Photochromic Polyphosphazenes with Spiropyran Units

Harry R. Allcock* and Chulhee Kim

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

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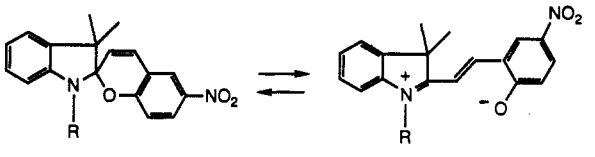
ABSTRACT: Photochromic spiropyrans were linked to polyphosphazenes through diethyleneoxy or triethyleneoxy spacer units. The reversion of photogenerated merocyanine groups to spiropyran units in these polymers in various solvents or in the solid state was investigated. The reversion rate in the polymeric solid state was much slower than in solution. In solution the rate decreased as the solvent polarity decreased. A phosphazene polymer with spiropyran units as the only side groups present showed a slower merocyanine to spiropyran reversion rate than did a mixed-substituent polyphosphazene with a lower loading of the chromophores. Presumably this is a consequence of steric effects. A polymer with spiropyran units linked via diethyleneoxy spacer groups underwent the merocyanine to spiropyran reversion at a slower rate than did a polymer with the spiropyran units connected through a triethyleneoxy spacer unit. Unlike the behavior of the free small-molecule spiropyran, the merocyanine relaxation in the polymeric species showed deviations from a first-order relationship in solution and in the solid state. Relaxations in THF and in the solid state were modeled by a biexponential process. The overall phenomena were explained by the solvation or aggregation of the polymer chains in solution as well as by the existence of two different environments for the merocyanine units.

Introduction

Spiropyrans[1] are well-known photochromic dyes, which have been used in polymeric systems in connection with morphological investigations[2-9] and conformational studies in solution.[10-17] They have potential applicability for optical data storage systems.[18-20] Spiropyrans are reversibly converted to ring-opened merocyanines when exposed to light or heat, or with changes in solvent polarity.[1]



spiropyran merocyanine

The photochromism involves the cleavage or formation of the C–O pyran bond and rotation of a part of the molecule to generate a pronounced change of conformation. This conformational change of the photochromic moiety is affected by the polymer chain conformation or mobility both in solution and in the solid state. Conversely, the conformation of polymer chains can also be influenced by the conformational change of bound photochromic groups. Therefore, photochromic spiropyrans can be used not only as probes to investigate polymer morphology or solution properties, but also as a trigger to change the polymer conformation.

Poly(organophosphazenes) are an important class of semiinorganic polymers that have a flexible phosphorus–nitrogen backbone and a variety of organic or inorganic side groups attached to the phosphorus atoms. Their unique morphological properties have been the source of some interest.[21-30] However, few studies have been reported of their solution properties. Thus, the photochemical behavior of poly(organophosphazenes) that bear a photochromic spiropyran moiety as a probe provides a method to understand both the solution and solid-state properties of phosphazene polymers.

In this paper, we discuss (1) the synthesis of photochromic poly(organophosphazenes) that bear spiropyran side units and (2) ultraviolet–visible spectrophotometric and kinetic studies of the reversion of merocyanine units to spiropyrans in solution and in the solid state.

Results and Discussion

Synthesis and General Properties. Synthetic approaches to link spiropyran groups covalently to phosphazenes were explored by use of a phosphazene cyclic trimer as a model. Thus, pentakis(trifluoroethoxy)monochlorocyclotriphosphazene was allowed to react with spiropyran 1 in the presence of sodium hydride in THF (Scheme I). The ^{31}P NMR spectrum of the product consisted of an AB_2 spin system (ν_A = 16.3 ppm, ν_B = 13.1 ppm, J_{PNP} = 92.4 Hz), which is typical of pentaalkoxy–monoaryloxy-substituted cyclic phosphazene trimers.[31,32] The mass (m/z) of the product was 981. Therefore, it is suggested that 2 undergoes a ring opening of the spiropyran, followed by the formation of a five-membered heterocyclic ring to form species 3, which then replaces the chlorine atom on the phosphorus of the trimer to yield trimer 4. This model reaction suggested that other functional groups are needed on the polymer for coupling of the spiropyrans rather than the use of a direct replacement of chlorine atoms by basic nucleophiles.

