Photopolymerizations. The monomer compositions were mixed with Irgacure 651 (1% by weight), melted, and aligned between rubbed glass plates separated by a 0.6-mm spacer. The films were submerged 0.5 in. in a thermostated water bath and positioned 9 in. from a 450-W Hg arc lamp for 30 s.

Optical and Thermal Measurements. A Perkin-Elmer 552 UV/vis spectrophotometer was used to measure the reflectance spectra of the materials as "apparent absorbance". Spectra were measured in the transmittance mode with Nujol in the reference cell. The DSC measurements were recorded with a Du Pont Model 900 thermal analyzer. Mesophase ranges were measured with a Leitz optical microscope using a Mettler FP5 and FP52 temperature control.

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Registry No. **2a**, 89734-62-3; **2a** (homopolymer), 91210-48-9; **2b**, 68091-11-2; (**2b**)·(**3a**) (copolymer), 91210-49-0; **2c**, 89734-64-5; **2c** (homopolymer), 91210-50-3; **2d**, 89734-63-4; (**2d**)·(**3d**) (copolymer), 91210-51-4; **3a**, 53816-29-8; (**3a**)·(**3c**) (copolymer), 91228-85-2; **3b**, 77225-90-2; **3b** (homopolymer), 77222-09-4; **3c**, 86689-87-4; **3d**, 79679-30-4; (**3d**)·(**3f**) (copolymer), 91228-86-3; **3e**, 79679-29-1; **3e** (homopolymer), 79702-51-5; **3f**, 86689-89-6; 2-hydroxyethyl methacrylate, 868-77-9; cholesteryl chloroformate, 7144-08-3.

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(21) Finkelmann and Rehage found that the optical properties of cholesteric poly(siloxanes) were also insensitive to changes in temperature below the isotropic transition.[7]
(22) The fine-grained textures are reminiscent of Shibaev's smectic polymer textures.[18] **Note Added in Proof**: X-ray diffraction data on the polymer film derived from **2c**, obtained after cooling from the isotropic melt, corresponds well with a smectic structure. This suggests that the cholesteric structure is metastable and heating to the isotropic transition allows the polymer to reorganize to a more stable smectic structure upon cooling.
(23) Addition of cross-linking agents to the monomer compositions also produces polymers that regenerate the cholesteric planar texture upon cooling from the isotropic melt.

"Zipper" Crystallization of Polymers with Spiropyran Side Groups

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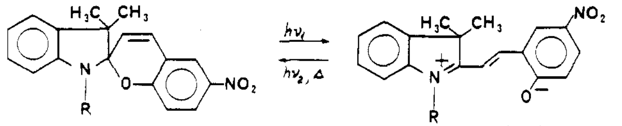
The transformation of spiropyrans into merocyanine dyes



A (spiropyran) B (merocyanine)

leads to substantial structural changes of macromolecules containing spiropyran groups (see references in previous papers[1,2] and ref 3). In particular, the capability of the merocyanine dyes to aggregate into giant molecular stacks[4] is a driving force for a new type of crystallization of atactic polymethacrylate bearing spiropyran side groups which was reported in a previous work.[1] A polymer of up to 40% crystallinity was obtained by slow evaporation of solvent from methyltetrahydrofuran (MTHF) solution of the polymer or by swelling of the amorphous polymer in this solvent. The crystallization of the polymer occurs cooperatively with the spiropyran–merocyanine conversion. The following crystallization mechanisms has been proposed: Slow precipitation of the polymer in MTHF leads to partial spiropyran–merocyanine conversion. This in turn results in incorporation of the merocyanine side groups into *inter*molecular stacks, with alternate antiparallel alignment of their molecular dipoles. Further development of this process brings about formation of crystalline domains, and the spiropyran side groups attached to the segments of the polymer chain adjacent to a domain are brought closer together. This and the increase of the polarity in the surroundings of the domains promote further solvatochromic spiropyran–merocyanine conversion followed by stacking of merocyanines and hence further ordering of the macromolecules. Evidently the ordering can proceed in the polymer only in the presence of solvent which enables segmental movement.

