Crystallization of Poly(spiropyran methacrylate) with Cooperative Spiropyran–Merocyanine Conversion

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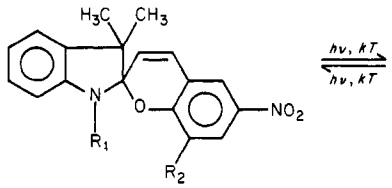
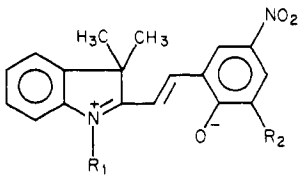
ABSTRACT: Atactic poly(spiropyran methacrylate) was prepared by free radical polymerization. Amorphous polymer, with negligible merocyanine content, separates on rapid precipitation. Crystalline polymer is obtained on slow precipitation or on swelling the amorphous polymer. Increased crystallinity is associated with increased merocyanine content. Polymers of up to 40% crystallinity were obtained. Visible absorption spectra of the polymer indicate that merocyanine side groups in the crystals interact similarly to cyanine dyes in H aggregates.

Introduction

Spiropyrans are the best known organic compounds with photochromic, thermochromic, and solvatochromic properties: they are converted reversibly to merocyanine dyes on irradiation with suitable light, on heating, or with increasing polarity of solvent:[1]



A (spiropyran)



B (merocyanine)

We showed earlier[2-5] that strong interactions arise between the solute molecules upon irradiation of spiropyrans dissolved in aliphatic hydrocarbons. The colored merocyanine molecules (B) interact with spiropyran molecules (A) to give A_nB (n = 1, 2) complexes. The A_2B absorption bands in the visible region are shifted bathochromically with respect to the AB bands. The A_2B complexes form highly dipolar microcrystals having a molecular stack structure. These microcrystals are coated with amorphous material composed of AB complexes, giving rise to a colloidal suspension of globules of about 0.1–0.4-μm diameter. The microcrystalline nuclei of these globules are responsible for their optical and electrical anisotropy. Further, the large dipole moment of the globules (>10^4 D) results in remarkable behavior of the dispersions in a constant electric field: at a field strength greater than 5 kV/cm the globules form string-of-bead structures which look macroscopically like colored threads aligned along the electric lines of force.

The ability of A_nB complexes to organize spontaneously into quasi-crystalline globules (crystalline core and amorphous envelope) is determined by the merocyanine moieties in the complexes. Many cyanine dyes are known to form in solution tightly bound giant molecular aggregates, the so-called Scheibe aggregates (considered to have a tilted deck-of-cards,[6] brickwork,[7] or herring-bone[8] structure). Two types of Scheibe aggregates are distinguished, usually by their visible absorption spectra: H aggregates, with their absorption band blue-shifted relative to that of the nonaggregate dye, and J aggregates, with a red-shifted band. In H aggregates the angle of the tilt of the dye molecules in a stack is greater than 54° and in J aggregates it is less than 54°.[9,10]

The tendency to organization into quasi-crystals is not very sensitive to the nature of substitutents R_1 and R_2. We find that in particular the spiropyran with methacrylate [$C_2H_4OCOC(CH_3)=CH_2$] for R_1 forms a quasi-crystalline dispersion on illumination.[4] One may expect that polymethacrylate molecules with spiropyran side groups would also exhibit a tendency to some ordering, though not necessarily of the quasi-crystalline type.

Copolymerization of monomers containing spiropyran groups with other vinyl monomers has been described earlier.[11] However, to our knowledge the homopolymer has never been studied. Here we report on the crystallization of poly(spiropyran methacrylate) prepared by free radical polymerization. As will be shown, during the crystallization process the spiropyran moieties open to merocyanine ester groups.

Experimental Section

The monomer SMA, 1-[β-(methacryloxy)ethyl]-3,3′-dimethyl-6-nitrospiro(indoline-2,2′-[2*H*-1]benzopyran), having R_1 = $C_2H_4OCOC(CH_3)=CH_2$ and R_2 = H, was prepared as described earlier.[12] It was polymerized in 15% methyltetrahydrofuran (MTHF) solution with 1% 2,2′-azobis(isobutyronitrile) at temperatures from 40 to 80 °C under vacuum. The polymer (PSMA) was precipitated by methanol, purified by repricipitation, and dried under vacuum at room temperature. The yield of the polymer was nearly 40%. The yield and crystallizability did not depend substantially on polymerization temperature. The 1:4 copolymer of SMA with methyl methacrylate (MMA) was prepared and purified by a similar method.