For this purpose, the new polyphosphazenes 9 and 10 with spacer groups and hydroxyl side-chain end groups were synthesized as illustrated in Scheme II. Both polymers 9 and 10 were prepared by using monoprotected diols 5 and 6. Characterization data for the polymers are summarized in Table I. As a representative example, the following pathways were involved in the preparation of polymer 9. Diethylene glycol was monoprotected by dihydropyran to yield compound 5. The sodium salt of 5 was allowed to react with poly(dichlorophosphazene) to produce polymer 7, which was soluble in common organic solvents such as THF, toluene, or chloroform. Polymers 7 and 8 became insoluble but swellable in THF if they were stored under dry condition for several days. Therefore, they were stored under *n*-hexane to maintain the solubility for further reactions. A high degree of chlorine replacement was confirmed by the singlet resonance at −8.1 ppm in the ^{31}P NMR spectrum, and by the elemental analysis. Molecular weight data from GPC experiments

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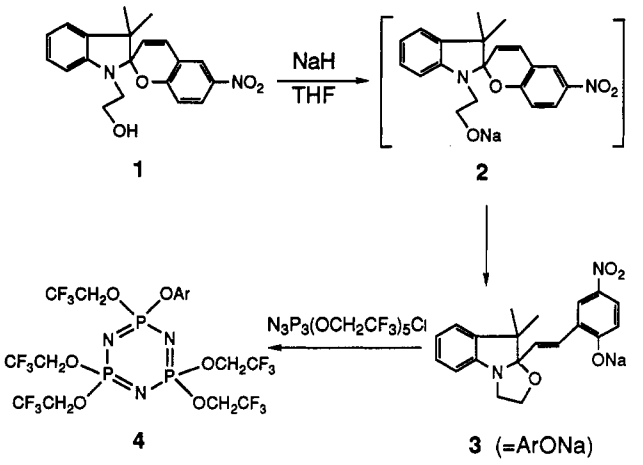
Scheme I



showed $M_w = 1.3 \times 10^6$ ($M_w/M_n = 36$). For the deprotection of the pyranyl moiety, polymer 7 was first dissolved in THF, and absolute ethanol was added to the point where the THF/ethanol ratio was 1/20–1/30. The polymer solution was then refluxed in the presence of pyridinium *p*-toluenesulfonate to yield polymer 9. It was confirmed that the deprotection was quantitative by ^{1}H NMR analysis and microelemental analysis for polymer 9. The ^{1}H NMR spectrum of polymer 9 showed a total disappearance of the resonances at 4.59 ppm and between 1.90 and 1.40 ppm, which was due to pyranyl groups. Polymers 9 and 10, with hydroxyl side-chain end groups, were soluble in water, methanol, ethanol, DMSO, and DMF.

Spiropyran 11 was introduced into polymers 9 and 10 by an esterification process to yield polymers 12 and 13, respectively. Spiropyran 11 was synthesized by using a literature procedure.[33] The polymeric products 12 and 13 were light tan materials, which were soluble in THF. Elemental microanalysis and ^{1}H NMR spectra showed that the esterification was quantitative. Polymers 12 and 13 were employed to study the effect of the spacer length on the photochemical process.

In order to investigate the effect of the spiropyran loading within the polymer on the kinetics of merocyanine conversion to spiropyran, the mixed-substituent photochromic phosphazene polymer 17 was prepared by using trifluoroethoxy groups as the cosubstituents. The synthetic pathways are described in Scheme III. Addition of the sodium salt of the monoprotected diethylene glycol in a controlled stoichiometric amount (ca. 20%) yielded polymer 14, which is partially substituted and hydrolytically unstable. Subsequent addition of an excess of sodium trifluoroethoxide produced polymer 15. This was a fibrous and film-forming polymeric product. The composition ratio of the mixed substituents (81% of trifluoroethoxy groups) in polymer 15 was determined by the integration ratio of the resonances from ^{1}H NMR and by elemental analysis. The pyranyl moiety of 15 was deprotected to yield polymer 16, which was esterified with spiropyran 11 to produce mixed-substituent phosphazene polymer 17. This polymer was soluble in THF and hexafluoro-2-propanol.

The glass transition temperatures of polymers 7, 8, and 15 with the pyranyl protected groups were −51, −54, and −49 °C, respectively. Removal of the six-membered pyranyl groups from the end of the side chains brought about a lowering of the glass transition temperatures. Polymers 9, 10, and 16, with total deprotection, showed T_g's at −63, −58, and −56 °C, respectively. Differential scanning calorimetric thermograms of polymers 12, 13, and 17 were complicated by the broad endotherm from the spiropyran group rearrangement.[9] The thermograms of polymer 12 are shown in Figure 1. In the first run, a broad endotherm appears due to the thermochromic behavior of the spiropyrans. From the second run, the broad endotherm disappears to show the glass transition at 77 °C. The glass transition temperatures of polymers 13 and 17 were 32 and 3 °C, respectively.

