Intramolecular Interactions in Photochromic Spiropyran-Merocyanine Polymers

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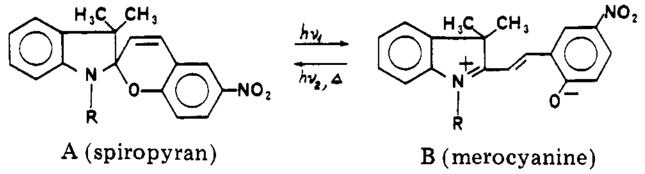
ABSTRACT: Methacrylate, acrylate, and styrene polymers with photochromic spiropyran side groups connected to the main chains through spacers of various lengths were prepared by free radical polymerization. The thermal back-reaction of photochemically formed merocyanines to spiropyrans in the polymer and monomer solutions was studied by flash photolysis. The reaction goes much slower in the polymer than in the monomer solutions. The longer the spacer, the higher the reaction rate in the polymers. Increased solvent polarity increases the rate in the polymer solutions and decreases it in the monomer ones. Whereas for polymer solutions in methyltetrahydrofuran the fading fits first-order kinetics, in benzene or toluene the fading kinetics is described by a superposition of two exponential decays. This is ascribed to the presence in the latter solvents of two types of merocyanines that also reveal different absorption spectra. It is proposed that the formation of intramolecular stacks causes these kinetic and spectroscopic effects.

Introduction

In a previous publication[1] we reported the synthesis of poly(spiropyran methacrylate) (PSMA) homopolymer which revealed a number of remarkable features as compared with copolymers of MMA-SMA (methyl methacrylate-spiropyran methacrylate), studied earlier by other authors.[2-5] The most interesting feature of PSMA is the cooperativity between the crystallization of the atactic homopolymer and the spontaneous spiropyran-merocyanine conversion. Polymer of up to 40% crystallinity was obtained by slow precipitation or swelling of the amorphous polymer. During this process additional spiropyran side groups were converted to merocyanine ones. It appears that these merocyanines interact and tend to undergo intermolecular stacking, and this is associated with the formation of three-dimensional crystalline domains. As a result, adjacent segments of the polymer chains were brought closer together. This, and the increase of the polarity in the surroundings of the domains, promoted further spiropyran-merocyanine conversion and hence further ordering. We called this mechanism "zipper crystallization".



A (spiropyran) B (merocyanine)

Attempts were undertaken to induce crystallization by UV irradiation of the polymer solution during slow evaporation of the solvent.[6] The idea was to induce the growth of the polymer crystals by creating by the irradiation an appropriate merocyanine concentration, sufficient to initiate the cooperative crystallization. However, polymer crystals were not obtained in this way.

To clarify the reasons for the failure of the photoinduced crystallization, flash photolysis studies of the merocyanine-spiropyran conversion in the polymer were performed, initially with PSMA in MTHF and benzene solutions.[7] It was shown that the rate of the merocyanine-spiropyran conversion was significantly lower than that of monomer in the same solvent. This was ascribed to the steric hindrance to the pyran ring closure by adjacent side groups.

In the present work these investigations have been extended to a variety of monomers and polymers in different solvents. Absorption spectra and the kinetics of the thermal decoloration of monomer and polymer solutions were studied, allowing us to propose a new mechanism for retardation of this reaction in the polymers.

Experimental Section

Materials. All solvents were purified by distillation, and methyltetrahydrofuran (MTHF) was, in addition, passed through a column of basic aluminum oxide before use. The following starting materials were distilled before synthesis: 2,3,3-trimethylindolenine (Aldrich), 2-iodoethanol (Aldrich), acrylic and methacrylic acids (Fluka).

6-Chloro-1-hexanol, 5-nitrosalicylaldehyde, and 4-chlorostyrene (all Aldrich) were used without further purification. *p*-Vinylbenzoic acid[8] was prepared by Grignard reaction from 4-chlorostyrene. 6-Iodo-1-hexanol[9] was obtained by action of KI on 6-chloro-1-hexanol. 1-(β-Hydroxyethyl)-3,3′-dimethyl-6′-nitrospiro[indoline-2,2′-[2*H*-1]benzopyran] (I) and 1-(β-hydroxyhexyl)-3,3′-dimethyl-6′-nitrospiro[indoline-2,2′-[2*H*-1]benzopyran] (II) were prepared by the method described in ref 10.

