Israelachvili and Dr. J. Klein for helpful discussions about the experimental aspects of this problem. This work was supported in part by the Department of Energy through Grant No. DE-FG03-87ER45288.

References and Notes

(1) Scheutjens, J. M. H. M.; Fleer, G. J. *Macromolecules* **1985,** *18,* 1882.

(2) Israelachvili, J. N.; Tandon, R. K.; White, L. R. *J. Colloid. Interface Sci.* **1980,** *78,* 430.

(3) Klein, J.; Luckham, P. F. *Macromolecules* **1984,** *17,* 1041.

(4) Almog, Y.; Klein, J. *J. Colloid. Interface Sci.* **1985,** *106,* 33.

(5) Rossi, G.; Pincus, P. A. *Europhys. Lett.* **1988,** *5,* 641.

(6) Dimarzio, E. A.; Rubin, R. J. *J. Chem. Phys.* **1971,** *55,* 4318.

(7) Edwards, S. *Proc. Phys. Soc., London* **1965,** *85,* 613.

(8) See; e.g.: Landau, L.; Lifshitz, I. *Quantum Mechanics;* Pergamon Press: Oxford, 1900; Chapter 7.

(9) de Gennes, P. G. *Rep. Prog. Phys.* **1969,** *32,* 187.

(10) This result can also be obtained from the Euler–Maclaurin series representation of the integral (see, e.g.: Mathews, J.; Walker, R. L. *Mathematical Methods of Physics,* W. A. Benjamin: New York, 1964; p 343), which can be summed exactly in this case.

(11) Ji, H.; Hone, D. *Macromolecules* **1988,** *21,* 2600.

(12) de Gennes, P. G. *Scaling Concept in Polymer Physics;* Cornell University: Ithaca, NY, 1979.

(13) Israelachvili, J. N.; Tirrell, M.; Klein, J.; Almog, Y. *Macromolecules* **1984,** *17,* 204.

Photochromism of Liquid-Crystal Polyacrylates Containing Spiropyran Groups

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ABSTRACT: Acrylic copolymers with mesogenic and spiropyran side chains yield a photochromic mesophase absorbing strongly in the visible region (λ_{max} 570–590 nm) on irradiation with UV light. The color disappears on irradiation with visible light or thermally. Thermodynamic spectroscopic and kinetic properties of the photochromic polymers were investigated. The structure of the mesophase is discussed.

Introduction

Incorporation of photo- and thermochromic spiropyrans side groups in polyvinyl macromolecules leads to substantial changes in the polymer structure stemming mainly from interactions between these side groups in their colored merocyanine form.[1–5] Conversion of spiropyran into merocyanine dye can be induced by UV irradiation, by heating of the polymer or by swelling of the polymer in a polar solvent. The dipolar and highly polarizable merocyanine groups have a very strong tendency to dimerization and further aggregation, which occurs both in solution and in bulk. The aggregation proceeds most efficiently on swelling or on heating the polymer above the glass transition temperature (T_g) when the segmental mobility of macromolecules is high enough to promote the dye aggregation, while irradiation below T_g produces mostly isolated dye molecules. At a high content of spiropyran groups in a copolymer, the aggregation may reach a degree at which the aggregates can be observed in an electron or even an optical microscope.[4] Moreover, swelling of a homopolymer containing only spiropyran units results in crystallization of the polymer by virtue of solvatochromic spiropyran–merocyanine conversion followed by self-assembly of the merocyanine groups into a three-dimensional crystalline lattice (so-called zipper-crystallization). The resulting polymer gave discrete Debye–Scherrer diffraction patterns and a degree of crystallinity of up to 40%.[1,3]

The absorption spectra and kinetic properties of the photochromic polymers are also strongly affected by aggregation. A hypsochromic shift of the visible band was observed when separated mercyanine groups form dimers or higher aggregates. The aggregates belong to the so-called H-type, which is characterized by antiparallel dipole–dipole interactions of molecules. The absorption bands of monomeric merocyanine molecules and aggregates usually overlap. However, important conclusions about the degree of aggregation can be drawn from the absorption band shift and the kinetics of the spontaneous merocyanine–spiropyran back-reaction.[2,6] For example, for many indoline–spiropyrans the visible absorption maximum was found to shift from ~580–590 to ~560 nm, and in thermal decoloration rate, to decrease about 5-fold when passing from isolated mercyanine molecules to dimers.[2,6]

Recently,[7–9] we reported thermochromic properties of liquid-crystal polyacrylic copolymers containing mesogenic and spiropyran side groups (Scheme I). Films of these mesomorphic copolymers change color on heating. At room temperature the electronic absorption bands of the films in the visible region lie in the range 460–600 nm, which is characteristic of merocyanine dyes both in the aggregated and nonaggregated form. Absorption bands with $\lambda_{max} \leq 560$ nm have been again ascribed to dimers and higher merocyanine aggregates, while the bands with $\lambda_{max} \geq 570$ nm belong apparently to nonaggregated merocyanines. The merocyanine aggregation leads to cross-linking of the macromolecules and network formation. A direct proof of such a physical cross-linking of the macromolecules was obtained by measurements of the copolymer melt viscosity as a function of temperature and spiropyran content.[7,8]

Similar properties were observed in liquid-crystal side-chain polysiloxanes containing spiropyran groups.[9,10] In