The molecular weight was estimated by ultracentrifugation (Spinco-Beckman Model E) and vapor pressure osmometry (Hitachi Perkin-Elmer LL5). This gave $M_w \sim 30\,000$ for the polymer obtained at 50 °C. Both the polymer and the copolymer were photochromic, and this hindered deterimination of M_w by light scatering. A very rough estimation of the M_w distribution showed a rather high content of the fraction with $M_w < 15\,000$.

T_g lies near 150 °C and did not changed significantly with degree of crystallinity.

Results and Discussion

A. Crystallization. The polymer precipitated with methanol from MTHF solution was an amorphous white powder and gave a diffuse X-ray diffraction pattern.

Crystallization of the polymer was carried out by very slow evaporation of the MTHF solution at room temperature. Improvement of crystallinity was achieved by subsequent swelling of the polymer in a small amount of MTHF (Figure 1). The resulting violet, polycrystalline precipitate exhibits birefringence. It is very heat stable and does not melt until the onset of decomposition at 250 °C. The powder X-ray diffraction reflections of the polymer are given in Table I. The degree of crystallinity estimated from reflection densities (Figure 2) is 40–50%. Indexing as prescribed in ref 13 gives a monoclinic unit cell with the following cell dimensions: a = 9.75 Å b =

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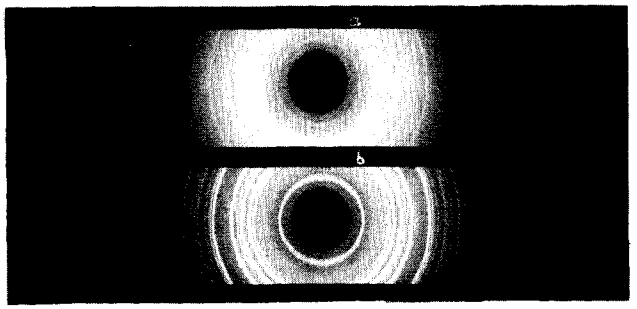

Figure 1. Debye-Scherrer patterns of PSMA: (a) after fast evaporation of solvent; (b) after swelling.

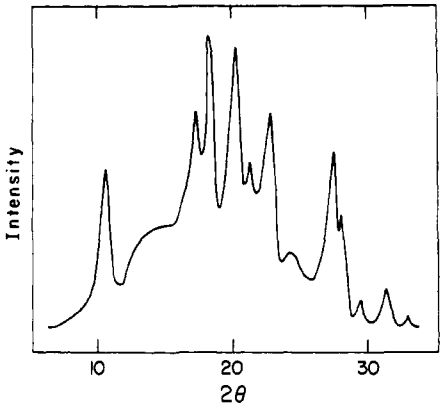

Figure 2. X-ray intensity curve of crystalline PSMA.

Table I
X-ray Powder Diffraction Reflections of Crystals[a]

material	interplanar spacings, D, Å
SMA, yellowish	10.58 (m), 8.83 (w), 7.93 (w), 7.13 (m), 6.88 (w), 6.03 (w), 5.62 (w), 5.26 (s), 5.05 (w), 4.74 (m), 4.41 (w), 4.28 (w), 4.08 (w), 3.81 (w), 3.66 (w), 3.48 (w), 3.35 (w), 3.16 (m)
SMA, violet	10.60 (m), 8.90 (w), 8.30 (w)*, 7.94 (w), 7.08 (m), 6.01 (w), 5.63 (w), 5.29 (s), 5.07 (w), 4.73 (s)**, 4.36 (m)**, 4.11 (w), 3.85 (m)**, 3.65 (w), 3.45 (w), 3.35 (w), 3.23 (w)*, 3.16 (m), 3.10 (w)*, 3.02 (w)*
PSMA, violet	8.32 (m), 5.12 (w), 4.79 (s), 4.35 (s), 4.15 (w), 3.86 (s), 3.21 (m), 3.13 (w), 3.00 (w)

[a] Relative intensities: s = strong, m = medium, w = weak; reflections with $D < 3.00$ Å are not listed in the table. See text for meaning of asterisks.

