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Self-Assembling of Spiropyran Polymers by Zipper Crystallization

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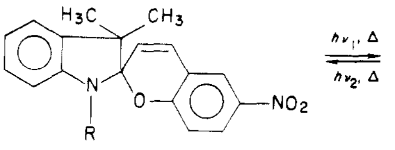
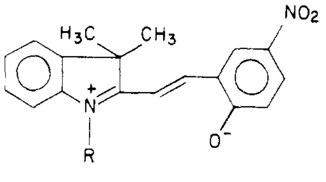
ABSTRACT: The early stages of crystallization of atactic methacrylate polymers with spiropyran side groups were studied by preparation of thin films from solution. The number of crystallization seeds formed on the films and the character of their order give information on the mechanism of crystallization associated with spiropyran → merocyanine conversion and the formation of the merocyanine molecular stacks.

Earlier we have reported a new type of crystallization of atactic vinyl polymers with spiropyran side groups by swelling of the amorphous polymers in THF or another moderately polar solvent.[1-3] The crystallization of the polymers goes cooperatively with the spiropyran–merocyanine conversion



A (spiropyran)



B (merocyanine)

The conversion is reversible in solution, and the equilibrium is shifted to the right with increasing solvent polarity. Swelling of a polymer results in the incorporation of the merocyanine side groups into intermolecular stacks with alternate antiparallel alignment of their molecular axes. This inhibits the merocyanine–spiropyran back-reaction. Further development of this process brings about formation of crystalline domains, which in turn promotes further solvatochromic spiropyran–merocyanine conversion and hence ordering of the macromolecules. The important feature of this process is the mutual stimulation of the chemical reaction and crystallization. The crystallization proceeds only in the presence of solvent, which enables segmental movement. The process was not observed with monomers. The crystallization is a "dark" process and cannot be induced by irradiation, which results in the fast photochromic process of merocyanine formation and irregular stacking.

We believed that a high degree of crystallinity of the polymers (up to 40%) was achieved because the cooperative spiropyran–merocyanine conversion occurs step-by-step along the polymer chains and called this process "zipper crystallization".

Comparison of polymers with main chains of different flexibility and with spiropyran side groups connected to the main chains by spacers of different length led us to the conclusion that both enhancement of the rigidity of the main chain and of the length of the spacer impede zipper crystallization.

The polymer crystals are stable even on heating up to 150 °C, unlike isolated merocyanine moieties in the amorphous polymers that are converted back to spiropyran on heating to 45–50 °C.

Formation of a three-dimensional crystalline lattice in an atactic polymer poses a problem regarding the effect of structural irregularities in the macromolecules on the crystallization process. This relates to the problem of relative efficiency of stack propagation along and across the polymer chains. These problems are difficult to resolve just by examination of the Debye–Scherrer diffractions patterns of the polymers after swelling, which give only rough estimates of the degree of crystallinity.

In the present work we found a very simple method of visual observation of the early stages of zipper crystallization, which allowed us to compare the rate of this process in different polymers. By using this method we make an attempt here to find answers to the problems formulated above.

Experimental Section

Materials. The synthesis of SMA, 1-(β-methacryloxyl)-3,3′-dimethyl-6′-nitrospiro(indolenine-2,2′-(2*H*)-1)benzopyran) and the free radical polymerization of the monomer were described in earlier publications.[1,4] The polymer was carefully purified from the monomer precipitating four times with methanol from methyltetrahydrofuran (MTHF) solution. The molecular weight measured by ultracentrifugation was $M_w = 40000$. Copolymerization with methyl methacrylate (MMA), purified according to ref 5, was conducted in MTHF at 70 °C. The content of SMA in the copolymer was estimated by the absorbance of the copolymer solution at 340 nm, corresponding to the spiropyran absorption band. The copolymer composition as a function of composition of the monomer SMA–MMA mixture is shown in Figure 1.

Film Preparation. Thin polymer films were prepared by spin coating from chloroform solution on a glass slide. Spinning of a ~80 g/L solution during a few seconds gave dry polymer films about 1-μm thick.

Electron Microscopy. Philips SEM 505 and Philips EM 300 instruments were used for scanning and transmission electron microscopy. The samples were prepared on a parlodium-coated glass slide and transferred on a grid after separation of the film from the glass on a water container.