Monomers. All spiropyran-substituted vinyl monomers listed in Table I were synthesized by the direct esterification of acrylic, methacrylic, or *p*-vinylbenzoic acid with I or II at room temperature, as is described in ref 11. The yields, melting points, and elementary analysis data are given in Table I.

Polymers. The polymerization procedure for preparation of homopolymers and copolymers was described elsewhere.[1] The mixtures for preparation of copolymers contained 5% or 25% of spiropyran monomers and, correspondingly, 95% or 75% of methylmethacrylate (MMA), methylacrylate (MA), or styrene, depending on the vinyl substituent attached to the spiropyran. We call the resulting copolymers 5% and 25% copolymer, taking into account that methacrylate-spiropyran (I) copolymers have the same composition as the initial mixture of monomers.[12] The molecular weights of the polymers (Table II) were measured by ultracentrifugation (Spinco-Beckman Model E).

Flash Photolysis. Flash photolysis was carried out as described in ref 13. The Corning 9863 filters were used to cut off the visible light fraction in the flash, thus preventing the photochemical merocyanine-spiropyran back-reaction.[13] In fact, it was shown earlier that photobleaching of the merocyanine form can be ignored in these conditions (the quantum yield of the coloration reaction is known to be near unity[15]). The apparatus was equipped with a Nicolet digital oscilloscope M206. A threefold decrease of the light intensity of the flash by a screen did not affect the resulting initial optical density of the solutions, indicating that the intensity was sufficient to transform all photochromic side groups into the merocyanine form. To decrease the initial spiropyran-merocyanine conversion, additional screens were used. The measurements were carried out on dilute monomer and polymer solutions (10^{-5}–10^{-6} M) in an argon atmosphere at room temperature. The solvents used were methyltetrahydrofuran

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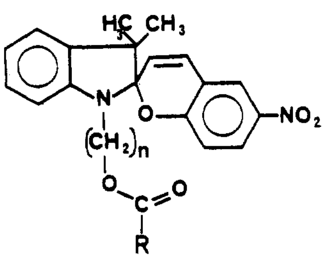
Table I
Spiropyran Vinyl Monomers



R	n[a]	yield,[b] %	mp,[c] °C	anal., % calcd C	calcd H	calcd N	found C	found H	found N
$-CH=CH_2$	2	45	100-101	67.96	5.45	6.89	67.85	5.41	6.91
$C(CH_3)CH_2$	6	57	63-64	70.56	6.77	5.88	70.51	6.74	5.90
$-Ph-CH=CH_2$	2	34	185-186	72.19	5.43	5.80	72.15	5.41	5.79
	6	32	101-102	69.13	6.36	5.20	69.08	6.33	5.21

[a] In the text the spacers with $n = 2$ and $n = 6$ are named C-2 and C-6, respectively. [b] The yield is given for the last stage - esterification and after crystallization. [c] Not corrected.

Table II
List of Synthesized Polymers

polymer[a]	$M_W \times 10^{-4}$	DP[b]
S_2	4.1	85
5% S_2	1.7	135
25% S_2	1.5	75
M_2	3.4	80
5% M_2	2.8	240
25% M_2	1.9	105
A_2	2.2	55
5% A_2	2.9	280
25% A_2	1.7	100
S_6	3.3	60
25% S_6		
M_6	2.9	60

[a] The general formula of a polymer unit is given in Table I. S_2, M_2, and A_2 correspond to $n = 2$ and $R = -Ph-CH=CH_2$, $R = C(CH_3)CH_2$, and $R = -CH=CH_2$, respectively. S_6 and M_6 correspond to $n = 6$ and $R = -Ph-CH=CH_2$ and $R = C(CH_3)CH_2$, respectively. [b] Degree of polymerization.