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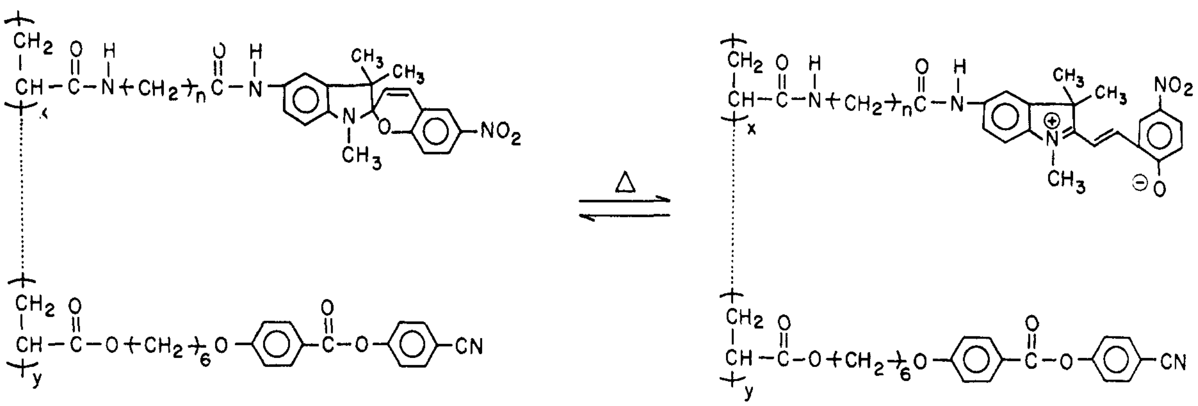
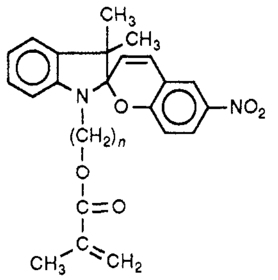
Scheme I

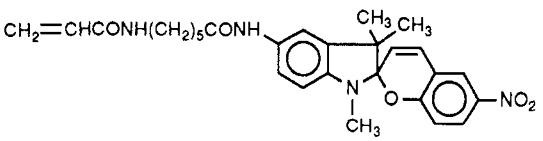


these systems both the thermochromic properties and the photochromism of polysiloxane copolymers were studied at various temperatures. At room temperature (above the glass transition point, T_g) the merocyanine groups formed on UV irradiation give dimers ($\lambda_{max} \sim$ 560 nm, red), which brings about network formation. At temperatures below −10 °C, at which the side chains are immobilized, isolated merocyanine groups are formed on UV irradiation ($\lambda_{max} \sim$ 580 nm, blue). On heating above −10 °C dimerization of the merocyanine occurs, and the blue film turns red. Irradiation of both the blue (below −10 °C) and the red (above −10 °C) films with visible light converts the merocyanine groups back into spiropyran (yellow).

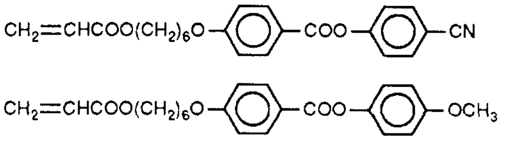
In the present paper we report the photochromic properties of side-chain liquid-crystal polyacrylates, containing spiropyran side groups of various structures. For this purpose the methacrylic- and acrylic-substituted T- and rod-shaped (lateral and linear) spiropyrans were copolymerized with acrylic monomers containing mesogenic groups:



lateral (T-shaped) spiropyran monomer (S_n^T)



linear (rod-shaped) spiropyran monomer (S_5^R)



monomers with the mesomorphic group (M_6^{CN} and M_6^{OMe})

The resulting liquid-crystal copolymers revealed strong photochromic properties. Investigation of thermodynamic, spectroscopic, and kinetic properties of the polymers enables us to draw some conclusions on the structure of the polymers.

Experimental Section

Materials. Mesogenic acrylate (M_6^{CN} and M_6^{OMe} and spiropyran monomers (S_n^T and S_n^R were synthesized according to refs 8, 11, and 12. (n indicates the number of methylene groups separating the spiropyran group from the methacrylate one; T and R relate to T- and rod-shaped spiropyrans.) The homopolymers denoted by $P(M_6)$ and copolymers denoted by $P(S_n^TM_6)$ and $P(S_n^RM_6)$ were prepared according to ref 8, by polymerization in solutions of tetrahydrofuran (THF) and toluene–THF mixtures. The composition of the copolymers was estimated as it was described earlier and is given as percentage of S; for example, 22% $P(S_n^RM_6)$ means that the copolymer contains 22 mol % of S^R (rod-shaped spiropyran). All copolymers were freeze-dried from benzene solution, except $P(S_5^RM_6^{CN})$, which was not soluble in benzene due to strong merocyanine aggregation.[8]

Material Characterization. The molecular weight distribution of the polymer was measured by GPC. The measurements were conducted in THF solutions by a TRACOR 985 liquid chromatograph with Lichrogel PS400, 20, and 4 columns and a TRACOR 970A variable-wavelength (UV) detector. The number-average molecular weight ($\bar{M}_n$) was calculated using a polystyrene calibration curve. Taking into account the complex copolymer structure, the molecular weight measurements should be considered only as approximations which give comparative characteristics of samples. Using THF as a solvent should diminish the aggregation of macromolecules during these measurements.[2]

Transition temperatures of the polymers were investigated by polarization microscopy and differential scanning calorimetry (DSC). A Wild M8 polarizing microscope with a Ernst Leitz Wetzlar hot stage was used. 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.[13]

X-ray diffraction experiments were performed on a Serle camera equipped with Franks optics and affixed to an Elliot GX6 rotating annode generator operating at 1.2 kW with a 200-μm focus. Specimens were held in either 1.5-mm quartz or glass X-ray capillaries, and the temperature was controlled by a water–alcohol bath flowing through the brass sample holder. Photographic measurements were made using Kodak DEF film, and exposure times ranged from ~16 to 54 h. The specimen to film distance was approximately 3 cm, calibrated by crystalline calcite.