Photochemical Behavior. The formation of merocyanines and their reversion to spiropyran groups were studied by UV–vis spectroscopy. Irradiation of polymers 12, 13, and 17 gave rise to new absorption maxima in the visible range, which were attributed to the merocyanine species.[22,23] As a representative example, irradiation of polymer 12 in THF solution generated a new λ_{max} at 576 nm with a shoulder at 555 nm as shown in Figure 2a. The absorbance of this λ_{max} in the visible range decreased as the merocyanine units relaxed to spiropyrans. In this case, there was no significant spectral change during the reversion of the merocyanine to spiropyran. The absorption spectra of polymer 12 after irradiation in a less polar solvent, for example in THF/toluene (1/4, v/v), are shown in Figure 2b. A shift of λ_{max} from 588 to 574 nm occurred during the reversion of the merocyanine to the spiropyran. In THF/toluene (1/1), λ_{max} was 586 nm and was shifted to 578 nm as the reversion to spiropyrans occurred. The solid film of polymer 12 on a quartz cell showed a λ_{max} at 584 nm, which was not changed significantly during the merocyanine relaxation. Polymer 13 showed a very similar spectral behavior. For the mixed-substituent polymer 17, λ_{max} after irradiation was 574 nm, with a small shoulder at 555 nm in THF, 568 nm in THF/toluene (1/1), 562 nm in THF/toluene (1/4), and 570 nm in a solid film. A shift of λ_{max} to a slightly shorter wavelength was observed during the merocyanine reversion to spiropyran.

The kinetics of the merocyanine to spiropyran conversion are dependent on the solvent polarity, spacer length between the polymer backbone and the dye moiety, and the spiropyran loading along the polymer chain. The kinetics in solution and in the solid state are also different. The half-lives (τ) of the merocyanine conversion to spiropyran under various conditions are summarized in Table II.

The half-lives in the solid state of all the polymers were much longer than those in solution. This can be ascribed to the rigidity of the solid polymeric matrix compared with the situation in solution. For a given solvent, or in the solid state, the half-lives of polymer 17 (with a 19% spiropyran incorporation in the side group) were much shorter than those of polymer 12 with 100% incorporation. This result suggests that the reduction of steric hindrance in polymer 12 increases the rate of the merocyanine reversion. This reduction of the steric bulkiness could result from the low incorporation of bulky spiropyran units and from the use of the small, flexible trifluoroethoxy cosubstituent. The shorter merocyanine half-life in polymer 13 than in polymer 12 is also explained by the reduction of steric hindrance that occurs by use of the longer spacer. The half-life of polymer 17 in a given solvent is slightly shorter or similar to those of the free small-molecule spiropyran 11. This is probably due to a combination of two factors. First, the steric problem in the side chain of polymer 17 could be greatly relieved by a low incorporation of spiropyran units. Second, the merocyanine form of the free spiropyran 11 can perhaps be stabilized by intra- or intermolecular hydrogen bonding through carboxyl and aryl oxide moieties and this would retard the merocya-