Table III
Half-Life Time (Measured at 580 nm) of Merocyanine Form of Monomers and Polymers with C-2 and C-6 Spacers (at 294 K)

polymer chain unit	spiropyran content in side groups, %	half-life (τ), 10^{-2} s benzene	toluene	MTHF
S_2	monomer	0.16	0.14	0.28
	5		0.27	0.31
	25		0.50	0.46
	100	1.7	2.3	0.95
M_2	monomer	0.13	0.12	0.24
	5		0.25	0.34
	25		0.69	0.46
	100	1.8	2.1	1.3
A_2	monomer	0.12	0.11	0.20
	5		0.22	0.27
	25		1.3	0.44
	100	1.6	1.8	1.2
S_6	monomer	0.20	0.18	0.23
	25	0.29	0.27	0.30
	100	0.35	0.51	0.45
A_6	monomer	0.19	0.16	0.28
	100	0.53	1.0	0.60

(MTHF), toluene, and benzene, purified as indicated above. The "Statistical Analysis System" was used for computations of the first and second order kinetics contstants as well as k_1, k_2, and x parameters in eq 1.

Absorption Spectra. Irradiations of 10^{-4}–10^{-5} M solutions of monomers and polymers were carried out with a 200-W high-pressure mercury lamp at room temperature. The absorption spectra were then measured with a Cary-14 spectrophotometer at lower temperatures, at which the fading of the solutions during measurement was negligible.

Results

A. Flash Photolysis. The kinetics of the merocyanine–spiropyran conversion are substantially different for monomers, copolymers, and homopolymers and depend, also, on the length of the spacer connecting the spiropyran moiety to the main chain and on the solvent polarity. Half-life times (τ) of the conversion are listed in Table III. The half-lives of monomers and 5% copolymers with C-2 spacer increase with solvent polarity. The 25% copolymers and homopolymers show the opposite tendency. In a given solvent the polymer half-lives are much larger than those of the monomers. For example, τ for the S_2 homopolymer in toluene is more than 15 times higher than for the S_2 monomer. All the homopolymers have their longest half-life times in toluene.

Figure 1 shows the logarithm of the optical density at 580 nm as a function of time after a flash for the S_2 homopolymer in MTHF. Thus this material in this solvent decays with first-order kinetics. All other monomers and polymers in MTHF, as well as monomers and 5% copolymers in benzene and toluene, obey the same kinetics. However, plots for 25% copolymers and homopolymers showed a distinct deviation from first-order kinetics in benzene and toluene. The curve for the A_2 homopolymer in toluene is shown in Figure 2a, as an example. Second-order kinetics also does not give a satisfactory fit to these results (Figure 2b). In this case the description of the merocyanine decay by superposition of two exponents gives the best agreement (see Figure 3):

$$D = D_0[xe^{-k_1t} + (1 - x)e^{-k_2t}] \qquad (1)$$

Here x and $1 - x$ are the fractions of the merocyanine moieties decaying with rate constants k_1 and k_2, respec-

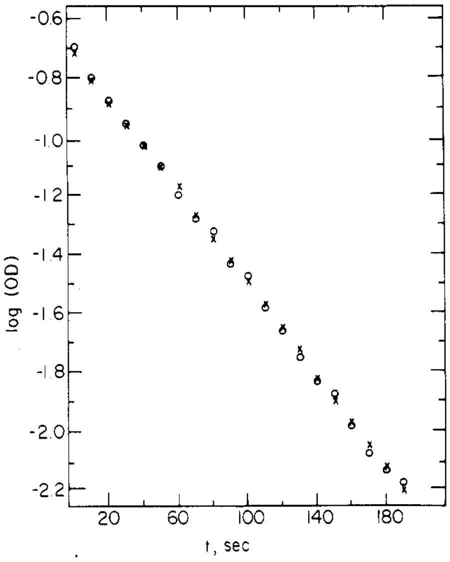


Figure 1. Kinetics of the merocyanine–spiropyran conversion for S_2 homopolymer in MTHF: (O) experimental data; (X) calculated data based on first-order kinetics.