Some of the polymer films were prepared from powder by melting above the clearing point and cooling to room temperature (below T_g) before spectroscopic investigation. Other films were cast from solution dried in vacuo and also melted and cooled. The film thickness varied from 2 to 7 μm.

Results and Discusion

Molecular Weight of Polymers. Typical results of molecular weight measurements of the photochromic copol-

Table I
Molecular Weight of Several Photochromic Polymers

polymer	polymerizn solvent	$\bar{M} \times 10^4$	$\bar{M}_w \times 10^4$ (±10%)	$\bar{M}_w/\bar{M}_n$
P(M_6^{CN})[a]	THF		2.5	
17% P($S_2^T M_6^{CN}$)	toluene–THF (4:1)	1.0	1.8	1.8
23% P($S_2^T M_6^{CN}$)	THF	1.0	3.2	3.2
14% P($S_2^T M_6^{OMe}$)	THF	0.9	2.7	3.0
21% P($S_5^R M_6^{CN}$)	THF	1.4	4.7	3.3

[a] Earlier measurement.[8]

ymers are given in Table I. Only P($S_2^T M_6^{CN}$) obtained by polymerization in a bad solvent, 4:1 toluene–tetrahydrofuran, has rather narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \sim 2$), which may be explained by precipitation of the polymer during polymerization. Other copolymers give rather broad molecular weight distribution, $M_w/M_n \sim 3$. Certain increases of molecular weight were observed for P($S_5^R M_6^{CN}$). Earlier[8] and in the present research we found that the copolymers with S_5^R are very prone to aggregation, which may explain the observed increase of molecular weight. On the other hand, we also found that the higher molecular weight, the stronger was the tendency to aggregation.

Phase Transitions. Phase diagrams of liquid-crystal polymers containing rod-shaped spiropyran groups were obtained by a combination of DSC and polarization microscopy. This is required because the enthalpy change on mesophase–isotropic phase transition is low (~0.5 J/g) and masked by noise, stemming probably from the interactions of photochromic groups. Copolymers with T-shaped spiropyrans gave substantially clearer DSC peaks; while microscopic observations were disturbed by the strong tendency of the copolymers to accept homeotropic orientation of mesogenic groups on the glass surface. Therefore, part of the microscopic observations was conducted with films aligned homogeneously on the surface in an electrostatic field.

DSC thermogram curves for T-shaped spiropyran copolymers contain an additional peak with $\Delta H \sim 3$ J/g in the first heating cycle. The peak lies at glass transition temperature (T_g) or slightly above it (Figure 1). The peak appears even on thermograms with a very high content of spiropyran which do not form mesophase. The peak does not appear on cooling and is substantially less pronounced or is not seen at all in the second heating cycle. At temperatures higher than T_g the thermograms usually have some exothermic inclination. Conceivably the low-temperature peak relates to a nonequilibrium phenomenon occurring on the first heating of the copolymers. One can assume that the side chains with the bulky photochromic groups somehow promote the effect because the peak appears only in a copolymer with spiropyran and grows with the increase of the spiropyran content.

Perhaps the exothermic inclination above T_g can be explained by a merocyanine aggregation process.

The phase diagrams for several copolymers are depicted in Figures 2–5. In Figure 2, the phase diagrams of P($S_2^T M_6^{CN}$) of different $\bar{M}_w$ are shown. While T_g is not affected markedly by $\bar{M}_w$ change, the clearing temperature (T_c) curve shows a clear increase in the mesophase stability with increasing $\bar{M}_w$. Marked effects of molecular weight and polydispersity on thermodynamic characteristics of liquid-crystal polymers were observed recently also by other authors.[14,15] The phase diagram in Figure 3 indicates that the homopolymer P(M_6^{OMe}) gives the smectic phase up to 85 °C, which was not observed in the copolymers. P($S_5^R M_6^{CN}$) (Figure 5) also deserves some discussion because the polymer reveals very strong thermal aggregation, as a result of which the copolymer could not be dissolved in benzene and could not be freeze-dried in this solvent. The low-temperature peak did not appear on the DSC thermograms of P($S_5^R M_6^{CN}$). For this copolymer the T_c and T_g lines go higher than those for any other studied copolymer, which is presumably also connected with very strong thermal aggregation of the polymer.

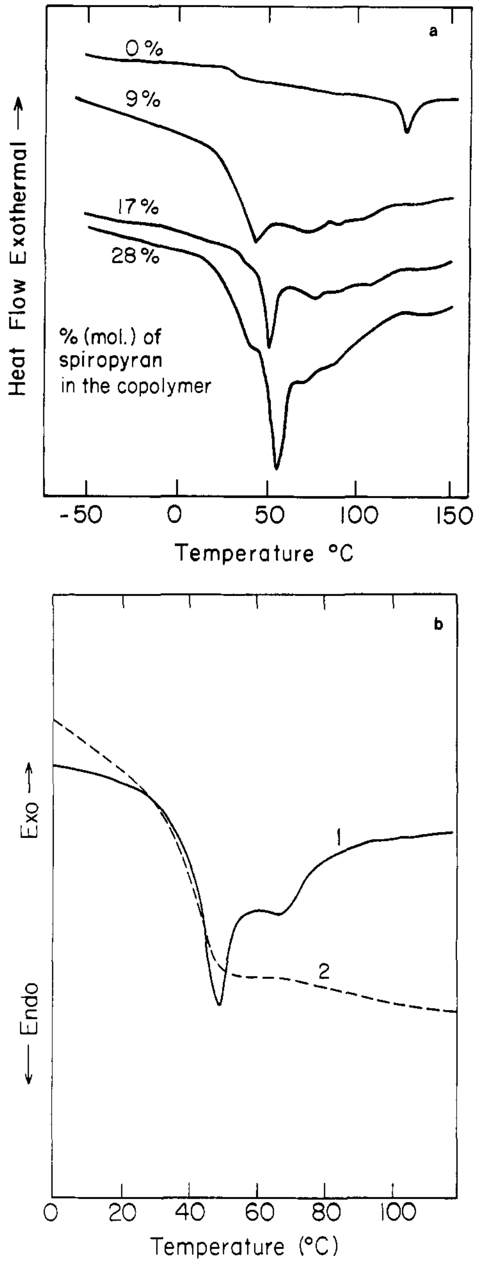


Figure 1. DSC thermograms: (a) homopolymer P(M_6^{CN}) and copolymers 9%, 17%, and 28% P($S_2^T M_6^{CN}$); (b) heating thermograms 26% P($S_6^T M_6^{CN}$), the first (1) and second (2) cycles.