The important feature of this process is the mutual stimulation of the chemical reaction and crystallization. Apparently a high degree of crystallinity is achieved if the cooperative spiropyran–merocyanine conversion occurs step-by-step along the polymer chains. We called this process "zipper crystallization".

While the above process was interpreted in terms of intermolecular stacks, the concept of *intra*molecular stack formation was proposed to explain our results from flash photolysis studies of different vinyl polymers with photochromic spiropyran side groups.[2] The merocyanine side groups organized in these stacks fade much more slowly than do isolated groups. These two types of merocyanines are differentiated also by other kinetic and spectroscopic prroperties. For instance, polar and nonpolar solvents affect oppositely the rates of the thermal merocyanine–spiropyran conversion of isolated merocyanines and those organized in the stacks. The effects of the polymer chain structure and of the length of the spacer connecting the photochromic side group to the main chain on the thermal fading and ability to form the intramolecular merocyanine stacks were also investigated. It is noteworthy that the polymers with the long, C-6 spacers did not reveal any tendency to stack formation.

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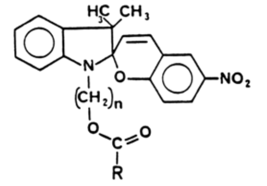
Table I
List of the Synthesized Polymers



symbol of polymer[a]	$M \times 10^{-4}$	DP	crystallizability
S_2	4.1	85	–
M_2	3.4	80	+
A_2	2.2	55	+
S_6	3.3	50	–
M_6	2.9	60	–

[a] S_2, M_2, and A_2 correspond to $n = 2$ and R = $-C_6H_4CH{=}CH_2$, R = $-C(CH_3){=}CH_2$, and R = $-CH{=}CH_2$, respectively. S_6 and M_6 correspond to $n = 6$ and R of S_2 and M_2, respectively. In the text the spacers with $n = 2$ and $n = 6$ were named C-2 and C-6, respectively.

Unlike intramolecular stack formation, zipper crystallization is a "dark" process and cannot be induced by irradiation. According to the explanation given in ref 2, the fast, irregular merocyanine stacking that proceeds under irradiation hinders disentanglement of the macromolecules and inhibits the slow, step-by-step formation of more regular intermolecular stacks along the polymer main chains.

Zipper crystallization has been found thus far only for one polymer, poly(spiropyran methacrylate). This raises the questions of how selective this process is and to what extent structural changes in the macromolecules affect it. In the present work we report such information, obtained from investigations of methacrylate, acrylate, and styrene-based polymers with spiropyran side groups connected to the main chains by spacers of different lengths.

Experimental Section

The synthesis of the monomers and polymers was described elsewhere.[1,2] The number-average molecular weights ($\bar{M}_n$) of the polymers were determined by ultracentrifugation (Spinco-Beckman Model E) and are listed in Table I. Crystallization of the polymers was carried out by slow evaporation of MTHF from a polymer solution in this solvent, followed by swelling in the same solvent. The swelling was performed by repeated additions of MTHF in such amounts as to avoid dissolving the precipitated polymer. The degree of crystallization was checked by X-ray diffraction, the diffraction intensity curves being measured with an automatic recording microdensitometer (Joyce Model MK III B).

Results and Discussion

Table I shows that only M_2 and A_2 polymers were obtained in crystalline form. No sign of crystallinity was found in the other polymers in many experiments using widely different conditions. X-ray patterns of M_2, A_2, and S_2 polymers after swelling are shown in Figure 1. The degree of crystallinity that was achieved in the M_2 polymer was 40%; in the A_2 polymer the highest degree of crystallinity did not exceed 20%. Indexing for both these polymers gives a monoclinic unit cell with the same dimensions: $a = 9.75$ Å, $b = 16.58$ Å, $c = 5.47$ Å, and $\beta = 101°$. This suggests that the packing in both the M_2 and A_2 polymer crystals is determined by the merocyanine side groups. Earlier[1] we suggested for the crystals a tilted layered structure where each layer consists of lamellae, composed of the merocyanine stacks, and interlamellar spaces. The polymer chains are apparently located in the interlamellar space, which allows the main chains to be arranged in a crystalline lattice. Other cases are known in which a stereoirregular main chain is incorporated into a crystalline lattice determined by polar side groups (ref 5).