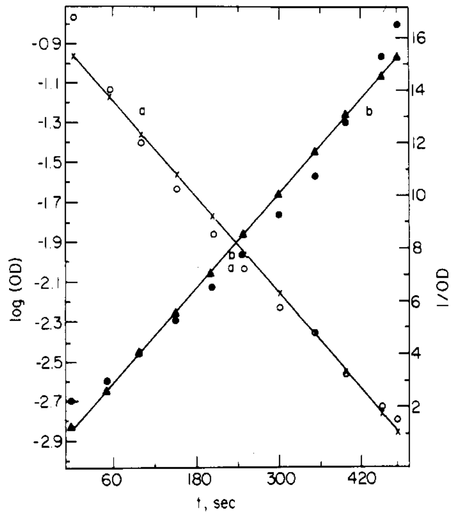


Figure 2. Kinetics of the merocyanine–spiropyran conversion for A_2 homopolymer in toluene: (a) comparison to first-order kinetics (X); (b) comparison to second-order kinetics (▲). O and ● correspond to experimental data.

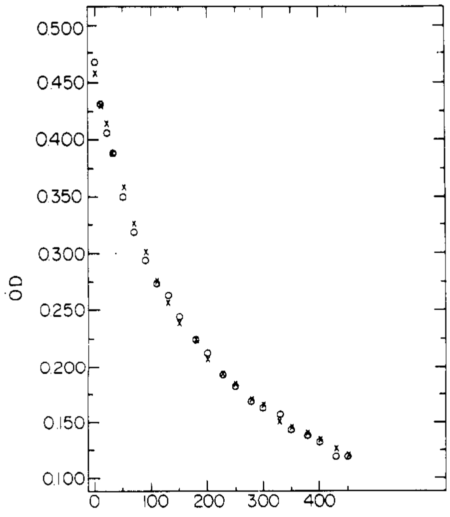


Figure 3. Kinetics of the merocyanine–spiropyran conversion for M_2 homopolymer in toluene: (O) experimental data; (X) data calculated according to the 2 exponential equation (1).

Table IV
Calculated Decay Rates of Long- and Short-Lived Merocyanines for M_2 Homopolymer in Toluene for Different Initial Conversions, Using Eq 1

OD_0[a]	α,[b] %	x,[c] %	$10^{-3}k_1$,[d] s^{-1}	$10^{-3}k_2$,[e] s^{-1}
0.57	100	56	1.0	6.4
0.46	80	56	1.2	6.4
0.25	49	56	1.3	6.4
0.16	28	56	1.5	6.4
0.059	10		3.3[f]	

[a] Initial optical density. [b] Degree of initial spiropyran-merocyanine conversion. [c] Fraction of merocyanines which are long-lived. [d] Decay rate of long-lived merocyanines. [e] Decay rate of short-lived merocyanines. [f] For low degrees of initial conversion the experimental curves are better described by monoexponential decay. Errors in x, k_1, and k_2 determinations are ±5%. The average values for x and k_2 are given.

Table V
Half-Lives of Merocyanine Form of M_2 Homopolymer in Toluene, Measured at Different Wavelengths (at 294 K)

α,[a] %	λ, nm	$10^{-2}\tau$,[b] s
100	540	2.5
100	580	2.1
100	620	1.8

[a] Degree of initial spiropyran-merocyanine conversion. [b] Half-life times of merocyanines (±5%).

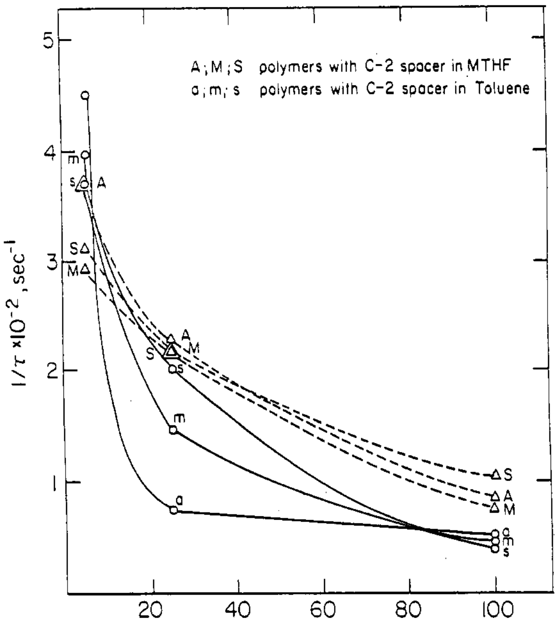


Figure 4. Dependence of the merocyanine–spiropyran conversion rates in polymers on spiropyran content (α = 100%).

tively. Table IV lists some of the experimental and calculated data for M_2 homopolymer in toluene for different degrees of the initial spiropyran–merocyanine conversion, changed by variation of flash intensity. One can see that x does not depend on the initial optical density for initial spiropyran–merocyanine conversions of 25–100%. However, for D_0 corresponding to less than 25% initial conversion, eq 1 is not longer necessary for description of the decay process, which is now well characterized by first-order kinetics.