Overall, incorporation of photochromic groups in the liquid-crystal polymer makes the polymer thermodynamic characteristics very sensitive to polymerization conditions and to sample preparation procedure.

X-ray Diffraction. The X-ray diffraction patterns of both the homopolymer and the T-shaped copolymers are characteristic of materials possessing a relatively low degree of order. Only two diffuse diffraction peaks are observed, one at ~5 Å and the second much weaker at ~12 Å in the X-ray diffraction pattern of copolymers with M_6^{CN}. The homopolymer P(M_6^{OMe}) forms a smectic

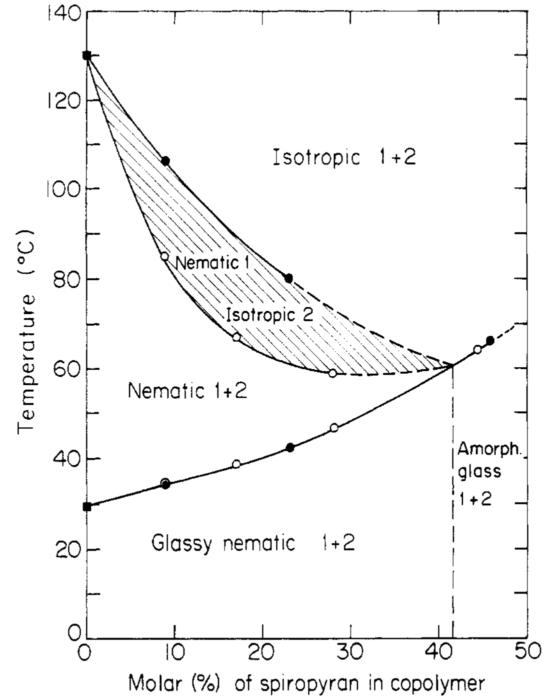


Figure 2. Phase diagrams of $P(S_2^{T}M_6^{CN})$: (1) copolymers polymerized in THF; (2) copolymers polymerized in THF–toluene (1:4) mixture.

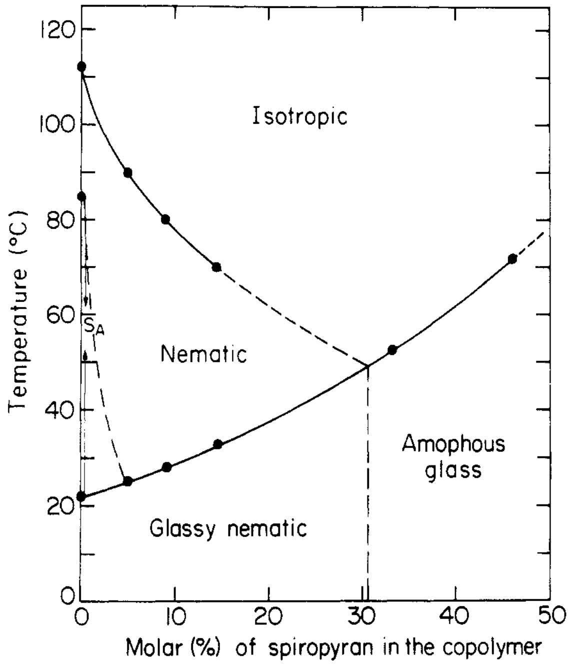


Figure 3. Phase diagram of $P(S_2^{T}M_6^{OMe})$(polymerization in THF).

phase, which may explain an additional diffuse peak at 25 Å. Incorporation of spiropyran groups in the polymer leads to disappearance of this peak.

Film Alignment in an Electric Field. Films of the copolymers, especially films of the copolymers $P(S_2^{T}M_6^{CN})$ and $P(S_6^{T}M_6^{CN})$, exhibit a strong tendency to spontaneous homeotropic alignment, which leads to vanishing birefrigence.

Films of the copolymers containing M_6^{CN} cast between parallel aluminium thin-film electrodes deposited on a glass slide could be easily aligned homogeneously parallel to the field in an electrostatic field of ~ 1 kV/mm at a temperature above T_g. Cooling the aligned films to room temperature (below T_g) in the electric field and subsequent UV irradiation of the aligned films produced dichroic absorption in the visible (Figure 6) region, which enabled us to estimate an order parameter for the merocyanine dye. The order parameter (S) of the dye is defined as

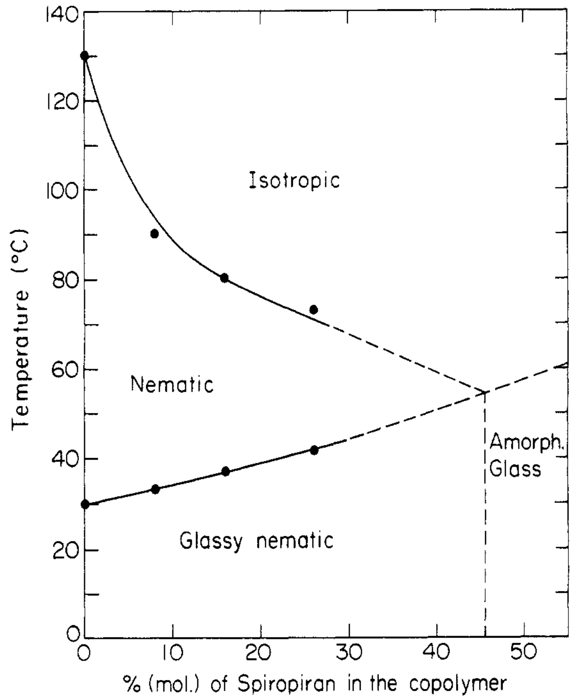


Figure 4. Phase diagram of $P(S_6^{T}M_6^{CN})$ (polymerization in THF–toluene, 1:4).