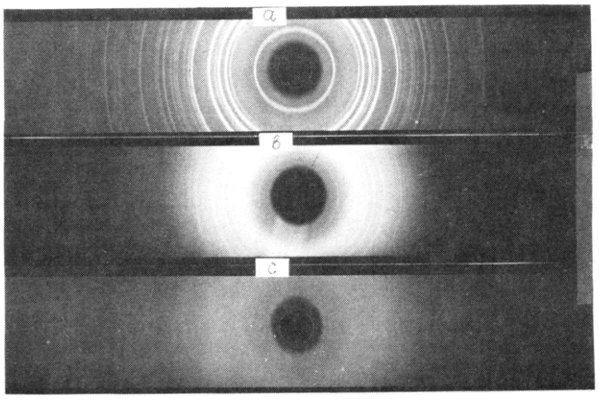


Figure 1. Debye–Scherrer patterns of (a) M_2, (b) A_2, and (c) S_2 polymers after swelling.

We could not obtain the S_2 polymer in a crystalline form. The powder diffraction pattern of this polymer (Figure 1) reveals two diffuse bands that are located between 3.64–4.27 Å and 6.23 Å. Though these halos point to some order in the this polymer (the middle of the first halo corresponds to the strong reflection 3.86 Å from the M_2 and A_2 polymer crystals), the lack of crystallinity can be explained as due to the rigidity of the polystyrene macromolecule.

The S_6 and M_6 polymers give only diffuse halos, characteristic of completely amorphous phases. This is consistent with the flash photolysis data on the photochromic behaviors of solutions of these polymers.[1,2] The formation of intermolecular merocyanine stacks was shown by S_2, M_2, and A_2 polymers but not by S_6 and M_6 polymers. This can be attributed to the high flexibility of the long spacers, which permits more free movement for the main-chain segments and spiropyran groups. This lowers the probability of close contacts between these side groups and hence the the probability of their transformation into merocyanine stacks. It is worthwhile recalling that "completely free" monomer molecules are precipitated from MTHF solution in spiropyran form with only small traces of merocyanine.[1]

Apparently the nature of the intramolecular stacks formed photochemically in the polymer solutions is very similar to that of the intermolecular stacks in the polymer crystals.[1,2] For instance, in the M_2 solution the maximum of the absorption spectra is shifted from 580 to 560 nm upon intramolecular stacking of the merocyanine side groups.[2] One can see the same shift on comparison of the absorption spectrum of the amorphous M_2 polymer, having only nonstacked merocyanines, to that of the crystalline polymers with the intermolecular stacks (Figure 2).

However, there is a substantial distinction between the processes leading to formation of the two types of stacks. Thus, the intramolecular stack formation in solution is less selective and occurs even in macromolecules that could not be crystallized (S_2 polymer and copolymers with spiropyran content more than 25%). The ability of the A_2 polymer and copolymers to form the intramolecular stacks is as good or even better than that of the M_2 polymer and copolymers, whereas the M_2 polymer can be obtained with a higher degree of crystallinity than the A_2 polymer. Further, whereas intramolecular stacking does not occur in MTHF, crystallization was carried out in this solvent.

In fact there are completely different mechanisms for the two types of stack formation: only merocyanine side

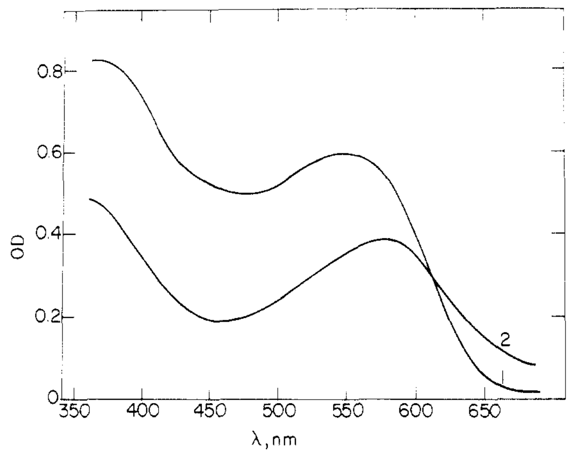


Figure 2. Diffuse reflectance spectra of crystalline (1) and amorphous (2) M_2 polymers. The amorphous polymer was obtained on fast evaporation of MTHF and consequent UV irradiation of the precipitated polymer.