16.58 Å, c = 5.47 Å, and β = 101° (Table II).

The violet color of the polymer crystals indicates that the side groups are, at least in part, in the merocyanine form or in the form of A_nB complexes. In part C we show that, in fact, in the crystals the side groups are all in the merocyanine form. One can suggest from the X-ray data that the crystals have a tilted layered structure, as do many other cyanine crystals.[14]

For comparison, the SMA monomer was crystallized from benzene and MTHF solutions as yellowish and violet crystals, respectively (the polymer is practically insoluble in benzene). The interplanar spacings of the monomer crystals are given in Table I. The yellowish (obviously spiropyran) crystals have spacings quite different from those of the polymer crystals. The diffraction pattern of the violet monomer crystals includes all reflections of the yellowish (spiropyran) crystals and additional reflections, marked with single stars in Table I. The relative intensities of a few other reflections (marked with two stars) are appreciably higher for the violet than for the yellow crystals, indicating that they hide beneath additional unresolved reflections. Obviously the violet precipitate contains small amounts of a new crystalline phase, characterized by the starred refections, apart from the spiropyran crystallites. A comparison with the polymer crystal pattern shows that the latter contains reflections that coincide with reflections of the violet monomer crystals but none that coincide with the reflections that belong to the pure spiropyran crystals. This implies that the violet monomer crystals, which, as we show below, have the photochromic groups in the merocyanine form, have the same lattice as the polymer crystals; this suggests that the packing in both crystals is dominated by the merocyanine groups and is not much affected by the presence or absence of the fairly rigid polymer backbone. The only feasible location of the polymer chains that would not lead to deterioration of the lattice is interlammelar space, and 79°

Table II
Observed and Calculated Interplanar Spacings of the PSMA Crystals

2θ	D	h	k	l	2θ	D	h	k	l
10.64	8.309	observed			41.63	2.168	observed		
10.67	8.283	1	1	0	41.57	2.171	2	0	2
10.67	8.287	0	2	0	41.63	2.168	4	3	−1
17.31	5.119	observed			41.66	2.166	0	7	1
17.32	5.115	1	0	−1	44.53	2.033	observed		
17.35	5.107	0	1	1	44.53	2.033	3	6	−1
18.52	4.788	observed			44.53	2.033	2	7	−1
18.54	4.781	2	0	0	47.31	1.920	observed		
18.53	4.784	1	3	0	47.28	1.921	5	0	−1
20.39	4.351	observed			47.28	1.921	4	5	−1
20.44	4.341	1	0	1	47.34	1.919	2	7	1
20.39	4.353	1	2	−1	47.30	1.920	1	8	−1
21.42	4.145	observed			51.08	1.787	observed		
21.44	4.141	2	2	0	51.03	1.788	4	4	−2
21.43	4.144	0	4	0	51.08	1.787	1	7	−2
23.04	3.856	observed			54.96	1.669	observed		
23.05	3.856	2	1	−1	54.94	1.670	3	2	−3
23.08	3.850	0	3	1	54.99	1.668	1	4	−3
27.75	3.213	observed			54.92	1.670	4	7	−1
27.75	3.212	2	1	1	54.93	1.670	2	9	−1
28.50	3.130	observed			55.98	1.641	observed		
28.49	3.130	3	1	0	55.95	1.642	5	3	−2
28.48	3.131	2	4	0	55.97	1.642	3	7	−2
28.47	3.132	1	5	0	56.03	1.640	0	8	2
29.72	3.003	observed			58.59	1.574	observed		
29.73	3.003	3	0	−1	58.61	1.574	1	4	3
31.72	2.818	observed			58.59	1.574	5	4	1
31.66	2.823	3	2	−1	58.58	1.575	0	5	3
31.74	2.817	2	3	1	64.11	1.451	observed		
31.70	2.821	0	5	1	64.09	1.452	5	0	−3
32.40	2.761	observed			64.13	1.451	6	5	−1
32.40	2.761	3	3	0	64.13	1.451	3	6	−3
32.38	2.762	0	6	0	64.12	1.451	4	9	−1
33.35	2.685	observed			64.12	1.451	3	10	−1
33.36	2.684	0	0	2	66.21	1.410	observed		
33.32	2.687	1	1	−2	66.22	1.410	0	10	2
35.30	2.541	observed			68.49	1.369	observed		
35.35	2.537	3	0	1	68.46	1.369	7	2	−1
35.26	2.543	2	5	−1	68.51	1.368	1	8	−3
36.90	2.434	observed			68.53	1.368	4	9	1
36.94	2.432	3	4	−1	68.49	1.369	2	11	1
36.95	2.431	1	6	−1	71.47	1.319	observed		
37.60	2.390	observed			71.44	1.319	7	1	−2
37.60	2.391	4	0	0	71.45	1.319	6	6	−2
37.57	2.392	2	6	0	71.51	1.318	1	11	−2
39.15	2.299	observed			77.67	1.228	observed		
39.19	2.297	4	2	0	77.73	1.228	6	5	−3
39.18	2.298	3	5	0	77.69	1.228	0	12	2
39.16	2.298	1	7	0	81.12	1.185	observed		
40.03	2.251	observed			81.15	1.184	5	3	−4
40.02	2.251	1	3	2	81.18	1.184	0	14	0
39.99	2.253	0	4	2					