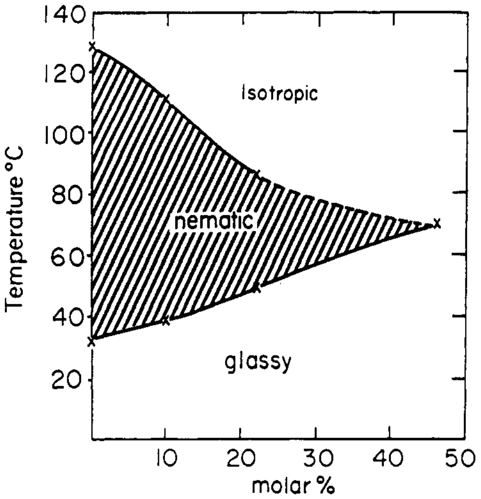


Figure 5. Phase diagram of $P(S_5^{R}M_6^{CN})$ (polymerization in THF).

$$S = (D_{\parallel} - D_{\perp})/(2D_{\perp} + D_{\parallel})$$

where $D_{\parallel}$ and $D_{\perp}$ are, respectively, the absorptions parallel and perpendicular to the liquid-crystal director. For several copolymers examined, roughly the same order parameter of the dye was obtained ($S \sim 0.1$).

Examination of the linear dichroism spectra of 4,4′-(dimethylamino)nitrostilbene (DANS) dissolved in the $P(M_6^{CN})$ homopolymer and in the 9% $P(S_2^{T}M_6^{CN})$ gave entirely different results (Figure 7). Two absorption maxima around λ = 460 nm can be seen in the spectra. The DANS order parameter estimated from the absorption spectra is ~0.5 both for the homo- and copolymer. The DANS fluorescence polarization spectra in 9%

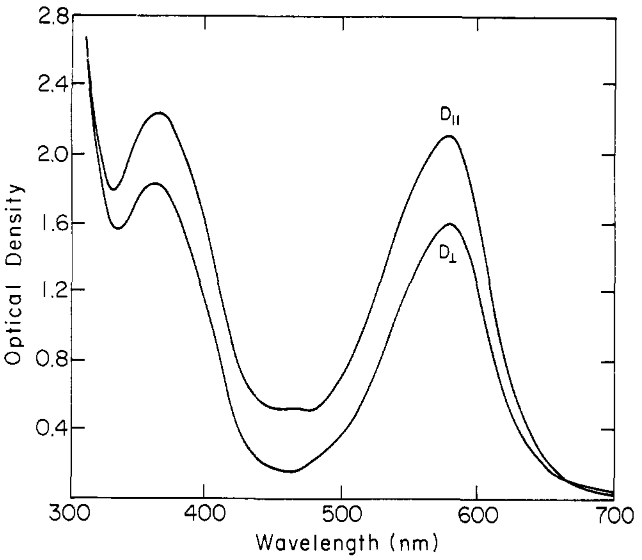


Figure 6. Polarization absorption spectra of 8% P(S$_6^T$M$_6^{CN}$) aligned in the electrostatic field (1 kV/mm) and irradiated with UV light. $D_\parallel$ and $D_\perp$ correspond to the measurements in light polarized parallel and perpendicular, respectively, to the mesophase director. Merocyanine order parameters $S \sim 0.1$.

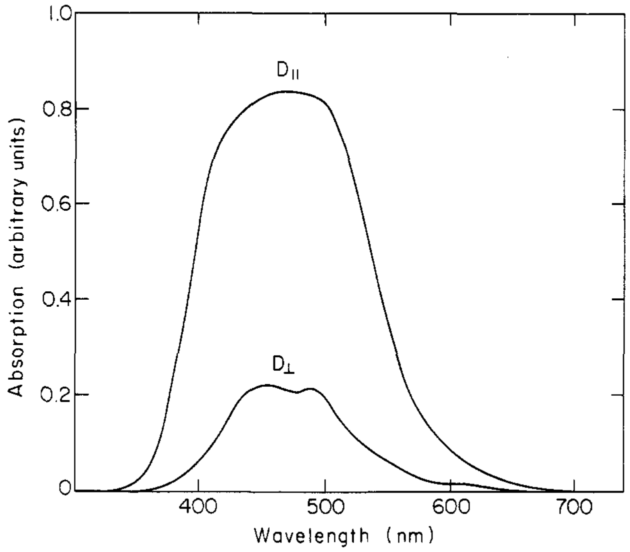


Figure 7. Polarization absorption spectra of 1 wt % DANS in P(M$_6^{CN}$) after alignment in the electric field. DANS order parameter $S \sim 0.5$. Similar spectra were obtained for DANS dissolved in 9% P(S$_2^T$M$_6^{CN}$).