Scheme II

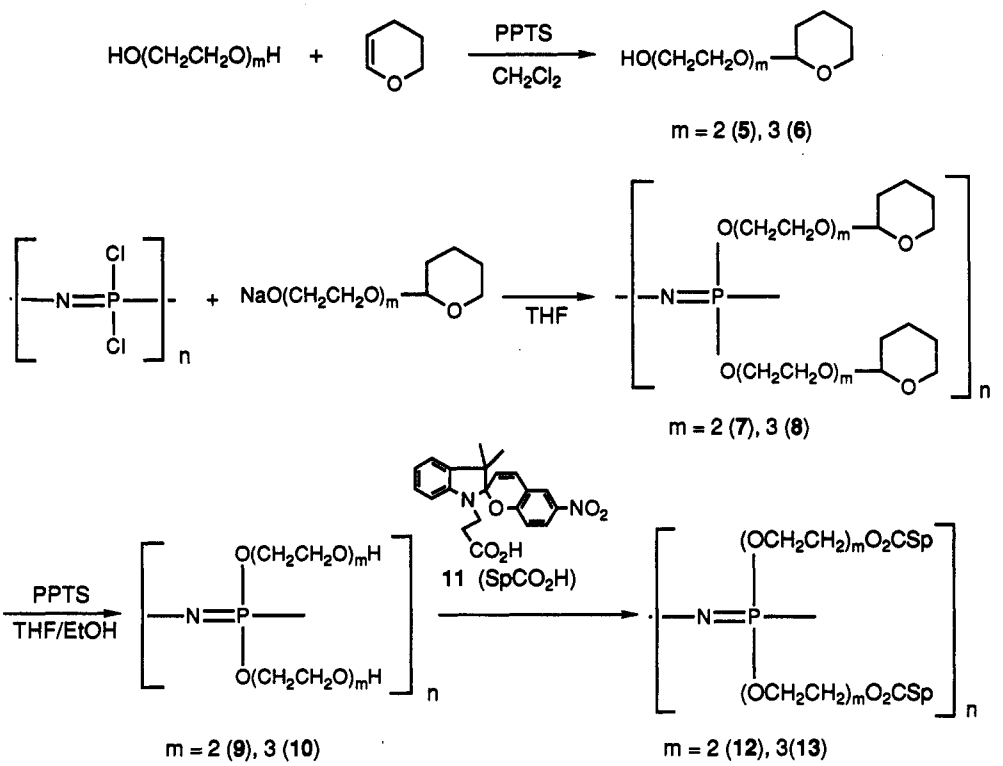


Table I
Characterization Data for Polyphosphazenes

polymer	^{1}H NMR,[a] δ	^{31}P NMR,[a] ppm	mol wt (GPC) M_w	M_w/M_n	T_g, °C	elem anal. calcd	elem anal. found
7	4.55 (br, s, CH, 1 H), 4.05 (br, s, $POCH_2$, 2 H), 3.95–3.35 (br, m, OCH_2, 8 H), 1.90–1.40 (br, m, CH_2, 6 H)	−7.9(s)	1.6×10^6	36	−51	C, 51.06; H, 8.09; N, 3.31; Cl, 0	C, 51.72; H, 8.51; N, 2.92; Cl, 0.074
8	4.50 (br, s, CH, 1 H), 4.00 (br, s, $POCH_2$, 2 H), 3.95–3.40 (br, m, OCH_2, 12 H), 1.90–1.40 (br, m, CH_2, 6 H)	−8.1(s)	6×10^5	19	−54	C, 51.66; H, 8.23; N, 2.74; Cl, 0	C, 51.48; H, 7.94; N, 2.82; Cl, 0.02
9	3.97 (br, s, $POCH_2$, 2 H), 3.65–3.25 (br, m, OCH_2, 6 H)	−8.1(s)	*b*		−63	C, 37.65; H, 7.11; N, 5.49; Cl, 0	C, 38.66; H, 7.35; N, 5.22; Cl, 0.02
10	4.00 (br, s, $POCH_2$, 2 H), 3.70–3.30 (br, m, OCH_2, 10 H)	−8.0(s)	*c*		−58	C, 41.98; H, 7.58; N, 4.08 Cl, 0	C, 39.52; H, 7.21; N, 4.46; Cl, 0.026
12	7.80–6.50 (br, m, ArH, vinyl), 5.75 (br, s, vinyl), 4.10–3.40 (br, m, OCH_2), 2.50 (br, d, CH_2), 1.60 (br, s, CH_2), 1.15 (br, s, CH_3), 0.95 (br, s, CH_3)	−8.0(s)	1×10^6	30	77	C, 61.29; H, 5.52; N, 7.15; Cl, 0	C, 60.77; H, 5.35; N, 6.99; Cl, <0.07
13	7.80–6.45 (br, m, ArH, vinyl), 5.80 (br, s, vinyl), 4.15–3.35 (br, m, OCH_2), 2.55 (br, d, CH_2), 1.65 (br, s, CH_2), 1.20 (br, s, CH_3), 0.95 (br, s, CH_3)	−7.8(s)	5×10^5	23	32	C, 71.37; H, 3.41; N, 7.71; Cl, 0	C, 70.79; H, 3.58; N, 7.54; Cl, <0.06
15	4.50 (br, s, CH), 4.30 (br, s, OCH_2CF_3), 4.20–3.40 (br, m, OCH_2), 1.90–1.40 (br, m, CH_2)	−8.1(s)	7×10^5	11	−49	C, 28.83; H, 3.50; N, 5.05; Cl, 0	C, 28.34; H, 3.18; N, 5.02; Cl, 0.041
16	4.30 (br, s, OCH_2CF_3), 4.1–3.4 (br, m, OCH_2)	−8.0(s)	5×10^5	14	−56	C, 23.29; H, 2.72; N, 5.71; Cl, 0	C, 22.74; H, 2.33; N, 5.87; Cl, <0.018
17	7.90–6.45 (br, m, ArH, vinyl), 5.75 (br, s, vinyl), 4.30 (br, s, OCH_2CF_3), 4.15–3.35 (br, m, OCH_2), 2.50 (br, d, CH_2), 1.65 (br, s, CH_2), 1.15 (br, s, CH_3), 0.95 (br, s, CH_3)	−8.1(s)	9×10^5	19	2	C, 39.93; H, 3.53; N, 6.44; Cl, 0	C, 38.43; H, 3.28; N, 6.12; Cl, 0.081