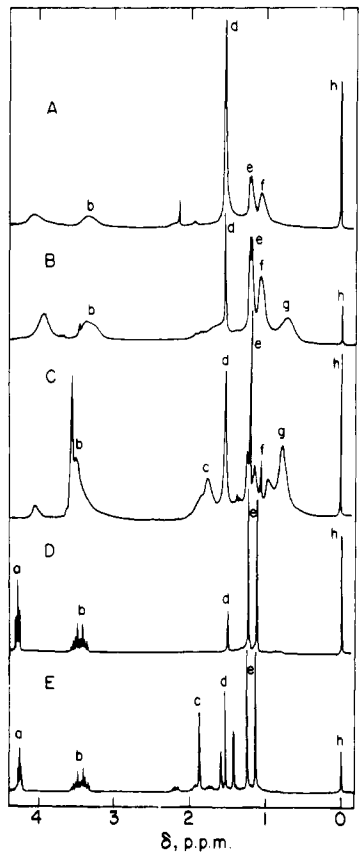

Figure 3. 270-MHz NMR spectra in chloroform: (A) poly(spiropyran acrylate); (B) PSMA; (C) 1:4 copolymer of MMA and SMA; (D) spiropyran acrylate monomer; (E) SMA monomer. a, $=CH_2$ group; b, C_2H_4 group; c and g, α-CH_3 group; d and f, CH_3 groups of spiropyran associated in dimers; e, CH_3 groups of nonassociated spiropyran; h, Me_4Si.

is probably the tilt of the long axis of the merocyanine moieties to the line connecting the centers of these groups. The MMA–SMA copolymer was precipitated on slow evaporation from MTHF in completely amorphous form.

B. Characterization of the Polymer by NMR. Polymethacrylates prepared by free radical polymerization at elevated temperatures are atactic as a rule.[16]

In order to estimate the stereoregularity of PSMA we attempted to convert it to poly(methyl methacrylate) by hydrolysis and subsequent methylation in accordance with ref 15. However, hydrolysis in concentrated H_2SO_4 at 50 °C for 24 h under vacuum did not go to completion and a tar was formed.

An indication of whether or not PSMA is stereoregular was provided by a comparison of the NMR spectrum of the polymer with spectra of poly(spiropyran acrylate) and corresponding monomers. (Synthesis of poly(spiropyran acrylate) will be described elsewhere.) The 270-MHz spectra in chloroform are given in Figure 3. The tendency of spiropyran molecules to give A_2 dimers in solution[5] leads to complication of the NMR spectra of the monomers. Similar A···A interaction is presumably facile in the polymer. Therefore we did not assign some peaks in the spectra. However, the comparison indicates unambiguously that the broad signal with a maximum at 0.78 ppm has to be assigned to α-CH_3 protons. One can see the same peak in the spectrum of the SMA–MMA copolymer. This indicates that the peak belongs to nonstereoregular macromolecules. The broadening of the peak should be ascribed to the overlap of proton signals from α-CH_3 groups of different tacticity, characterizing an atactic polymer with

