110294-68-3; $(A_{2,3})(B_2)$ (copolymer), 87318-28-3; $(A_{2,3})(B_2)$ (SRU), 110294-69-4; $(A_{2,4})(B_2)$ (copolymer), 87318-29-4; $(A_{2,4})(B_2)$ (SRU), 110294-70-7.

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Physical Cross-Linking of Mesomorphic Polymers Containing Spiropyran Groups[†]

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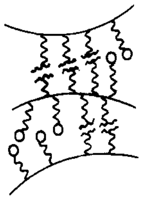
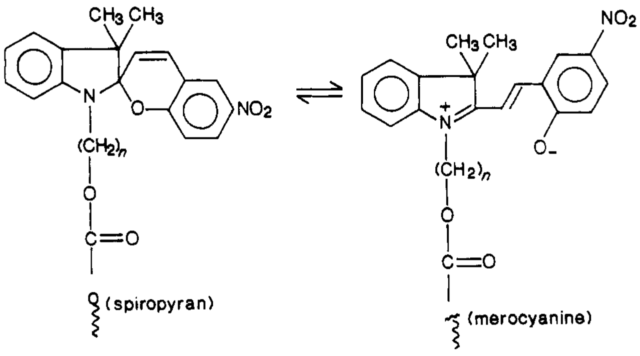
ABSTRACT: Acrylic copolymers with mesogenic and spiropyran side chains give a mesophase, which on heating is converted to an isotropic melt, displaying strong dynamic birefringence. This effect is connected with the thermochromic spiropyran–merocyanine transformation resulting in the physical cross-linking of the macromolecules due to merocyanine aggregation.

Earlier, we reported[1,2] a new type of crystallization of atactic vinyl polymers bearing spiropyran side groups, by swelling in polar solvents. Solvatochromic spiropyran–merocyanine conversion and self-assembly of merocyanine groups into giant molecular stacks are the driving forces for this crystallization.





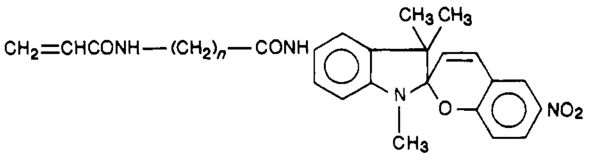
We believe that the high degree of crystallinity of the above polymers (up to 40%) was achieved because the cooperative spiropyran–merocyanine conversion occurs step-by-step along the polymer chains, a process which we called "zipper crystallization". The tendency of the merocyanine groups to self-assembly is so strong that even in a 1:1 copolymer of a spiropyran methacrylate with methyl methacrylate it proceeds rather fast, though it does not result in crystalline order.[3]

The assumed structure of the assemblies resembles the structure of side chain liquid crystal polymers, though the factors that give rise to these structures are completely different: the merocyanine stacks, formed in the course of swelling, belong to the so-called H-type, which is characterized by antiparallel dipole–dipole interactions of the molecules.[4] The liquid crystalline structure, on the other hand, is determined mainly by the steric factor connected with the geometrical anisotropy of the mesogenic groups.[5]

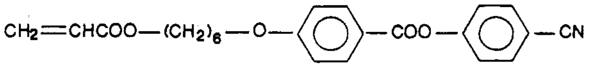
Recently, we have shown that the combination of thermochromic spiropyran and mesogenic groups in a low molecular weight molecule gives a new kind of mesophase, quasi-liquid crystals.[6,7]

One can expect that in copolymers containing both spiropyran and mesogenic side groups the competition between merocyanine interactions and liquid crystalline ordering of mesogenic groups will give rise to new, interesting structural changes of the mesophase, taking into account that spiropyran can be effectively converted into merocyanine both by light and by heat.

To test these expectations, and in order to make spiropyran groups more compatible with mesogenic ones, new spiropyran acrylate monomers



were now synthesized (Table I), in which the acrylic group is attached through a flexible spacer to the indoline part of the spiropyran. Copolymerization with an acrylic monomer containing a mesogenic group[8]



leads to liquid crystal copolymers with thermochromic properties. We now report structural transformations occurring in such copolymers: Physical cross-linking of the macromolecules due to aggregation of the dye moieties gives rise to formation of a network responsible for the

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[†] Dedicated to Prof. Ernst Fischer on the occasion of his 65th birthday. His pioneering studies on spiropyrans inspired our long-lasting interest in these fascinating substances.