P(S$_2^T$M$_6^{CN}$) and in the homopolymer were also measured (Figure 8). The fluorescence spectra measured in the nonpolarized light have one peak and a wide red-shifted shoulder. In the light polarized parallel to the sample alignment two overlapping emission bands with $\lambda_{max} = 610$ and 660 nm were observed. In the light polarized perpendicular to the alignment only one band with $\lambda_{max} = 630$ nm was observed. The DANS order parameter estimated from the fluorescence polarization spectra is also ~0.5. A two-band fluorescence spectrum was also observed in nonpolarized light by Fischer and co-workers[16] for DANS dissolved in nonpolar hydrocarbon solvent at −50 °C. In polar solvent the spectrum had only one red-shifted peak. The authors did not discuss the origin of the two peaks. One should take into account that there is a very strong tendency to the dye association in nonpolar solvents at low temperature, which can be responsible for the appearance of one of the peaks. Meredith et al.[17] studied the second harmonic generation by DANS dissolved in the liquid-crystal polymer matrix and poled in the electrostatic field. These studies led the authors to the conclusion that DANS easily associated in the polymer matrix.

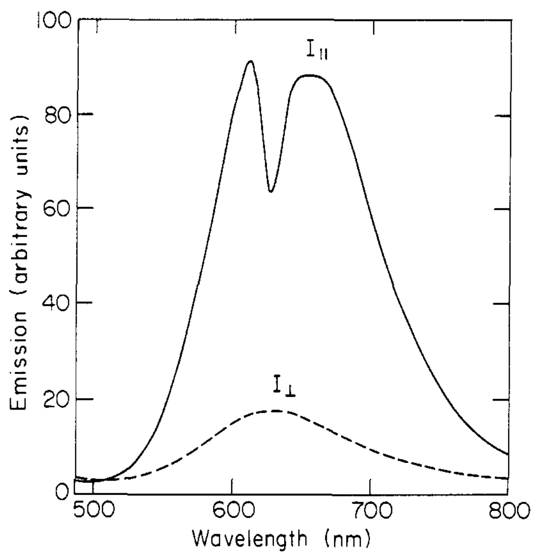


Figure 8. Polarization emission spectra of 1.5 wt % DANS in 9% P(S$_2^T$M$_6^{CN}$) aligned in the electric field $I_\parallel$ and $I_\perp$ correspond to the measurements with light polarized parallel and perpendicular to the mesophase director $S \sim 0.5$.

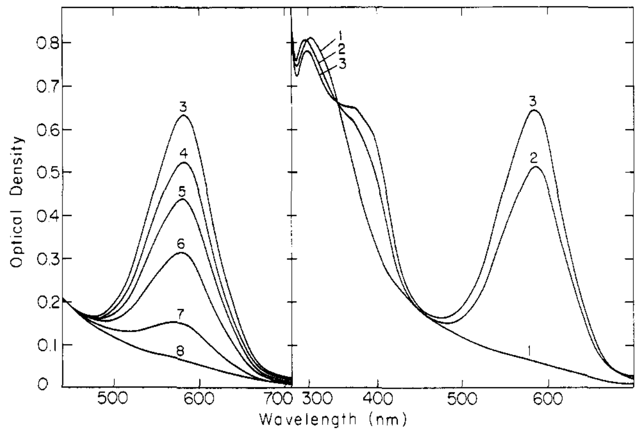


Figure 9. Absorption spectra of 9% P(S$_2^T$M$_6^{CN}$): before irradiation (1) and after UV irradiation ($\lambda = 365$ nm) for 2 and 10 min (2, 3); successive exposures to visible light ($\lambda > 500$ nm) for 1 min (4), 1 min (5), 2 min (6), 6 min (7), and 10 min (8).

The polymer alignment obtained in the electrostatic field was not affected when the films were irradiated with UV or visible light. This was true both for homogeneously and homeotropically aligned films. The polymers containing M$_6^{OMe}$ could not be aligned in the field.

Electronic Absorption Spectra. The thermochromic properties of the copolymers with T-shaped spiropyrans are similar to those of the copolymers with rod-shaped spiropyrans. However, the spiropyran ⇔ merocyanine equilibrium is shifted more to the left for the T-shaped photochromes, probably due to the lower tendency to aggregation of the corresponding merocyanine molecules. As a result, the copolymers of T-shaped spiropyrans are practically colorless at room temperature.

Irradiation with UV light of a glassy film, formed after cooling of the mesomorphic copolymers below T_g, produced deep blue color in copolymers with both rod- and T-shaped spiropyrans (λ_{max} in the range 570–590 nm; Figures 9 and 10). Irradiation of the film with visible light ($\lambda > 500$ nm) led to erasure of the visible absorption band. For the copolymers with S$_6^R$ and S$_6^T$, which exhibit a strong

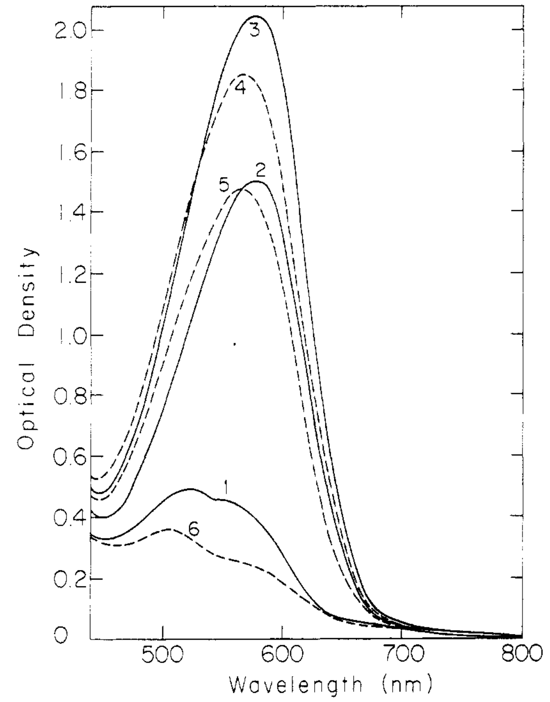


Figure 10. Absorption spectra of 21% $P(S_5^RM_6^{CN})$: before irradiation (1) after 12 and 24 min of successive UV irradiation (2, 3); after 17 h of thermal color decay at 25 °C (4); 3-min and 1-h irradiation with visible light (5, 6).