The apparent decay rate depends on the wavelength at which the optical density is measured. Table V shows half-lives of M_2 homopolymer at different detecting wavelengths in toluene. The half-life measured at 540 nm

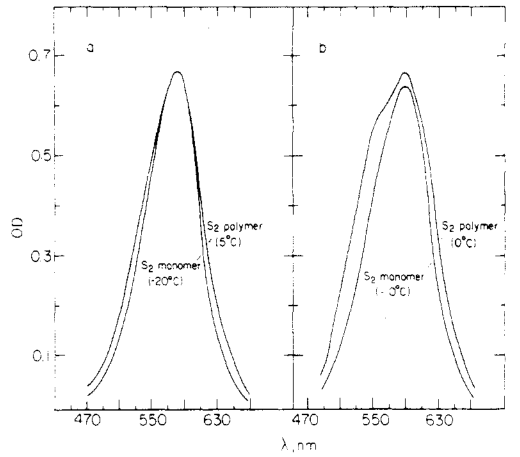


Figure 5. Absorption spectra of irradiated S_2 monomer and S_2 polymer solutions in MTHF (a) and toluene (b).

is distinctly longer than that measured at 620 nm.

The rates of the merocyanine–spiropyran conversion as functions of the spiropyran content in polymers are shown in Figure 4. One can see that for toluene solutions the rate drops sharply with the increase of spiropyran content from 5 to 25%. Thus, for the A_2 homopolymer of spiropyran content 25%, in this solvent, the rate drops almost to that of the corresponding homopolymer. In MTHF the change of the rate is less drastic.

We return now to the results in Table III; this table lists also the half-lives for S_6 and M_6 monomers and polymers, which have long C-6 spacers. One can see that the differences between the rate constants for monomers and polymers are smaller for C-6 spacers than for the short spacers shown in this table. The fading of the monomers and polymers with long spacers in all solvents are well fitted by first-order kinetics.

B. Spectroscopic Data. Absorption spectra, in the visible region, of irradiated S_2 monomer and polymer solutions in MTHF are shown in Figure 5a. These spectra have maxima at 580 nm that are due to the merocyanine moieties[1,14]. There is no significant difference in absorption of polymer and monomer merocyanines. Figure 5b shows the absorption spectra of the same compounds in toluene. The homopolymer absorption spectrum in toluene differs from that of the monomer in this solvent and from that of the polymer in MTHF, in that it has an absorption shoulder at 560 nm. To check the relationship between the 560 and 580-nm peaks, the absorption spectra of monomer and polymer solutions were measured for different exposures to irradiation (pumping) and for different intervals of time after the last irradiation (relaxation). In MTHF no significant changes as functions of time were observed. Figure 6a shows the pumping spectra of M_2 homopolymer in toluene, which are similar to the spectra observed for all other homopolymers in this solvent. On pumping, as the merocyanine content increases, the dominant peak becomes the short-wavelength one, rather than that at 580 nm. The upper curve corresponds to about 25% spiropyran–merocyanine conversion. A shift of the absorption maximum from 580 to 560nm occurs also during the back-conversion of merocyanines to spiropyrans. An example is shown in Figure 6b.

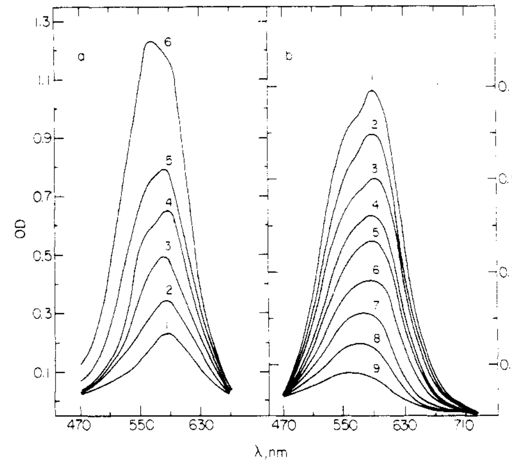


Figure 6. Absorption spectra of irradiated M_2 homopolymer solution in toluene: (a) pumping (light exposure increases from spectrum 1 to 6), $\alpha_{max} \sim 25\%$; (b) relaxation (fading time increases from spectrum 1 to 9), $\alpha_{max} \sim 15\%$.

