxane backbones determine T_g.

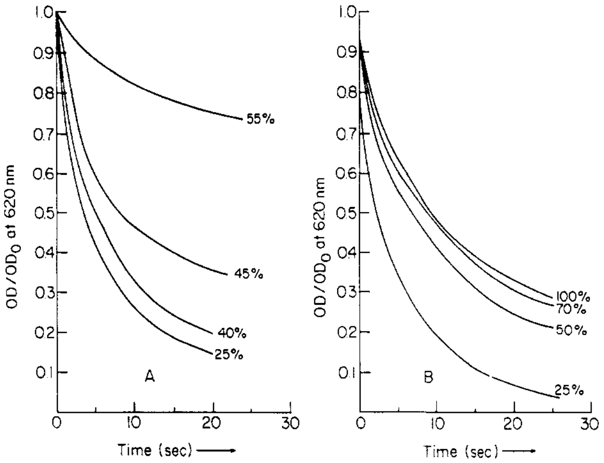


Figure 5. Kinetics of the fast color decay measured by flash photolysis at 610 nm for linear polysiloxane polymers with different contents of the photochromes: A, spirooxazine VI; B, spirooxazine VII.

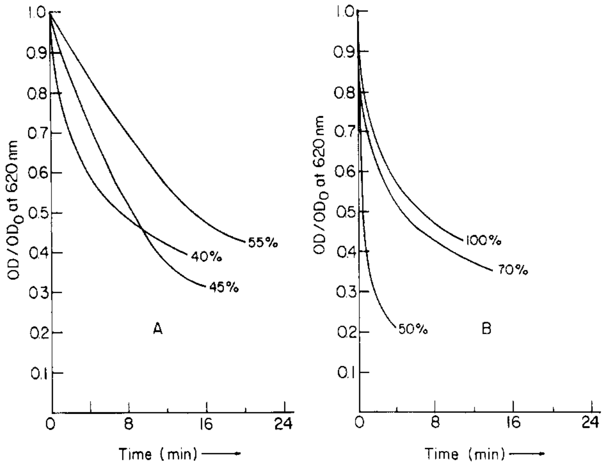


Figure 6. Kinetics of the slow color decay for linear polysiloxane polymers with different contents of the photochromes: A, spirooxazine VI; B, spirooxazine VII.

Spectra and Color Decay Kinetics. The absorption spectra resulting from UV irradiation of the photochromic polysiloxanes in the rigid films and in tetrahydrofuran solution are similar (film spectra are given in Figure 4) and remain unchanged when the temperature or concentration of the photochromic side groups is changed. Similar spectra were reported by us for photochromic, polymeric, and low molar mass liquid crystals containing spirooxazine units.[8,15] The absorption maximum at 610 nm and a pronounced shoulder around 580 nm indicate two overlapping bands. As suggested earlier,[16] the bands were ascribed to two merocyanine isomers which are in thermal equilibrium with each other. The shape of the spectra remains unchanged during the thermal color decay of the irradiated polymer films (Figure 4), which is in agreement with the two-isomer assumption. Unlike polymers containing spiropyran photochromic groups,[6] we found no spectral indication of aggregation of merocyanine formed from spirooxazine.

Typical kinetics of decoloration processes of UV-irradiated films are shown in Figures 5 and 6. The color decay does not obey first-order kinetics. The initial fast decay (Figure 5) is followed by a slower decay (Figure 6). Thus, e.g., curve 55% in Figure 6A is actually a continuation of the same curve in Figure 5A. It is evident that the fraction of fast initial decay decreases at higher spirooxazine contents, in particular with VI. At 25% spirooxazine content decoloration is practically first order and involves only the fast stage. On the other hand, at the highest spirooxazine content, the second stage of decay is followed by a still slower stage, as may be seen in Figure 4. As a first approximation, the color decay can be described by a sum of two exponential equations, with "fast" and "slow" rate constants.[17,18] For linear polysiloxanes, the rate of the slow and the fast stage decreases with increasing concentration of photochromic groups in the polymer (Figures 7 and 8). The slowest decay was