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Table I

			analysis %					
			calcd			found		
n^a	yield,^{b} %	mp,^{c} °C	C	H	N	C	H	N
2	37	126–130	64.92	5.67	12.11	64.96	5.60	12.10
5	71	102–104	66.65	6.39	11.10	66.68	6.31	11.08
11	43	85–88	69.36	7.53	9.52	69.40	7.50	9.60

^{a} In the text the monomers with n = 2, 5, and 11 are named S_2, S_5, and S_{11}, respectively. ^{b} The yield is given for the last-step of synthesis. ^{c} Not corrected.

appearance of a new rheooptical effect, observed above the clearing point. Preliminary observations of this effect have already been reported.[9]

Experimental Section

Materials. All solvents were purified by distillation, and tetrahydrofuran (THF) was, in addition, passed through a column of basic aluminum oxide before use. The following starting materials were distilled before synthesis: 1,3,3-trimethyl-2-methyleneindoline (Fisher's base), acryloyl chloride, and acrylic acid (all Fluka).

The following were used without further purification: 6-chloro-1-hexanol, 4-cyanophenol, di-*tert*-butyl dicarbonate (all Fluka); 4-hydroxybenzoic acid, β-alanine, 6-aminohexanoic acid (all BDH), dicyclohexylcarbodiimide (Merck), 5-nitrosalicylaldehyde (Eastman Kodak), and 12-aminododecanoic acid (Aldrich).

The acryloylamino acids were prepared by procedures described in the literature: 3-acryloylaminopropanoic acid [I],[10] 6-acryloylaminohexanoic acid [II],[11] and 12-acryloylaminododecanoic acid [III].[12] 5-Amino-1,3,3-trimethyl-6′-nitrospiro(indole-2,2′-[2*H*-1]-benzopyran) ("5-aminospiropyran") was synthesized according to ref 13.

Monomers. The mesogenic acrylate (M_6) was prepared according to ref 8. The spiropyran monomers (Table I) were synthesized by reacting in situ the symmetrical anhydrides of I, II, or III with 5-aminospiropyran. In a typical example, II (0.002 mol) was dissolved in 16 mL of dry 1,2-dimethoxyethane. The solution was cooled in an ice–water bath while dicyclohexylcarbodiimide (0.001 mol) was added with stirring. After about 2 h, the N,N′-dicyclohexylurea was removed by filtration. 5-Aminospiropyran (0.001 mol) and 4-(dimethylamino)pyridine (0.0001 mol) were then added and the reaction was allowed to proceed at room temperature overnight. The solvent was evaporated, the residue dissolved in methylene chloride, the solution washed with water, 5% acetic acid solution, 5% sodium bicarbonate solution, and again with water and dried ($MgSO_4$), and the solvent evaporated in vacuo to give a reddish oily solid. The materials were purified by flash chromatography with ethyl acetate/hexane mixtures and reprecipitated from CH_2Cl_2/hexane.

Polymers. The homopolymers (denoted by $P(S_n)$ and $P(M_6)$) and copolymers (denoted by $P(S_nM_6)$) were prepared by polymerization of a 20–30% THF solution with 2% 2,2-azobis(isobutyronitrile) at 55 °C under vacuum. The polymers were precipitated by methanol, purified by reprecipitation, and dried under vacuum at room temperature. The yield of the polymers (40–70%) depended substantially on the solution concentration: the higher the concentration, the better the polymer yield.

Characterization of the Polymers. Gel permeation chromatography carried out in THF with Lichrogel PS400, 20, 4 columns, and narrow-distribution polystyrene standards gave estimated $\bar{M}_n$ values of 2.5×10^4 for the LC homopolymer, 8×10^3 for the $P(S_5M_6)$ copolymer containing 22% spiropyran units, and 1.2×10^4 for the $P(S_5)$ homopolymer.

The liquid crystalline behavior and the transition temperatures of the polymers were investigated by polarization microscopy and differential scanning calorimetry (DSC). A Wild M8 polarizing microscope with a Ernst Leitz GmbH 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.[14]

The rheooptical measurements were carried out with a simple parallel-disk-type rheometer with transparent glass disks of 1-cm diameter. The rheometer was made from a glass syringe and mounted on the stage of the polarizing microscope. The sample thickness was controlled by a 12-μm Mylar spacer between the glass disks. The shear rate was 290 s^{-1} at the rim of the device. The torque measurements were performed with a Caldwell (Model 75) dynamometer and the transmitted polarized-light intensities were measured with a photodiode–amplifier–recorder setup.