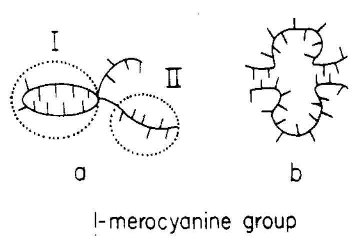


Figure 7. Scheme of interaction of side groups in a macromolecular coil: (a) (I) merocyanine stacks and (II) separated merocyanines; (b) supposed irregularities in photoinduced crystallization.

Discussion

The experimental results allow us to divide the merocyanine side groups of the C-2 homopolymers dissolved in toluene and benzene into two types, characterized by different kinetic and spectroscopic behaviors. Conversion of each of these types of merocyanine into spiropyran follows first-order kinetics. The "long-" and "short-lived" merocyanines fade with the rate constants k_1 and k_2 (Table IV), respectively, that were determined from measurements at 580 nm, where the overlap of the two forms is strong. The net kinetics were described by a superposition of two exponential decays. The long-lived merocyanines absorb at shorter wavelength than do the short-lived ones. This is confirmed qualitatively by measurements of the τ's at 540 and 620 nm (Table V), but even at these wavelengths the overlap of the spectra is still significant and does not permit direct determination of k_1 and k_2. On pumping, the relative contribution of the long-lived species in the absorption becomes more substantial than that of the short-lived ones. Therefore the pumping spectra are shifted to the blue (Figure 6a). For all degrees of conversion, α, of above 25% the relative population of the two types of merocyanines remains about the same: x in Table IV is approximately a constant. The relaxation spectra (Figure 6b) also show enrichment of the polymer molecules with the long-lived species on fading (the peak at 560 nm becomes the dominant one, rather than that at 580 nm). Thus our results indicate that photopumping leads first to 580-nm merocyanines and subsequently to both types of merocyanine, in a proportion which is constant above 25% conversion. The 580-nm merocyanines fade more rapidly so that, on relaxation, the 560-nm species remain as the dominant one.

In MTHF solutions the merocyanine–spiropyran reaction in homopolymers obeys first-order kinetics, with rate constant about the same as k_2. The "pumping" and "relaxation" spectra coincide and have a single maximum at 580 nm.

Earlier[1,14] we came to the conclusion that merocyanines with absorption maximum at 560 nm belong to molecular stacks formed in loops or other closely spaced segments of macromolecules (Figure 7a (I)). In light of the above discussion it is these merocyanines which are the longer lived. The data obtained in this work can be interpreted on the basis of this assignment. Probably the long lifetime of these merocyanine molecules is due to the fact that their transformation into the spiropyran form requires either escape of the merocyanine moiety from the stack structure or disruption of this structure. Nonpolar, "bad" solvents may play a double role. On the one hand they cause the polymer coils to pack more densely, and hence bring the macromolecular segments closer together. On the other hand, they solvate poorly the polar merocyanines and force them to form stacks with antiparallel alignment of alternate merocyanine dipoles, diminishing in this way the net dipole moment. The merocyanine groups are attached to the main chain and thus cannot be totally organized into stacks. Apparently, that part of the merocyanines that is not organized in stacks fades faster (short-lived merocyanines, Figure 7a (II)).

Further, the fact that x is constant for initial conversions of more than 25% to merocyanines indicates that probably for such high converions the coils reach some limit of rigidity and do not change their dimensions substantially at higher α. The slightly larger k_1 at lower α (Table IV) can be interpreted as being due to a lower average number of merocyanines in a stack. Therefore, under these conditions the contribution of the merocyanines at the ends of the stacks becomes more substantial. Obviously these merocyanines are easily converted to spiropyrans, thus increasing the net k_1. For a <25% the merocyanine–spiropyran conversion obeys first-order kinetcs, probably because k_1 increases so markedly that we can no longer differentiate the two types of merocyanines kinetically, though it can be done spectroscopically (Figure 6); at these conversions the merocyanine population in a coil is so low that the possibility of intermerocyanine interaction becomes very small, and this results in domination of the peak at 580 nm over that at 560 nm (Figure 6a, spectrum 1).