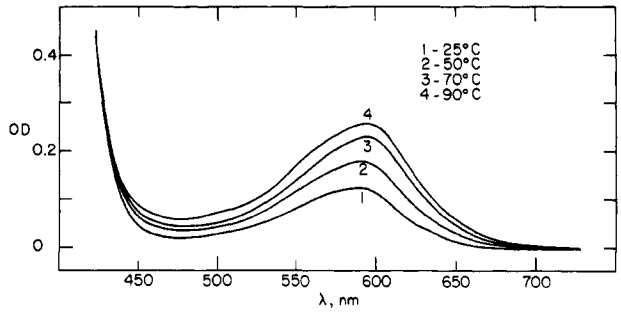

Figure 4. Absorption spectra of a 0.2 M SMA solution in MTHF at various temperatures. Optical path 2 mm.

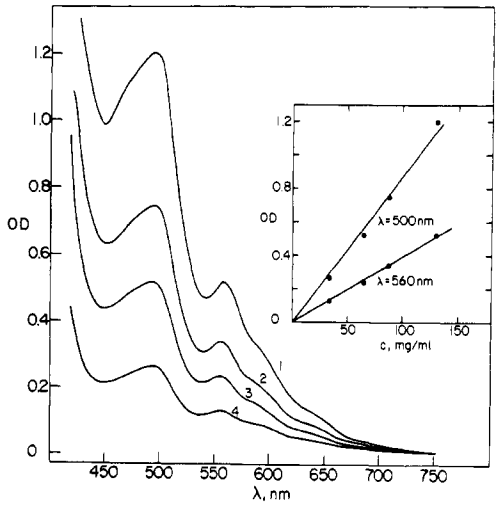

Figure 5. Absorption spectra of PSMA solution in MTHF. Concentration of PSMA per monomer unit: (1) 0.2; (2) 0.135; (3) 0.1; (4) 0.05 M. Optical path 2 mm. Top right, optical density at 500 and 560 nm as a function of concentration of PSMA.

aromatic ester groups.[16] Thus the PSMA main chains are not stereoregular and tend to be unordered in polymer crystals.

C. Visible Absorption Spectra of SMA and PSMA. Visible absorption spectra of a 0.2 M SMA monomer solution in MTHF at different temperatures are shown in Figure 4. The spectra have a maximum at ~600 nm, which belongs apparently either to the merocyanine molecules or to A_2B complexes.[17,18] The concentration of the solution is the same as the initial concentration of the monomer on polymerization. Taking into account that the molar extinction coefficients of the merocyanine form and A_2B are in the range 10^4–10^5 cm^{-1} M^{-1} (see ref, 1, 2, and 18), we can estimate the equilibrium concentration of the monomer in the open merocyanine form at the temperatures of polymerization. It is 10^3–10^4 times less than the concentration of the spiropyran monomer. This means that practically only the monomer in the spiropyran form participates in polymerization because the reactivity of methacrylates does not depend strongly on the nature of the ester groups. For example, MMA and SMA have comparable reactivities.[18]

The spectrum of the polymer solution in MTHF (Figure 5) differs markedly from the spectrum of SMA. It has two absorption maxima, at ~500 and ~560 nm, and only barely visible shoulders near 600 and 640 nm. Solutions of PSMA obey Beer's law (Figure 5) up to concentrations of the polymer close to saturation, indicating that intermolecular complexation and aggregation of macromolecules are insignificant.

Assignment of the absorption band with λ_{max} 500 nm is rather obvious: our previous results[3,5,17] indicate that the

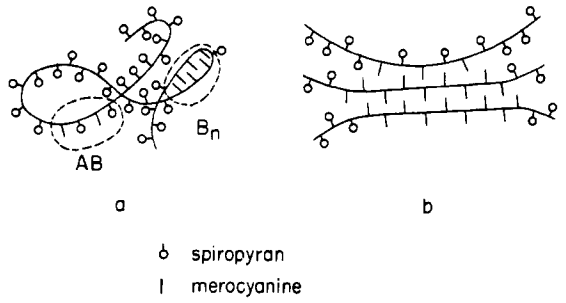

Figure 6. Scheme of interaction of macromolecule side groups: (a) in solution; (b) on crystallization.