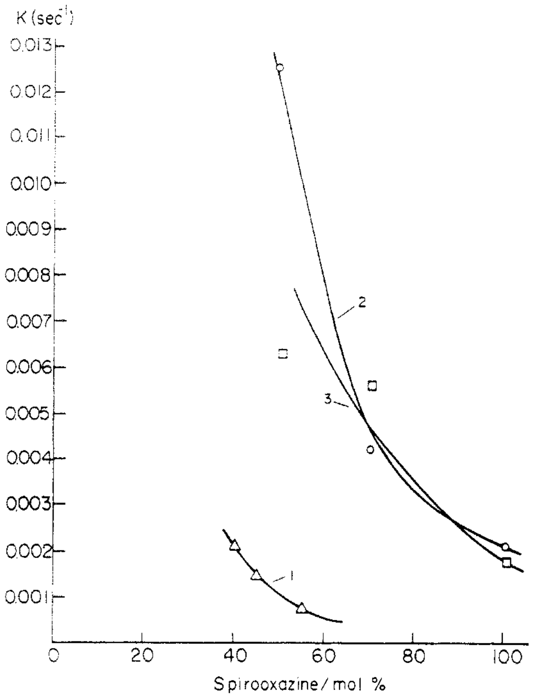


Figure 7. Dependence of the slow decoloration rate constants on the photochrome content in the linear polymers [1 (△), spirooxazine VI; 2 (○), spirooxazine VII] and in the cyclic tetrasiloxane [3 (□), spirooxazine VII].

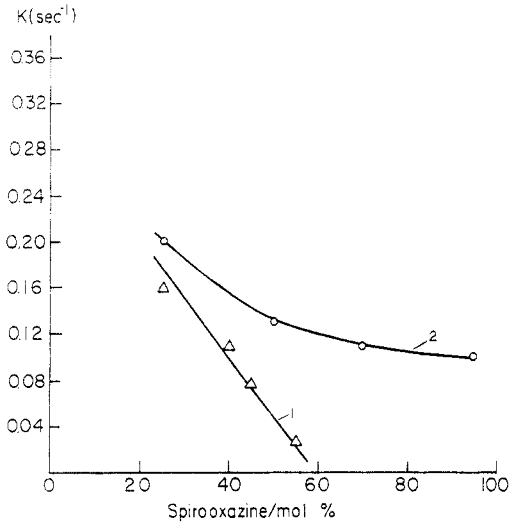


Figure 8. Dependence of the fast decoloration rate constants on the photochrome content in the linear polymers [1 (△), spirooxazine VI; 2 (○), spirooxazine VII].

observed in the polymer containing the highest possible concentration of spirooxazine groups. In the cyclic polymers containing the photochrome with a long spacer, the color decay occurs practically with the same rate as in the linear polymers (Figure 7).

Comparison of the kinetic curves with the T_g dependence on the photochrome concentration (Figure 3) indicates that there is no direct connection between the temperature of the glass transition (presumably also the polymer density) and the decoloration kinetics. Apparently, the deviation from first-order kinetics and the retardation of the color decay at high concentration of the photochrome in polysiloxane stem from the steric hindrance by adjacent bulky photochromic groups. Similar kinetic behavior of acrylic and methacrylic photochromic polymers with spiropyran–mercocyanine photochrome proved to be connected with the merocyanine aggregation.[17,18]

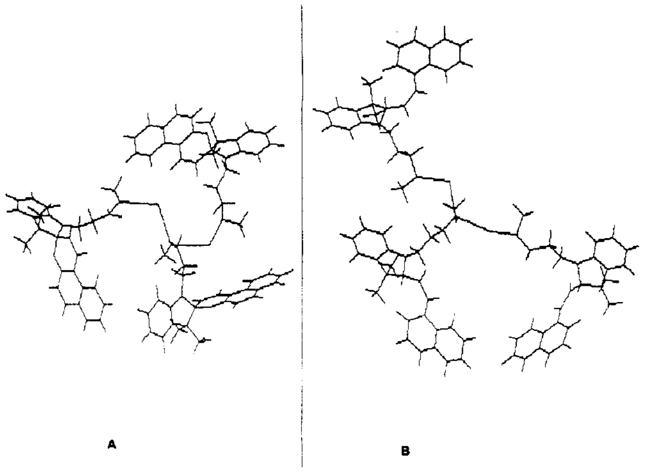


Figure 9. Conformation of a fragment of the macromolecules with the $(CH_2)_3$ spacer minimized over energy: photochrome in the form of (A) spirooxazine and (B) merocyanine.