A very rough estimation of the gain in energy resulting from stack formation can be made from the shift in the absorption spectra (580–560 nm). This gives 7.5 J/mol and approximately corresponds to the difference in activation energies of the merocyanine to spiropyran reactions estimated from the ratio k_1/k_2.

For homopolymers in MTHF at any α the effect of stack formation is not displayed distinctly. This presumably is due to good solvation of the polymer, resulting in looser polymer coils, so that merocyanines of type II (Figure 7a) predominate in this case. The retardation of the merocyanine–spiropyran conversion in polymer in this solvent, as compared with the monomer, we attribute to the steric effects of adjacent bulky side groups. Presumably also in copolymers dissolved in MTHF these steric effects determine the retardation of the merocyanine–spiropyran reaction, which proceeds with higher rate the lower the spiropyran content (Figure 4). The sharp change of the rate constants for copolymers dissolved in toluene at spiropyran content of 20% may be explained by assuming that at higher concentration of the photochromic units the stack formation begins to play a substantial role. This tendency is displayed most markedly for A_2 polymers, probably due to the flexibility of the main chain.

The opposite effect of solvent polarity on the fading rate of monomers and low spiropyran content copolymers, on the one hand, and on the homopolymers and high spiropyran content copolymers, on the other hand, can be understood if one takes into account that the polar solvent stabilizes the zwitterionic merocyanine structure[15] but apparently weakens the merocyanine–merocyanine interactions in the macromolecular coils of the polymers with high spiropyran content. The competition of these effects determines the shape of the curves in Figure 4.

Retardation of the merocyanine–spiropyran reaction in polymers with long spacers (S_6 and A_6 in Table II) is relatively weak as compared to that in the short spacer polymers. The obvious reason for this is the larger flexibility of the long spacers, which permits the merocyanine side groups to escape from stacks more easily and avoid steric hindrance.

Such increase of the reaction rate with the length of the spacer (the spiropyrans were attached to 5′-position of the indoline) was observed earlier by Labsky et al. (ref 5) and was attributed by them to the higher frequency factor corresponding to the longer side chain. Unfortunately the authors dealt only with copolymers having a low content of spiropyrans (2–3%) and thus stack formation did not affect the kinetics of the decoloration reaction, and the reaction proceeded in toluene much faster than in acetone (as for monomers).

Our data on polymers with C-2 spacers are compatible with the results reported earlier by Irie et al.[3] on the reversible change of viscosity of M_2 copolymer solution during UV irradiation. While in benzene solution the viscosity decreased markedly during UV irradiation, in THF, methyl acetate, and other polar solvents there was no such marked change. The change in viscosity was explained in ref 3 by intramolecular solvation of merocyanines by methyl ester side groups. The possibility of merocyanine–merocyanine interaction was rejected because the S_2 copolymer did not exhibit any response to irradiation, and for M_2 copolymer the maximum effect was observed at rather low spiropyran content—17% (Irie et al. did not study homopolymers and limited themselves to 40% copolymer). Comparing these results with ours we can suggest that the photoviscosity effect is determined by the merocyanine stack formation. On this basis the lack of photoresponse in S_2 copolymer would be due to the rigidity of the main chain while the maximum effect at 17% spiropyran content in M_2 copolymer can be connected with decrease of the polymer chain flexibility at higher content of the bulky side groups. Unfortunately the largest content of spiropyrans in the copolymer for which the viscosity measurements were carried out was 40%. Our attempts to measure viscosity of homopolymers did not give definite results because of the very low solubility of our homopolymers in aromatic solvents.