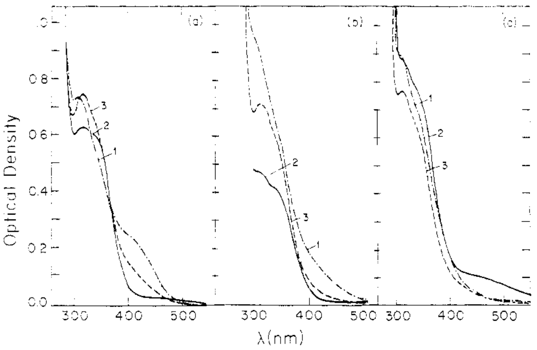

Figure 1. Absorption spectra in THF solution. (a) Monomers: (1) S_2, 8.2×10^{-4} M; (2) S_5, 6.1×10^{-4} M; (3) S_{11}, 1×10^{-3} M. (b) Homopolymers: (1) $P(S_2)$, 8.9×10^{-4} M; (2) $P(S_5)$, 6.3×10^{-4} M; (3) $P(S_{11})$, 8.3×10^{-4} M. (c) Copolymers: (1) 16% $P(S_2M_6)$, 5.2×10^{-3} M; (2) 22% $P(S_5M_6)$, 4.4×10^{-3} M; (3) 9% $P(S_{11}M_6)$, 7.3×10^{-3} M. Optical path, 1 mm.

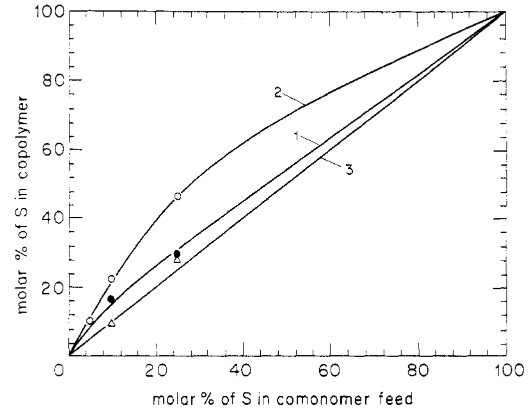

Figure 2. Composition of the $P(S_nM_6)$ copolymers as a function of the monomer mixture composition. (1) n = 2; (2) n = 5; (3) n = 11.

Results and Discussion

A. Copolymer Composition. The composition of the copolymers $P(S_nM_6)$ was assessed by spectrophotometry of their solutions. The spectra of the monomers and corresponding homo- and copolymers in THF solutions are shown in Figure 1. Comparison of the spectra indicates that the spiropyran homopolymers and related copolymers spectra are very similar, while the monomer spectra (except for S_{11}) are substantially different. Therefore, we used the extinction coefficients of the homopolymers per monomer unit at λ = 340 nm to estimate the composition of a copolymer. The copolymer composition as a function of the feed composition is plotted in Figure 2. The monomer reactivity ratios $r_1 = K_{ss}/K_{sm}$ and $r_2 = K_{mm}/K_{ms}$, estimated from copolymer–feed compositions are given in Table II.