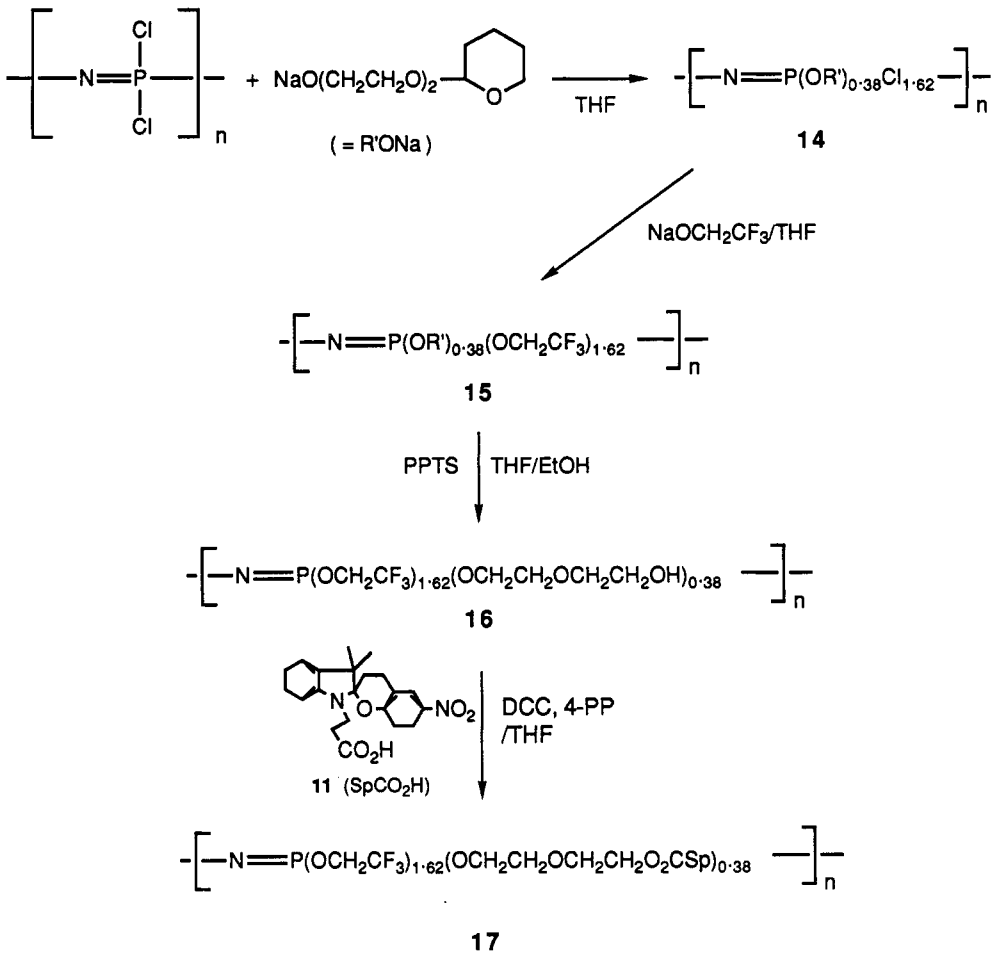
[a] In $CDCl_3$ except 9 and 10 (DMSO-d_6). [b] η_{inh} = 0.98 dL/g (*c* = 0.5 g/dL, ethanol). [c] η_{inh} = 0.84 dL/g (*c* = 0.5 g/dL, ethanol).

nine reversion, which is not expected in polymer 17. For a given polymer, the reversion half-lives are longer in less polar solvents.

The merocyanine reversion of polymer 12 in THF solution followed a first-order relationship until ca. 55% conversion, where deviations occurred. After the conversion of ca. 85%, the decay fitted a different first-order relationship. The whole conversion process can be better described by a biexponential expression as in eq 1 (Figure 3). In this equation, x and $1-x$ are the fractions of merocyanines with decay rates k_1 and k_2. This treatment assumes that two types of merocyanines exist, depending on the solvation or stacking condition.[15] The conversion of merocyanine in a solid film of polymer 12 showed a similar decay pattern. However, the conversion in THF/

$$A = A_0[xe^{-k_1t} + (1-x)e^{-k_2t}] \quad (1)$$

Scheme III



toluene (1/2 or 1/4) showed deviations from both a first-order relationship and a biexponential expression (Figure 4). For polymers **13** and **17**, the decay patterns were similar to those of polymer **12** in solution and in the solid state. For free spiropyran **11**, the merocyanine reversion in solution showed a first-order relationship.

A study of the morphological or conformational changes of polyphosphazenes induced by the photochromic behavior will be a subject for further study.

Experimental Section

Materials. Hexachlorocychlotriphosphazene (Ethyl Corp.) was purified by recrystallization from *n*-hexane followed by sublimation at 40 °C (0.5 mmHg). Poly(dichlorophosphazene) was prepared by the bulk thermal ring-opening polymerization of hexachlorocyclotriphosphazene at 250 °C.[34-36] Tetrahydrofuran (THF) and toluene were dried over sodium benzophenone ketyl and were distilled under nitrogen before use. Silica gel (60–200 mesh, Fisher) was used for column chromatography. All the other reagents (Aldrich) were used as received.