groups participate in the intramolecular stacking whereas the intermolecular stacking involves also the spiropyrans, which are then converted into merocyanines along the direction of the propagation of the crystallization process (possibly along the macromolecular main chains). The merocyanine groups that appear randomly (for example, due to irradiation) *only impair* the zipper crystallization.

In conclusion, it is worthwhile emphasizing that in spite of the ephemerality of the isolation merocyanine moieties, they have a strong tendency to form rather stable phases: quasi-crystals[6,7] and polymer crystals. The stabilization of the merocyanines in these materials is by their dipole–dipole interaction, which is most effective in certain phases. Thus, in the M_2 polymer crystals, the merocyanines are stable even on heating up to 150 °C. (Further heating leads just to destruction of the polymer.) In amorphous polymers fast thermal merocyanine–spiropyran conversion begins at 45 °C (color disappears during a few seconds).

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Registry No. S_2, 91191-22-9; M_2, 57981-89-2; A_2, 89908-24-7; S_6, 91191-23-0; M_6, 89908-30-5.

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Communications to the Editor

Importance of Structure Regularity in Polymer Association[1]

In past years, we have shown that very weak interchromophore interactions, almost undetectable in small-molecule systems, are enhanced in polymers and bring about polymer association even in an extremely dilute solution.[3-7] Exciplex emission from a pair of electron-donating and electron-accepting chromophores bonded to a polymer and its dependence on polymer concentration provide information on self-association of exciplex-forming polymers. Although an exciplex is by definition a complex formed only in the excited state, the pairing chromophores having essentially donor (D) and acceptor (A) natures induce a more or less electron donor–electron acceptor (EDA) interaction in their ground state. The effect is, however, negligibly small in monomer model systems whereas the weak EDA interaction drives polymer association very greatly when D and A units are arrayed along a polymer chain either as main-chain components or as side groups.

Detailed investigation on the effect of polymer molecular weight,[5-7] solvent,[5,7a,c] and polymer main-chain rigidity[7d] on concentration-dependent exciplex emission led to the conclusion that interlocking of EDA chromophores along a polymer chain (zipping) is the origin of polymer association. Observation of an allosteric effect on polymer association in a good solvent[5] further reinforced this conclusion. Furthermore, the rise time of interpolymer exciplex formation is shorter than that of intramolecular exciplex by small model compounds,[8] indicating polymer association prior to photoexcitation.

It is extremely difficult to prove such polymer association in the concentration region of 10^{-5} M (10^{-3}–10^{-4} wt %) by orthodox methods presently available for solution property study. However, we recently succeeded in proving association of exciplex-forming polymers by pulse polarographic determination of diffusion constant as a function of polymer concentration in the concentration region comparable with that of fluorescence spectroscopy.[9] Decrease of diffusion constant was observed for exciplex-forming polymers but not for excimer-forming polymers when the polymer concentration increased.

The structural regularity of the D and A array should promote polymer association. In the following, we will show that an irregular arrangement of D (*N*,*N*-dimethylanilino) and A (1-pyrenyl) groups reduces interpolymer association greatly.

Results and Discussion. The structures of the samples employed are shown in Figure 1. We have previously reported that I[7a,b] as well as V[7b,c] forms strong interpolymer exciplexes at chromophore concentrations below 10^{-5} M. As a measure of interpolymer exciplex formation, the value of $(F_e/F_m)_c(F_e/F_m)_{c\to0}$ was taken, where F_e and F_m indicate the maximum fluorescence intensities of exciplex and monomer emission and the subscript c on the parentheses is the chromophore concentration. This index expresses the magnitude of interpolymer interaction relative to intrapolymer interaction, the value being unity at infinite dilution.

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