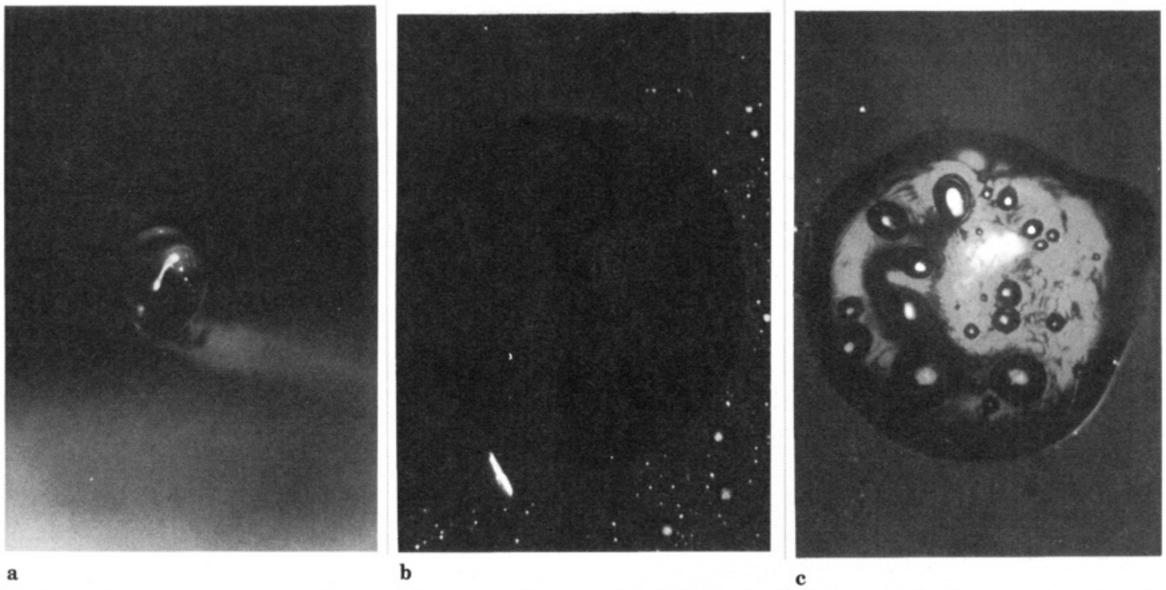

Figure 3. "Sparkling phenomenon" in droplets of 22% $P(S_5M_6)$ at 95 °C. (a) A droplet observed without crossed polarizers (×10); (b) undisturbed droplet observed with crossed polarizers (×41); (c) the disturbed droplet between crossed polarizers (×41).

Table II
Reactivity Constants

n	r_1	r_2
2	<0.1	0.5
5	4.0	0.5
11	3.0	1.4

The data indicate that the polymer radicals ending with the spiropyran unit with the longer spacers react more actively with their own monomers than with the mesogenic monomer, which can be explained by the strong tendency of spiropyrans to associate in solution.[15] This effect is not observed for the monomer with the short spacer (S_2) probably due to significant steric hindrance. The composition of the copolymers is given as percentage of S; for example, 22% $P(S_5M_6)$ means that the copolymer contains 22 molar % of S.

B. Visual Microscopic Observations. Observation with a polarizing microscope revealed that the clearing points of the copolymers are lower the higher the content of spiropyran units in the copolymer, going down from 129 °C (liquid crystal homopolymer $P(M_6)$) (Table III). The copolymers with a high content of spiropyran do not give a mesophase at all. The most remarkable feature of the isotropic films formed above the clearing point by the copolymers with low concentration of spiropyran is their very strong transient translucence between cross polarizers when they are squeezed between two glass slides or even lightly touched with the tip of a spatula.

The liquid crystal homopolymer, which does not contain spiropyran, does not exhibit this effect.

Usually such instant birefringence during mechanical disturbance is considered as an indication of homeotropic (orthogonal to solid surface) orientation of mesogenic molecules.[16] Therefore, one could conclude that instead of nematic–isotropic transition at the clearing point we observe a transformation of orientation of mesogenic groups of macromolecules from parallel to perpendicular to the surface.

To check this, we treated the glass surface with cremophor[17] and nylon[18] which promote the planar orientation of liquid crystals and with 1-dodecanol[17] for the homeotropic alignment. We found no effect of the surface on the "sparkling phenomenon". A decisive experiment was performed with droplets of the copolymers in an isotropic phase having a relatively small area connected with a surface (Figure 3). For these droplets again even a very gentle touch gave remarkable sparkling, though in this case the effect of the surface must be insignificant. This suggests that the transient brightening is caused by at least partial restoration of liquid crystalline order, induced by mechanical disturbance.

Table III
Transition Temperatures (°C)

copolymer (molar % of S)	glass transition	clearing pt	disappearance of dynamic birefring.	range of dynamic birefring.
$P(M_6)$	33	129[a]	129	0
$P(S_2M_6)$ (16%)	55	92	106	14
$P(S_2M_6)$ (29%)	95	no	123	>18
$P(S_5M_6)$ (10%)	39	112[a]	127	15
$P(S_5M_6)$ (22%)	50	86[a]	114	28
$P(S_5M_6)$ (46%)	70	no	no	0
$P(S_{11}M_6)$ (9%)	40	85[a]	101	16
$P(S_{11}M_6)$ (28%)	53	no	106	>20

[a] Measured by DSC.