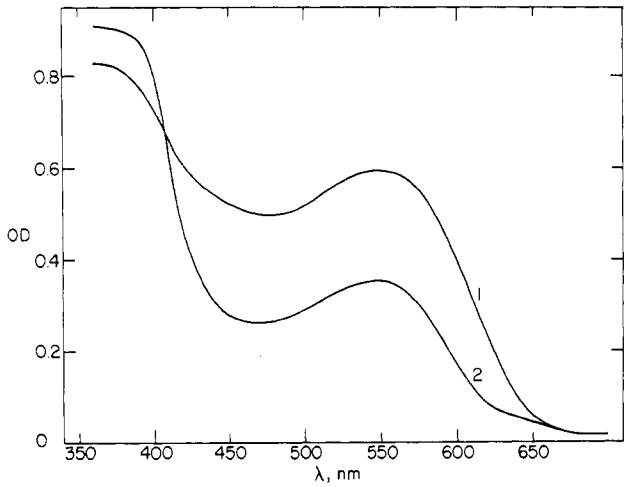

Figure 7. Diffuse reflectance spectra of crystalline powders: (1) polymer; (2) monomer.

band belongs to AB complexes. Presumably these complexes are formed by two adjacent side groups on a polymer chain (Figure 6a). As mentioned above, the shoulder at 600 nm belongs to the side groups in either form B or A_2B.

The band with λ_{max} 560 nm is the only band in the visible region which is found in the diffuse reflectance spectra of the polymer and monomer powders after crystallization from MTHF solution (Figure 7). The bands with λ_{max} 500 and 600 nm are not observed at all, although they are the main absorption bands of PSMA and SMA solutions, respectively.

It is unlikely that the band with λ_{max} 560 nm belongs to A_nB complexes with $n > 2$: formation of such complexes by side groups of an isolated macromolecule in solution is improbable. To explain the results we suggest that the band with λ_{max} 560 nm arises from B_n stacks of merocyanine side groups (in the polymer) or merocyanine molecules (in the monomer).

In solution these stacks are presumably formed in loops of macromolecules (Figure 6a) whereas in crystals they form a three-dimensional lattice (Figure 6b). The hypsochromic shift relative to the absorption of B or A_2B (λ_{max} 600 nm) indicates that the B_n stacks are of the H type, with an angle of tilt greater than 54°. The crystallographic data (part A) give an angle of 79°, which is compatible with our assumption. The type of stacking most probable in the polymer is the H type since the adjacent merocyanine molecular dipoles in a stack are directed oppositely (Figure 6), which makes a tilt of more than 54° energetically favorable.[4]

The molar extinction coefficient of AB in solution was determined earlier[2] (3×10^4 cm^{-1} M^{-1}). Using this value, we estimate that the concentration of AB in the polymer solution is 10^3 times less than the concentration of spiropyran side groups. Similarly the concentration of B_n stacks in solution (λ_{max} 560 nm) is very small. This can be explained if we take into account that the macromolecules do not interact with each other in solution and that intramolecular stacking is possible only in loops of favorable geometry. We cannot now make any unambiguous assigment of the slight absorption shoulder at 640 nm which could belong to the dimer B_2.

Mechanism of Crystallization. There are a number of publications on ordering of atactic polymers by virtue of side-group interaction. The type of ordering varies from the so-called lateral order ("chain-to-chain spacing")[19,20] to that found in liquid-crystalline polymers (see, for example, ref 21 and 22 and references therein). Only a few publications are concerned with intrinsic three-dimensional crystals[23-25]

The most relevant results are those on the crystallization of poly[(acryloyloxy)benzoic acid] and poly[(methacryloyloxy)benzoic acid], reported in ref 23. Hydrogen bonding between side groups—benzoic acid—is mainly responsible for the formation of the crystalline structure. The crystals also have a lamellar structure, with side groups tilted with respect to the lamellar plane. Probably only the lamellar structures allow the nonregular main chain to be arranged in a crystalline lattice. The structures of the polymer and monomer crystals reported in ref 23 are different, indicating, presumably, that the rather rigid attachment of the side groups to the main chain affects the crystal lattice.