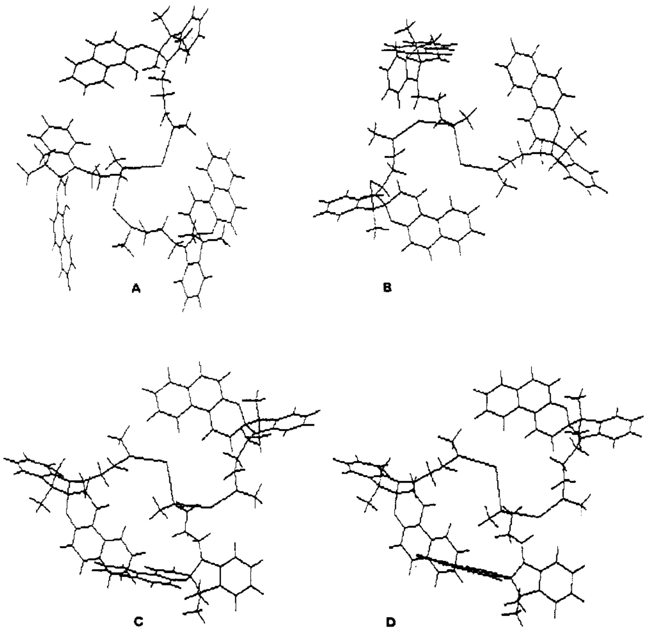


Figure 10. Examples of rotated (only C–C bonds) conformations of the macromolecule with the photochrome in the spirooxazine form: A, B, allowed conformation; C, D, forbidden conformations (the covalently unbound atoms contact each other).

Computer Simulation of Molecular Conformations. The Oxford Molecular Graphics program was used for conformational analysis and visualization of possible steric interactions of the bulky photochromic groups incorporated in the polymer through the hydrocarbon spacers.

In the first stage the macromolecule was separated into the three "quasi" constrained fragments: (1) polymer main chain (polysiloxane); (2) fragment of the molecule consisting of the $(CH_2)_3$ and $(CH_2)_6$ spacers; and (3) photochromic spirooxazine or merocyanine side groups.

In the process of the energy minimization for these constrained groups, we used the library of the specific bond lengths and bond angles partly obtained from X-ray data.[19]

The conformation of each constrained group, at this stage, was calculated independently. During the minimization we checked the bonds and angles between covalently bound atoms, restraining the distances between Si and O in polysiloxanes (=3 Å), the distances between C and C in spacers (=1.5 Å), etc. Then we connected all three independent fragments together, creating a fragment of the whole macromolecule, and ran energy minimization

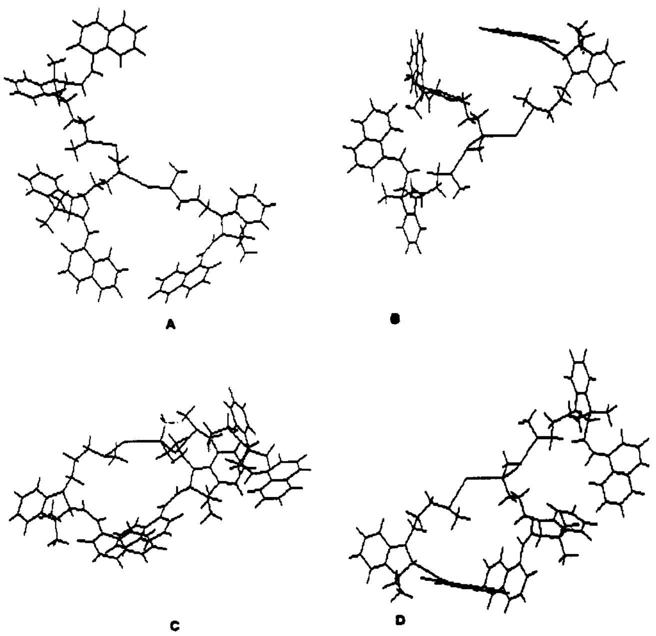


Figure 11. Examples of rotated (along C–C bonds) conformations of the macromolecule with the photochrome in the merocyanine form: A, B, allowed conformations; C, D, forbidden conformations.