Instruments. The ^{1}H NMR spectra were recorded with the use of a Bruker WP-360 spectrometer operated at 360 MHz. Chemical shifts are relative to tetramethylsilane at $\delta = 0$. ^{31}P NMR (^{1}H-decoupled) spectra were obtained with a JEOL FX90Q NMR spectrometer operated at 36.2 MHz or a Bruker WP-360 spectrometer operated at 144.8 MHz. ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 at 0 ppm with positive shift values downfield from the reference. Electron impact or chemical ionization mass spectra were obtained with the use of a Kratos MS9/50 spectrometer. Molecular weights were determined by using a Hewlett-Packard HP1090 gel permeation chromatograph with an HP-1037A refractive index detector and Polymer Laboratories PL gel (10 μm) column. The samples were eluted with a 0.1% solution of tetra-*n*-butylammonium bromide in THF. The GPC column was calibrated with polystyrene standards

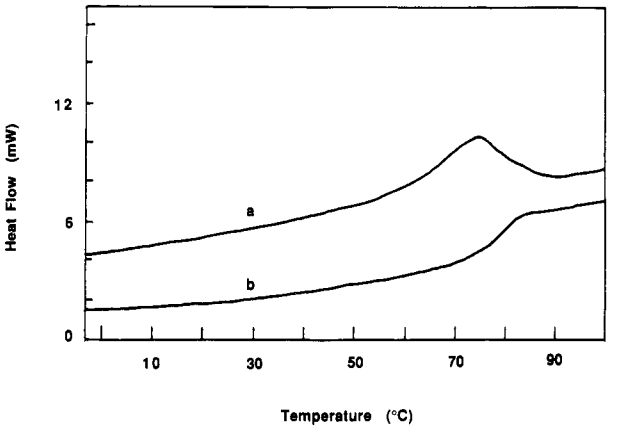


Figure 1. Differential scanning calorimetry thermograms of polymer **12**; (a) first run, (b) second run.

(Waters) and with fractionated samples of poly[bis(trifluoroethoxy)phosphazene] provided by Drs. R. Singler and G. Hagnauer of the U.S. Army Materials Technology Laboratories, Watertown, MA. UV–vis spectra were recorded with Hewlett-Packard 8450A UV–vis spectrophotometer. The kinetic study was carried out with the use of a Perkin-Elmer Lamda 4C UV–vis spectrophotometer combined with a Perkin-Elmer Series 7300 computer. During the experiments the sample was maintained at a constant temperature of 25 °C by means of a water jacket device. UV irradiation was performed by using UV lamps (100 or 450 W) with a visible filter (Oriel 50380). Samples were irradiated until the highest merocyanine absorbance was obtained. The use of a high-pressure mercury lamp (450 W) did not affect the absorbance of samples already irradiated by a 100-W lamp. Thus, it was assumed that most of the spiropyran units were converted to merocyanines by irradiation. The Direct Searching Simplex Method was used for biexponential curve

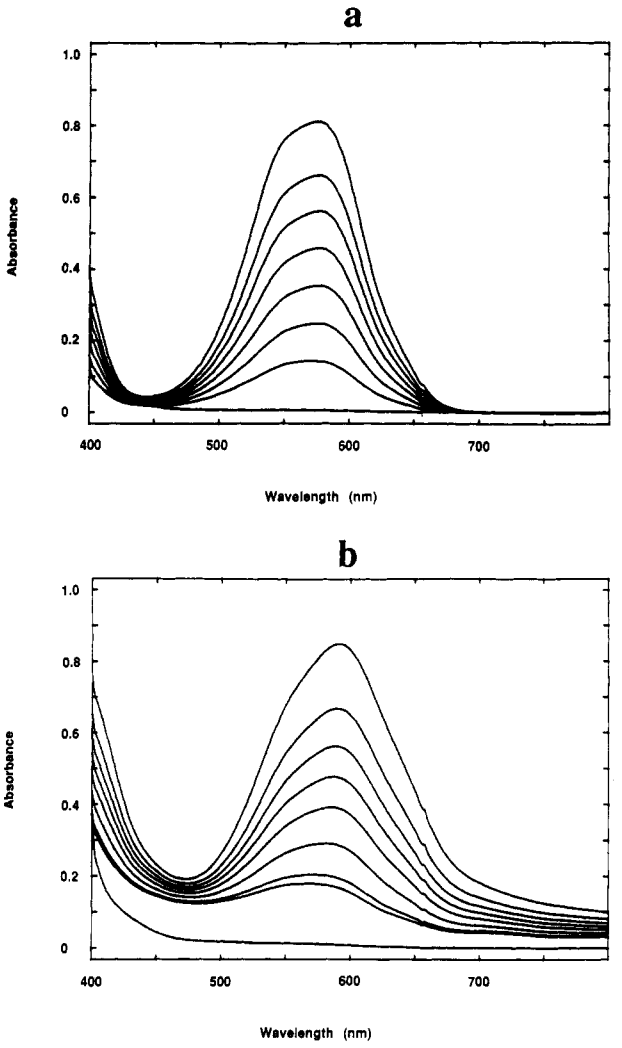


Figure 2. Absorption spectra of irradiated polymer 12 in (a) THF and (b) THF/toluene (1/4). The relaxation time increases as the absorbance decreases. These spectra were selected to illustrate the changes in the spectral profile. The actual changes in absorbance as a function of time are shown in Figures 3 and 4.