The identity of the crystal structures of SMA and PSMA is apparently determined by the C_2H_4 spacer and hence by the flexible linkage between the merocyanine moiety and the main chain. The importance of such decoupling for odering of liquid-crystalline polymers with mesogenic side groups was demonstrated by Ringsdorf and co-workers.[26,27]

The most remarkable feature of the crystallization is the cooperation of this process with the chemical reaction spiropyran → merocyanine. In polymer solution, aggregation of polymer molecules was not observed even at concentrations close to saturation, and the concentration of merocyanine side groups is extremely low. In accordance with the conclusion made in part C, the crystallization is dominated by interaction between merocyanine side groups of different macromolecules. The degree of crystallinity which was achieved in the polymer indicates that more than 40% of the side groups were in the merocyanine form and were involved in the intermolecular interaction.

One can envisage the process as follows: Precipitation of the polymer enhances the probability of *inter*molecular stacking of merocyanine groups and formation of three-dimensional crystalline domains. The segments of polymer chains adjacent to the domains are thus probably brought closer together. This and the increase of the polarity in the surroundings of the domains promote further solvatochromic spiropyran → merocyanine conversion and hence further ordering. Evidently the ordering can proceed in the precipitate only in the presence of solvent when segmental movement is possible. Fast evaporation of the solvent leads to a lowering of the degree of crystallinity and swelling substantially enhances it (Figure 1).

The peculiarity of the process under consideration is the mutual stimulation of the chemical reaction and crystallization. Here, as well as in quasi-crystals, spiropyrans reveal an astonishing capability for self-organization.

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Effect of Strain Energy in the Theory of Polymer Crystallization

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ABSTRACT: A theory is developed to establish the basic relationship between minimum strain energy and an equilibrium crystal shape in strained states. Changes in crystal shape have been investigated as a major phenomenon in macromolecular crystals. Many familiar observations, such as the thickening of lamellae and extended chain fibers during annealing and stretching, respectively, and the thinning of lamellar crystals under pressure, can be explained adequately by the theory in terms of a single parameter—the strain energy. With irreversible thermodynamics, the nonequilibrium annealing behavior is analyzed with the same strain energy function as the driving force. The theoretical prediction is in good agreement with experimental data and the existing theory of Sanchez, Colson, and Eby which is based on a surface free energy consideration.

Introduction

The thickening of lamellae during annealing and the lengthening of fibrils during stretching are well established in the literature[1,2] and illustrate the important effect of strain energy in the formation of macromolecular crystals. It is generally recognized that polymer crystals are thermodynamically metastable and the crystallization process is controlled by nucleation theory[3,4] under the postulate of local equilibrium. Annealing and stretching may be considered as two opposite irreversible processes.[5,6] The former moves toward the lowest energy state of a crystal and the latter away from it. Energy variations during deformation as a function of crystal shape—the fundamental part of the problem—have not been determined because the role of strain energy in the theoretical treatment of crystallization is not well established.[7] The main objective of this work is to explain the change in shape of polymer crystals in terms of strain energies applied to or released from the system. A functional relationship between the minimum strain energy and the equilibrium shape of a strained crystal is derived for an equilibrium morphology. Assumptions concerning the crystal morphology[8-11] and detailed descriptions of the strain energy are avoided at the present time to preserve the generality of the theory. The fundamental relation between strain energy and crystal shape is applied to interpret various stress effects on crystallization in polymers, such as the crystallization induced by stretching, stress relief by annealing, and the effect of pressure. The theoretical interpretation is then compared with experimental observations. As an example, the strain energy of ultraoriented high-density polyethylene fibers[12] is estimated and the mechanical and thermal implications are discussed.

In the search for a unified approach to the equilibrium and nonequilibrium changes in crystal shape, the time dependence of crystal thickening during annealing was analyzed as an irreversible process driven by the strain energy gradient instead of a surface free energy gradient proposed by Sanchez, Colson, and Eby.[5] The present theory is then compared with their theory and experimental crystal thickening data.

Theoretical Development

The free energy of crystallization from the melt can be written as

$$\Delta G = G_{\text{crystal}} - G_{\text{melt}} \tag{1}$$

The free enthalpy of a crystal consists of bulk and surface contributions

$$G_{\text{crystal}} = G_{\text{bulk}} + \sum_i \gamma_i A_i \tag{2}$$

where γ_i represents the surface free energy per unit area

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