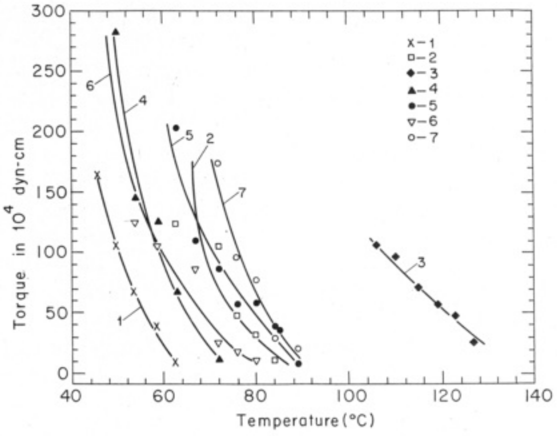

Figure 4. Dependence of the torque on temperature: (1) $P(M_6)$; (2) 16% $P(S_2M_6)$; (3) 29% $P(S_2M_6)$; (4) 10% $P(S_5M_6)$; (5) 22% $P(S_5M_6)$; (6) 9% $P(S_{11}M_6)$; (7) 28% $P(S_{11}M_6)$.

C. Rheooptical Measurements. The torque required to rotate the upper disk of the rheometer was measured as a function of the polymer melt temperature (Figure 4). The torques of both the liquid crystalline homopolymer

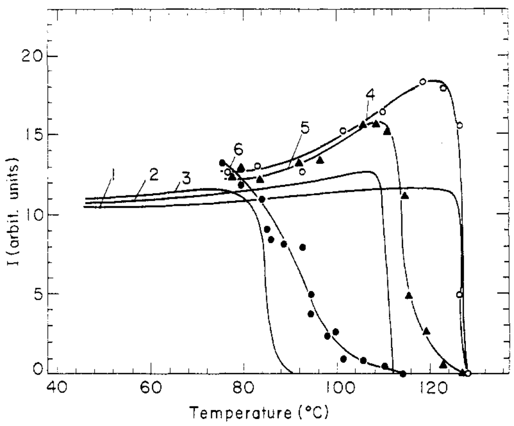

Figure 5. Transmitted polarized light intensities (I) vs temperature. "Static" regime: (1) $P(M_6)$; (2) 10% $P(S_5M_6)$; (3) 22% $P(S_5M_6)$. (4–6) as 1–3 but under "dynamic" regime.

and copolymers decline sharply above the glass transition points. In this region the flow character of the fluids is non-Newtonian and very complex. Therefore, the data were not amenable to conversion to viscosity units.[19] However, since the viscosity is a monotonically increasing function of the torque,[19] we can conclude that the viscosity of the copolymer is much higher than that of the homopolymer at the same temperature. The viscosity of $P(S_5M_6)$ and $P(S_{11}M_6)$ with approximately the same content of spiropyran is very similar, while $P(S_2M_6)$ copolymers give much higher viscosity. A drastic increase of viscosity upon the introduction of a relatively small portion of the thermochromic groups indicates a very substantial effect of these groups on the interaction between macromolecules. As we have shown earlier,[20] spiropyran–merocyanine conversion in melts of low molecular weight spiropyran containing mesogenic groups brings about contraction of the fluid, due to aggregation of the merocyanine formed in the melt. One may assume that in the case of the copolymers the interaction of the merocyanine groups, formed on heating, gives rise to the aggregation of macromolecules in a network with high viscosity. Apparently $P(S_2M_6)$, where the spiropyran groups are separated from the backbone by short spacers, give a much more dense network than $P(S_5M_6)$ and $P(S_{11}M_6)$, resulting in the higher viscosity of the melt.

The polarized light intensity–temperature relationships for the liquid crystalline homopolymer and the $P(S_5M_6)$ copolymers are shown in Figure 5 as an example. The clearing points are indicated by a sharp fall of "static" birefringence. In the dynamic regime, the transmitted light intensity reaches a maximum near the clearing points. This can be explained by a decrease of the number of defects with viscosity decrease and domain growth induced by shear.[21] At low temperatures, the viscosity becomes so high that it was impossible to perform the shearing measurements. The viscosity increases also with the spiropyran content; for example, 46% $P(S_5M_6)$ forms a red, tar-like material on melting, which gives neither mesomorphic nor dynamic birefringence.