Table II
Half-Life of Merocyanine Form of Polymers and Small-Molecule Spiropyran

	half-life (τ), min			
compounds	THF	THF/tol (1/2)	THF/tol (1/4)	solid
spiropyran 8	0.25	0.27	0.27	
polymer 12	1.20	4.69	8.29	121.0
polymer 13	0.79	1.57	3.66	113.0
polymer 17	0.16	0.20	0.39	74.6

fitting. Perkin-Elmer 7 thermal equipment was used to obtain differential scanning calorimetric thermograms. Solution viscosities were measured by using a Cannon-Ubbelohde capillary viscometer. Elemental microanalyses were obtained by Galbraith Laboratories, Knoxville, TN.

Preparation of 2-[2-(Tetrahydropyranyloxy)ethoxy]ethanol (5) and 2-[2-[2-(Tetrahydropyranyloxy)ethoxy]ethoxy]ethanol (6). Compounds 5 and 6 were prepared by following the same procedure. As a representative example, 5 was prepared by the following procedure. A methylene chloride solution (200 mL) of dihydropyran (16.82 g, 0.2 mol) with pyridinium *p*-toluenesulfonate (PPTS; 5.03 g, 0.02 mol) was slowly added to the solution of diethylene glycol (21.22 g, 0.2 mol) in methylene chloride (500 mL). The solution was stirred for 4 h at room temperature. The oily product was isolated from di- and unprotected diethylene glycol by column chromatography on a silica gel (R_f = 0.40 in diethyl ether; yield, 14.12 g, 37%).

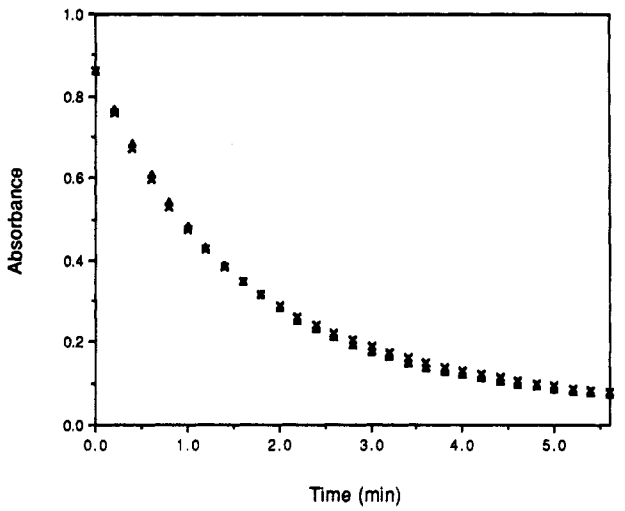


Figure 3. Absorbance decay at 576 nm for polymer 12 in THF. (△) Experimental data; (×) calculated data obtained from biexponential eq 1.

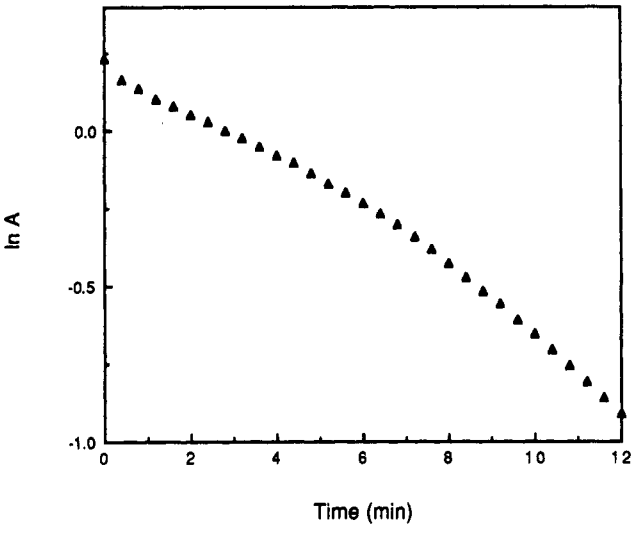


Figure 4. Kinetics of the merocyanine–spiropyran conversion for polymer 12 in THF/toluene (1/4).

For 5: ^{1}H NMR ($CDCl_3$) δ 4.60 (t, OCHO, 1 H), 3.90–3.40 (m, OCH_2, 10 H), 1.85–1.40 (m, CH_2, 6 H); IR (thin film on KBr) 3700–3050 cm^{-1} (br, OH), 2940 (s, CH), 1120 (s, COC); MS (CI) found 190, calcd 190.

For 6: ^{1}H NMR ($CDCl_3$) δ 4.60 (t, OCHO, 1 H), 3.90–3.40 (m, OCH_2, 14 H), 1.90–1.40 (m, CH_2, 6 H); IR (thin film on KBr) 3700–3050 (br, OH), 2950 (s, CH), 1120 (s, COC) cm^{-1}; MS (CI) found 234, calcd 234.