Table II
Thermal Color Decay Rate of UV-Irradiated Copolymers

polymer	color decay rate, s^{-1}	λ_{max}	glass phase
9% $P(S_2^TM_6^{CN})$	$(5 \pm 3) \times 10^{-6}$	580	mesomorphic
17% $P(S_2^TM_6^{CN})$	$(8 \pm 3) \times 10^{-6}$	580	mesomorphic
45% $P(S_2^TM_6^{CN})$	$(5 \pm 3) \times 10^{-6}$	580	isotropic
8% $P(S_2^TM_6^{OMe})$	$(1 \pm 0.2) \times 10^{-5}$	580	mesomorphic
28% $P(S_2^TM_6^{OMe})$	$(7 \pm 0.2) \times 10^{-5}$	580	isotropic
5% S_2^T solution in $P(M_6^{OMe})$	$(12 \pm 0.2) \times 10^{-4}$	560	mesomorphic

tendency toward aggregation, the λ_{max} was blue shifted during the decoloration (Figure 10; curves 4–6) or a pronounced shoulder at 560 nm appeared. The remaining absorption (Figure 10, curve 6) is not easily erasable with visible light because it belongs to aggregates formed thermally on polymer melting. The absorption at 560 nm is characteristic of the merocyanine dimers while the absorption maximum around 500 nm may be tentatively ascribed to trimers.[6]

Thermal Decay of the Photoinduced Color. Measurements of the thermal decoloration rate of a UV-irradiated polymer were conducted with $P(S_2^TM_6)$ films at room temperature (~25 °C). The color decay at λ_{max} did not obey the first-order kinetics and can be described only by at least two exponential equations (see also refs 2 and 6). However, the decay can be satisfactorily described by one exponential equation during the initial stage of the reaction (less than 20%). The comparison of the first-order rate constants in the early stage of decay for different copolymers $P(S_2^TM_6)$ is given in Table II.

The merocyanine form in copolymers with M_6^{CN} is very stable. The rate constants are about the same in glassy mesophase and isotropic glass ($\sim 5 \times 10^{-6}$ s^{-1}). Decoloration of the irradiated mesomorphic copolymers with M_6^{OMe} goes with the same rate or slightly faster than that in the copolymer with M_6^{CN}. However, with M_6^{OMe} in an isotropic glass the rate constant was almost 1 order of magnitude higher than that in the mesomorphic one.

Apparently; the solvatochromic effect of CN-substituted mesogenic groups stabilizes the merocyanine form of the photochrome strongly enough to screen the steric hindrance of the decoloration reaction by the mesophase. In case of methoxy-substituted mesogenic groups some stabilization by the mesomorphic structure can be seen clearly. When the monomer S_2^T was dissolved in the homopolymer $P(M_6^{OMe})$, the stabilization by the mesomorphic structure was not observed.

Structure of the Polymers. Incorporation of spiropyran groups into liquid-crystal polymers brings about marked structural changes, including thermal cross-linking of macromolecules. Yet the phase diagrams of the copolymers indicate that the mesophase is very "tolerant" to introduction of bulky nonmesogenic spiropyran groups. This may be accounted for by the assumption that the photochromic groups are accommodated outside the domains of mesogenic groups. The low-order parameter of the merocyanine groups in a polymer film aligned in an electrostatic field, no impact of photochromic conversion on the film alignment, and rather weak influence of mesophase on the decoloration kinetics seem also to be interpretable on the basis of photochromic and mesomorphic site separation due to strong structural incompatability of spiropyran groups and mesogenic ones. DANS molecules give a 5-fold higher order parameter apparently because of their higher compatability with the mesogenic domains.

In total, the observations reported in this and previous publications support the hypothesis of the existence of two sites in side-chain liquid-crystal polymers: mesogenic domains and amorphous sites. Main chains and photochromic side chains are presumably located in the amorphous site, which is expanded with an increase of spiropyran content until the mesophase finally vanishes. Yet a certain "mixing" of mesogenic domains and photochromic groups occurs which is manifested in a nonzero-order parameter of merocyanine units and certain retardation of thermal color decay in some cases. Rheooptical effect,[7] effect of aggregation on phase transitions, and the tendency to hopmeotropic orientation of the copolymers indicate the existence of indirect interactions which apparently involve the main chain.

It is worthwhile mentioning here that there have been found two sites, one amorphous and one liquid crystalline, in the low molecular mesophase formed by quasi-liquid crystals (low molar mass molecules containing spiropyran and mesogenic units).[18,19]

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References and Notes

(1) Krongauz, V. A.; Goldburt, E. S. *Macromolecules* **1981**, *14*, 1382.
(2) Goldburt, E.; Shvartsman, F.; Fishman, S.; Krongauz, V. *Macromolecules* **1984**, *17*, 1225.
(3) Goldburt, E.; Shvartsman, F.; Krongauz, V. *Macromolecules* **1984**, *17*, 1876.
(4) Wismontski-Knittel, T.; Krongauz, V. *Macromolecules* **1985**, *18*, 2124.
(5) Goldburt, E.; Krongauz, V. *Macromolecules* **1986**, *19*, 246.
(6) Eckhardt, H.; Bose, A.; Krongauz, V. A. *Polymer* **1987**, *28*, 1959.
(7) Cabrera, I.; Krongauz, V. *Nature (London)* **1987**, *326*, 582.
(8) Cabrera, I.; Krongauz, V. *Macromolecules* **1987**, *20*, 2713.
(9) Cabrera, I.; Krongauz, V.; Ringsdorf, H. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 221.
(10) Cabrera, I.; Krongauz, V.; Ringsdorf, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1178.