The dynamic birefringence of $P(M_6)$ disappears at the clearing point almost as sharply as does the static one, while that of the copolymers extends much beyond the clearing points, though it declines gradually after that point. The range between the clearing point and the temperature where the dynamic birefringence is not observed anymore increases with the spiropyran content in the copolymers (Table III). In other words, even though the spiropyran–merocyanine groups disturb the mesophase thermal stability, they promote the dynamic restoration of an ephemeral order in the isotropic phase.

D. DSC Measurements. The DSC measurements give endothermic peaks at temperatures that coincide with the microscopic observation of the clearing points. This confirms that the static birefringence disappearance relates to the mesophase–isotropic phase transition.

E. Electric Field Effect. Films of the copolymers casted onto a glass slide with interdigital electrodes can be aligned in an electrostatic field (>0.5 kV/mm) below the clearing point. Above this temperature, the alignment disappears, which proves again the isotropic character of the melt. The order parameter for 22% $P(S_5M_6)$, estimated spectrophotometrically as described earlier,[13] was 0.3.

F. Electronic Absorption Spectra. The electronic absorption spectra of films of $P(S_2M_6)$ and $P(S_5M_6)$ with low spiropyran content (Figure 6a,b) show an increase of visible absorption with rising temperature. The transition from amorphous to liquid crystalline phase is accompanied by formation of a broad plateau in the range 460–585 nm. The optical density in this range does not change with temperature up to the clearing point. The transition from mesophase to isotropic phase coincides with the appearance of an absorption band with a $\lambda(\max) = 585$ nm (a correction for the light scattered by the mesophase was made when the spectra were plotted). The band vanishes reversibly on cooling.

Comparison of the above spectra with the spectral data obtained by us earlier[1,6,22] brings us to the conclusion that the broad absorption in the range 460–585 nm is connected with association of merocyanine molecules in molecular stacks (probably very short ones, mostly dimers). The absorption of these associates overlaps apparently with the absorption of isolated spiropyran ($\lambda(\max) = 370$ nm) and merocyanine ($\lambda(\max) = 585$ nm) side groups. This confirms our theory that the elevated viscosity of the copolymer melt with high spiropyran content may be explained by such association which results in formation of a network. Apparently, the number of the cross-linked merocyanine groups does not change markedly with the temperature below the clearing point. The reversible absorption band with $\lambda(\max)$ at 585 nm, characteristic of nonaggregated merocyanine groups, becomes pronounced above the clearing point when formation of the network is completed and restricted segmental mobility hinders further merocyanine association.

The spectral changes occurring with films of $P(S_{11}M_6)$ are quite different (Figure 6c). Heating of an original amorphous film above the clearing point leads to appearance of an absorption spectra with two distinct bands, (λ at 590 and 520 nm), which according to our assignment correspond to isolated and associated (apparently dimers) merocyanine groups. Cooling of the melt brings about widening and growth of the merocyanine absorption bands with a pronounced jump in optical density accompanying the transition from isotropic to mesophase.

The spectral changes are reversible and seem to be opposite to those observed for $P(S_2M_6)$ and $P(S_5M_6)$. A possible explanation of these changes may be based on the assumption that interactions between merocyanine and mesogenic side groups become stronger on cooling of the melt. The interactions bring about the widening and growth of the absorption bands. The optical density jump below the clearing point might be explained by assuming that the parallel arrangement of side groups in the mesophase is favorable for these interactions.

In order to stimulate the merocyanine association at room temperature, we swelled a 22% $P(S_5M_6)$ film in