Preparation of Poly[bis[2-[2-(tetrahydropyranyloxy)ethoxy]ethoxy]phosphazene] (7) and Poly[bis[2-[2-[2-(tetrahydropyranyloxy)ethoxy]ethoxy]ethoxy]phosphazene] (8). Polymers 7 and 8 were prepared by the same procedure. As an example, the procedure for 7 is as follows. Into a THF (300 mL) suspension of the sodium salt of 5, prepared from compound 5 (14.76 g, 78 mmol) and sodium hydride (1.87 g, 78 mmol), was added a THF solution (70 mL) of poly(dichlorophosphazene) (3.0 g, 26 mmol). The solution was stirred for 48 h at 40 °C. The polymer solution was concentrated by the evaporation of the solvent and was poured into water to obtain the precipitate of the polymeric product, which was further purified by repeated precipitation into water and *n*-hexane (5.6 g, 51%). An average yield for 8 was 50–60%.

Preparation of Poly[bis[2-(2-hydroxyethoxy)ethoxy]phosphazene] (9) and Poly[bis[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]phosphazene] (10). The same procedure was employed for the preparation of polymers 9 and 10. The typical procedure for 9 is as follows. Polymer 7 (5.0 g, 12 mmol) was first dissolved in THF (10 mL) and absolute ethanol (300 mL) was

added slowly with PPTS (2.25 g, 9 mmol). The solution was refluxed for 30 h and dialyzed against water for 5 days and against methanol for 2 days, and the solution was concentrated by evaporation of the solvent. Precipitation into *n*-hexane produced an adhesive polymeric product, which was dried in vacuum (2.3 g, 75%). For **10**, the yield was 70–80%.

Preparation of Polymers 12 and 13. Polymers **12** and **13** were prepared by using the same procedure. The procedure for **12** is as follows. To a DMSO solution (30 mL) of polymer **9** (1.53 g, 6 mmol) was added compound **11** (11.40 g, 30 mmol) with *N,N*-dicyclohexylcarbodiimide (6.18 g, 30 mmol) and 4-pyrrolidinopyridine (0.60 g, 4.0 mmol). Compound **11** was prepared by following a literature procedure.[33] The reaction mixture was stirred for 2 days at room temperature and for an additional 2 days at 40 °C. The white precipitate of *N,N*-dicyclohexylurea was filtered off and the filtrate was poured into methanol to obtain a polymeric precipitate, which was purified by repeated precipitation from THF into methanol and *n*-hexane. (3.40 g, 58%). An average yield for **13** was 55–70%.

Preparation of Polymer 15. A THF suspension (50 mL) of the sodium salt of compound **5**, prepared from **5** (2.05 g, 10.8 mmol) and sodium hydride (0.26 g, 10.8 mmol), was added to a THF solution (30 mL) of poly(dichlorophosphazene) (3.13 g, 27 mmol). The reaction mixture was stirred for 24 h at room temperature to yield the partially substituted polymer **14**. Into this solution was added a THF solution (150 mL) of sodium trifluoroethoxide (108 mmol) and the solution was stirred at 40 °C for additional 24 h. The reaction mixture was concentrated by removal of the solvent at reduced pressure and was poured into water to isolate a polymeric precipitate. Purification of the polymeric product was carried out by repeated precipitation from THF into water and *n*-hexane. (4.5 g, 60%).

Preparation of Polymer 16. Into a THF solution (5 mL) of polymer **15** (2.0 g, 7.2 mmol) was added absolute ethanol (100 mL) with pyridinium *p*-toluenesulfonate (0.9 g, 3.6 mmol). The solution was refluxed for 30 h and was concentrated. The polymeric precipitate was obtained by pouring the solution into water. The product was purified by repeated precipitation from THF into water and *n*-hexane. (1.4 g, 79%).

Preparation of Polymer 17. Into a DMSO (15 mL) solution of polymer **16** (0.9 g, 1.4 mmol with respect to hydroxyl group) were added spiropyran **11** (3.04 g, 8.0 mmol) and dicyclohexylcarbodiimide (2.06 g, 10 mmol). 4-Pyrolidinopyridine (0.88 g, 6.0 mmol) was then added. After 48 h at room temperature, the reaction mixture was stirred at 40°C for an additional 48 h. The urea precipitate was removed by filtration. The filtrate was poured into methanol to isolate the product. Further purification was carried out by repeated precipitation from THF into methanol, water, and *n*-hexane (yield 1.1 g, 78%).

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References and Notes

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Registry No. **1**, 16111-07-2; **4**, 132911-78-5; **5**, 2163-11-3; **6**, 60221-37-6; $N_3P_3(OCH_2CF_3)_5Cl$, 55975-53-6; dihydropyran, 110-87-2; diethylene glycol, 111-46-6; triethylene glycol, 112-27-6.