Macromolecules **1990**, *23*, 713–718

(11) Portugall, H.; Ringsdorf, H.; Zentel, R. *Macromol. Chem.* **1982**, *193*, 2311.
(12) Goldburt, E.; Shvartsman, F.; Fishman, S.; Krongauz, V. *Macromolecules* **1984**, *17*, 1225.
(13) Fischer, E. *Mol. Photochem.* **1970**, *2* (1), 99.
(14) Gray, G. W.; Lacye, D.; Nester, N.; Toyne, K. J.; White, M. S. *Abstracts*; International Conference on Liquid Crystal Polymers, Bordeaux, France, 1987.
(15) Sagane, T.; Lenz, R. *Polym. J.* **1988**, *20*, 923.
(16) Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 3907.
(17) Meredith, G. R.; Vandusen, J. G.; Willimans, D. J. *Macromolecules* **1982**, *83*, 816.
(18) Meirovitch, E.; Shvartsman, F.; Krongauz, V.; Zimmerman, H. *J. Phys. Chem.* **1985**, *89*, 5522.
(19) Shvartsman, F.; Cabrera, I.; Weis, A.; Wachtel, E.; Krongauz, V. *J. Phys. Chem.* **1985**, *89*, 3941.

Registry No. M_6^{CN} (homopolymer), 83847-15-8; $(S_2^{T})(M_6^{CN})$ (copolymer), 124401-69-0; $(S_2^{T})(M_6^{OMe})$ (copolymer), 124401-70-3; $(S_5^{R})(M_6^{CN})$ (copolymer), 108764-09-6; S_2^{T}, 25952-50-5.

A Nonradiative Energy Transfer Fluorescence Study: Blends of Poly(vinyl chloride) and Poly(methyl methacrylates) of Different Tacticities and Molecular Weights

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ABSTRACT: The nonradiative energy transfer (NRET) technique has been used to investigate the influence of tacticity and molecular weight of poly(methyl methacrylate) (PMMA) on its miscibility with poly(vinyl chloride) (PVC). These investigations were carried out by labeling PVC with both naphthyl (fluorescence donor) and anthryl (fluorescence acceptor) chromophores assuming that the efficiency of energy transfer is dependent upon the extent of random dispersion of the PVC chains. Comparative measurements lead to the observation of differences of miscibility at a molecular level between different PVC/PMMA blends prepared under identical conditions and all exhibiting a single glass transition temperature. These results indicate that an increase in isotactic content and molecular weight of PMMA results in more nonrandom dispersion of the PVC chains, i.e. reduces its miscibility with PVC. It is shown that this behavior can be related to a tacticity and molecular weight dependent lower critical solution temperature of these mixtures.

Introduction

The nonradiative energy transfer (NRET) technique has been used as a tool of investigation of ion-pair interchange in ionomer solutions,[1] chain interpenetration in bulk and solution,[2] morphology of polymer colloids,[3] miscibility of polymer blends,[4,5] and formation of micelles in block copolymers,[6] as reviewed recently by Morawetz.[7]

Morawetz et al. were the first to use this fluorescence technique to study the miscibility of polymer blends in the solid state,[4,7-9] which involves grafting fluorescent donor and acceptor molecules to the polymers. The efficiency of the nonradiative energy transfer, after the photoexcitation of the donor, depends upon the average distance between the donor and acceptor molecules; measurements of the relative emission intensities of the donor and acceptor, characterized by their emission intensity ratio, indicate the extent of interpenetration of the chains, giving information about the miscibility of the polymeric species. It has been demonstrated[4,5] that a suitable choice of the donor–acceptor pair, e.g. naphthalene–anthracene or carbazole–anthracene, leads to an efficient energy transfer over a distance of about 3 nm. It is then assumed that changes of the energy transfer efficiency is related to the evolution of the miscibility of the donor- and acceptor-containing polymers at this molecular level.

However, in a previous investigation, using naphthyl (donor) and anthryl (acceptor) chromophores,[10] we have critically examined this fluorescence method and shown that, in studies of the miscibility of polymer blends, the reference emission intensity ratio in the absence of energy transfer has to be measured in the bulk instead of being made in organic solutions. This ratio is important to establish an energy transfer scale. Furthermore, the fluorescence quenching effect of the polymers must be examined because it can lead to a variation of the relative fluorescence quantum yields of the donor and acceptor as a function of blend composition. In other words, if fluorescence quenching occurs, a change of the emission intensity ratio of the donor to acceptor can be observed without changing the miscibility level of the blend. Therefore, the interpretation of energy transfer data must be done with caution.

Nevertheless, in the present article, we will show that, under suitable conditions, the NRET technique provides useful information about the miscibility of polymer blends. It is particularly sensitive to small differences of polymer miscibility at the molecular level, differences which cannot be detected by other conventional techniques such as, for example, differential scanning calorimetry (DSC).

More specifically, the NRET technique will be used to investigate the influence of the tacticity and molecular weight of poly(methyl methacrylate) (PMMA) on its miscibility with poly(vinyl chloride) (PVC). Miscibility is generally observed in these blends, under suitable conditions of blend preparation.[11-13] The origin of this miscibility is attributed to the presence of hydrogen-bonding interactions involving the carbonyl group of PMMA and the α-hydrogen[14] as well as the β-hydrogens[11] of PVC. It will be shown that the NRET technique allows direct measurements of small miscibility differences between

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