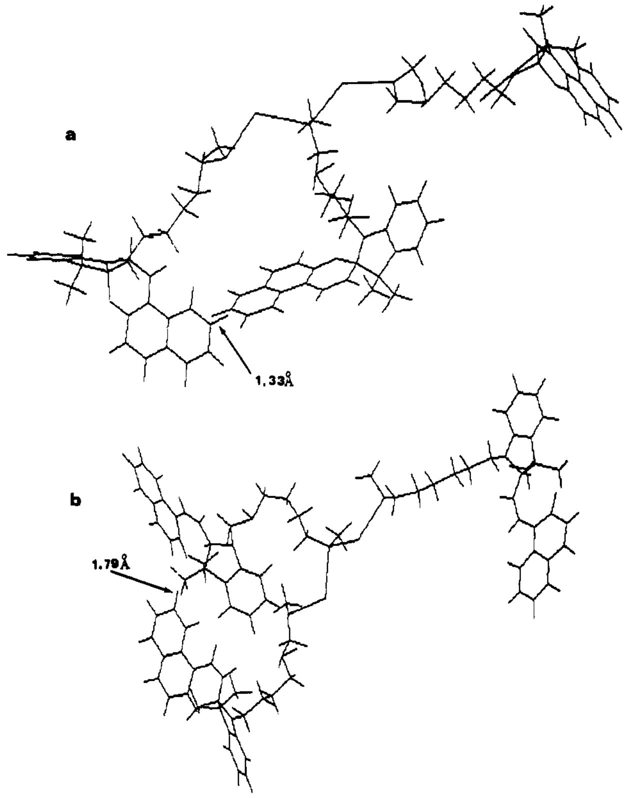


Figure 12. Closest positions of the photochromic groups for the $(CH_2)_6$ spacer: a, spirooxazine; b, merocyanine.

for this system. After several iterations, we checked all distances and bond angles between the neighboring atoms. All of these parameters corresponded to standard library values. After constructing a fragment of the whole macromolecule, we used the rotations of the photochromic groups along all of the C–C bonds in the $(CH_2)_n$ spacers to reveal the contacts between covalently nonbound atoms in a macromolecule and possible unreasonable conformations.

The results of computer simulations confirm the conclusions about the steric hindrance of reactions by the bulky groups. The contacts between the different atoms of the adjacent photochromic groups were found only in the macromolecules with the short spacers $(CH_2)_3$. The conformation of the molecule after energy minimization, but before rotation around C–C bonds of a spacer, is depicted in Figure 9. The series of rotations leading to the sterically forbidden conformations for $(CH_2)_3$ spacer are presented in Figures 10 and 11.

The same simulations were performed for the linear polysiloxanes with the long $(CH_2)_6$ spacers between the main chain and photochrome. In this case, the photochromic groups never "touch" each other at any rotation around the C–C bonds of the spacer. This was proven for both spirooxazine and merocyanine photochromes. The shortest distances between the unbound C atoms of the spirooxazine or merocyanine groups in macromolecules are 1.79 and 1.33 Å, correspondingly. This is illustrated in Figure 12.

These distances are smaller than those allowed by van der Waals interactions, which apparently explains the retardation of the thermal decoloration reaction at high contents of the photochromic groups. However, this does not prevent the nearly 100% substitution of the polymer by the photochromic groups.

In the case of the short $(CH_2)_3$ spacers, the forbidden conformations prevent the incorporation of the photochromic groups in a proportion higher than ~50–60%. The photochromic groups interacting with the macromolecule seem to accept a variety of positions in the course of the reaction, and if some of them are forbidden in the transition state, the reaction does not proceed.

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