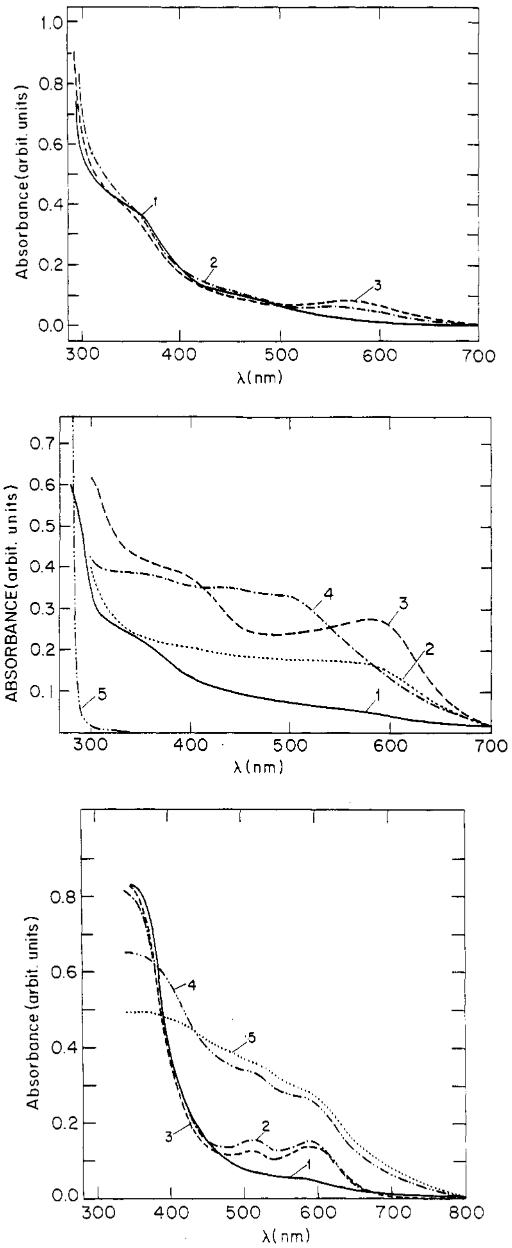

Figure 6. Absorption spectra of polymer films. (a, top) 16% $P(S_2M_6)$: (1) amorphous film (26 °C); (2) 60 °C; (3) 95 °C. (b, middle) 22% $P(S_5M_6)$: (1) amorphous film (26 °C); (2) 82 °C; (3) 95 °C; (4) swelled film at room temperature (26 °C); (5) $P(M_6)$ (26 °C). (c, bottom) 9% $P(S_{11}M_6)$: (1) amorphous film (26 °C); (2) 90 °C; (3) 120 °C; (4) 75 °C; (5) cooled mesophase (32 °C).

chloroform. The film was previously heated in order to form a birefringent texture. After swelling and drying, the static birefringence disappeared but a very distinct dynamic birefringence was observed even at room temperature. The film acquired a high viscosity and a deep red color with absorption plateau from 380 to 520 nm (Figure 6b). At longer wavelengths, the absorption goes down, which indicates that the contribution of isolated merocyanine moieties to the absorption is negligible. This supports the assumption that merocyanine association leads to dynamical birefringence.

Conclusion

To explain the results, let us consider the effect of the liquid crystal–isotropic phase transition on the main chain conformation. According to Kuzma,[23] in the liquid crystal phase, the parallel arrangement of mesogenic groups effects the conformation of the macromolecular backbone. Above the clearing point, this effect of the mesogenic side groups becomes insignificant and the macromolecules accept a coil conformation, which provides maximum entropy, and is in general different from the conformation in the mesophase. Formation of the transient liquid crystalline order by shearing or other mechanical perturbation results not only in restoration of the parallel arrangement of the mesogenic groups but in a certain reconstruction of the main chain coils, causing a decrease in entropy.

Presumably, formation of the network favors the preservation by macromolecules of the conformation acquired in the mesophase even above the clearing point due to a more rigid structure. This makes the dynamic ordering easier.

Earlier Finkelmann et al[24] observed the occurrence of birefringence, above the clearing point, on stretching side chain liquid crystal polysiloxane elastomers. This observation is consistent with our conclusion that dynamic birefringence stems from macromolecular aggregation.

Acknowledgment. Support from the Minerva Foundation, FRG, the US–Israel Binational Science Foundation, and the US Army European Research Office (Contract DAJA45-C-0030) is gratefully acknowledged.

Registry No. S_2, 110419-14-2; S_5, 108764-08-5; S_{11}, 110419-15-3; M_6, 83847-14-7; $P(M_6)$ (homopolymer), 83847-15-8; $P(S_2M_6)$ (copolymer), 110433-30-2; $P(S_5M_6)$ (copolymer), 108764-09-6; $P(S_{11}M_6)$ (copolymer), 110433-31-3.

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