Finally we are able to answer the question, why we could not photochemically initiate polymer crystallization. In the beginning of the crystallization, when the amount of solvent incorporated within the polymer is still large enough, the stack formation on irradiation of the polymer solution leads to macromolecular coil shrinking. This shrinking prevents intermolecular interaction of the side groups which requires disentaglement of the main chains. Later on, as evaporation of the solvent leads to precipitation of the major amount of the polymer, random formation of intermolecular merocyanine stacks on irradiation results, presumably, in formation of holes and other irregularities in the polymer structure (Figure 7b). Apparently only step-by-step spiropyran–merocyanine conversion, as occurs in zipper crystallization, allows formation of more regular intermolecular stacks along the polymer main chains.

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Registry No. S_2-homopolymer, 89908-21-4; $(S_2)\cdot$(styrene) (copolymer), 89908-22-5; M_2-homopolymer, 57981-89-2; $(M_2)\cdot$(MMA) (copolymer), 51816-58-1; A_2-homopolymer, 89908-24-7; $(A_2)\cdot$(MA) (copolymer), 89908-25-8; S_6-homopolymer, 89908-27-0; $(S_6)\cdot$(styrene) (copolymer), 89908-28-1; M_6-homopolymer, 89908-30-5; S_2-monomer, 89908-20-3; M_2-monomer, 25952-50-5; A_2-monomer, 89908-23-6; S_6-monomer, 89908-26-9; A_6-monomer, 89908-31-6.

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Mass Spectrometric Studies on Cyclo- and Polyphosphazenes. 1. Polymerization of Hexachlorocyclophosphazene

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ABSTRACT: The polymerization of hexachlorocyclophosphazene $[(NPCl_2)_3]$ to poly(dichlorophosphazene) $[(NPCl_2)_n]$ has been carried out in the ionization chamber of a mass spectrometer. The mechanism of the reaction has been studied in detail under different experimental conditions, with the aid of linked scans, mass analyzed ion kinetic energy spectra, collisionally activated decomposition experiments, and energy release measurements. Comparison of the mass spectrometric reaction with the bulk thermal polymerization of $(NPCl_2)_3$ has given substantial evidence of the identity of the two reaction mechanisms.

Introduction

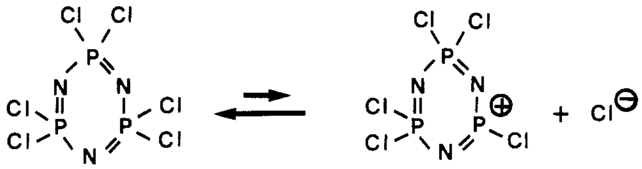
It is well-known[1] that poly(organophosphazenes) (POP) are an unusual class of inorganic polymers whose main chain is based on a sequence of P–N repetitive units.

As far as their synthesis is concerned, they possess a nearly unique characteristic; i.e. they are all prepared by reacting the same parent compound, the highly unstable poly(dichlorophosphazene), $(NPCl_2)_n$ (I), with suitable nucleophilic groups, so obtaining a complete replacement of the chlorine atoms bonded at the phosphorus of the polymer chain. $(NPCl_2)_n$ is in turn prepared by the thermal bulk polymerization of the low molecular weight cyclic trimer, the hexachlorocyclophosphazene, $(NPCl_2)_3$ (II).

In spite of the fact that there has been a great increase of the basic investigations and technical development of POP during the last two decades,[2,3] the mechanism of the reaction which leads hexachlorocyclophosphazene II to poly(dichlorophosphazene) I is not yet fully understood.[4]

The normal experimental procedure for the preparation of I involves a reaction of II at 250 °C for 8–30 h in evacuated, sealed glass tubes, followed by separation of the residual II, for instance by vacuum sublimation.[5]

Scheme I



In the past, several possible reaction mechanisms have been considered[4] for this reaction, in an attempt to obtain a satisfactory explanation of all the reported experimental findings; however, it is now widespread opinion that the polymerization process occurs via the cation mechanism.[6]

The primary initiation step of the reaction is believed to be the heterolytic scission of a P–Cl bond of II, leading to the formation of a P^+Cl^- ion couple (Scheme I).

The propagation step of the polymerization is supposed to be a successive electrophilic attack by P^+ ion on the unpaired electron pair of a nitrogen atom of a second II molecule, followed by the opening of the cyclophosphazene ring. The positive charge on the phosphorus atom is in this way transferred from the P cation on the phosphazene ring to the P atom at the end of the chain, so enabling the

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