Results

A. Visual Microscopic Observations. A typical film of the SMA homopolymer prepared by spinning is shown in Figure 2a. The film is not uniform and contains dark spots spread throughout the light-yellow surface. The spots are substantially thicker than the bright area of the film, exhibit birefringence, and look like nodules on the flat surface. Better contrast can be obtained by photochromic coloring of the film resulting from irradiation with UV light. While the area between nodules acquires a blue color, the nodules and the colorless area around them remain unchanged (Figure 2b).

The photoinduced color disappears on heating of the film above 50 °C, while the color of the nodules was preserved even above 150 °C. In order to study the effect of molecular weight of the polymer on the extent of the nodule formation, we separated the homopolymer into two fractions with $M_w = 50000$ and $M_w = 20000$ by fractional precipitation. The films prepared from the high molecular

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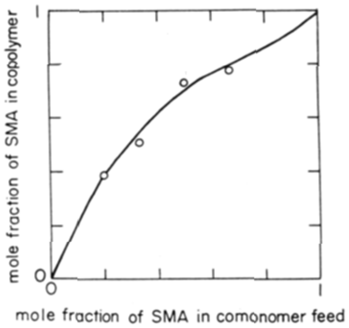

Figure 1. Composition of the SMA-MMA copolymer as a function of the monomer mixture composition.

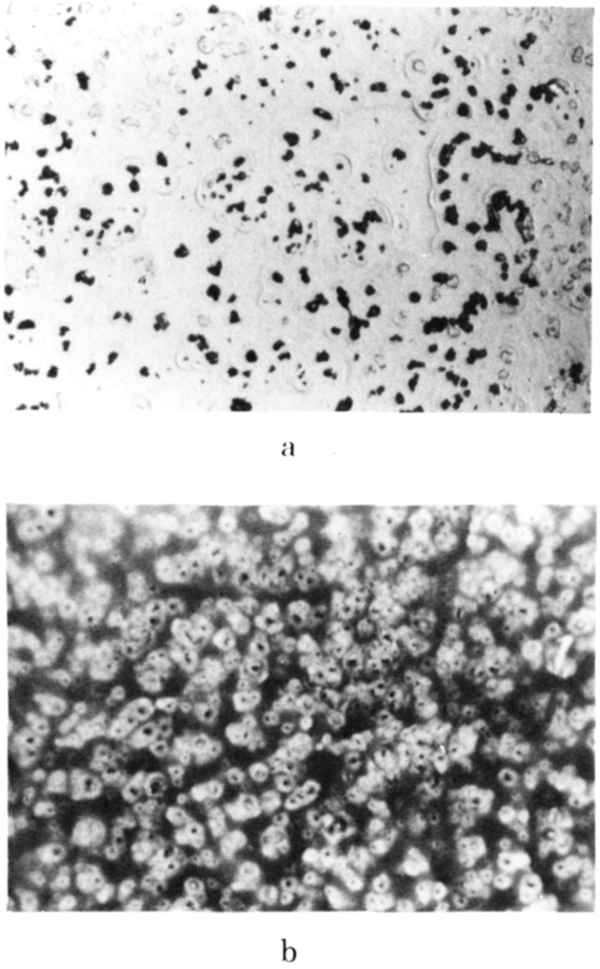

Figure 2. (a) Film prepared by spinning of the homopolymer solution. (b) Same film after irradiation with UV light (65X).

weight fraction contained about ten times more nodules per area unit than the films prepared from the low molecular fraction.

The films prepared from the SMA-MMA copolymers with 75 and 50% content of SMA also contained the nodules on the surface. The number of the nodules was less than on the films of the high molecular weight homopolymer but larger than on the films of the low molecular weight fraction.

B. Electron Microscopy. An electron micrograph and electron diffraction pattern of the homopolymer nodules are shown in Figure 3 parts a and b. The nodules are about 30–50-μm long and have rather sharp edges. They are too thick for electron diffraction measurements and we usually examined small fragments or edges of the nodules. The nodules on the copolymer films either are smaller or have burst (apparently on further growth). (Figure 3c.) The

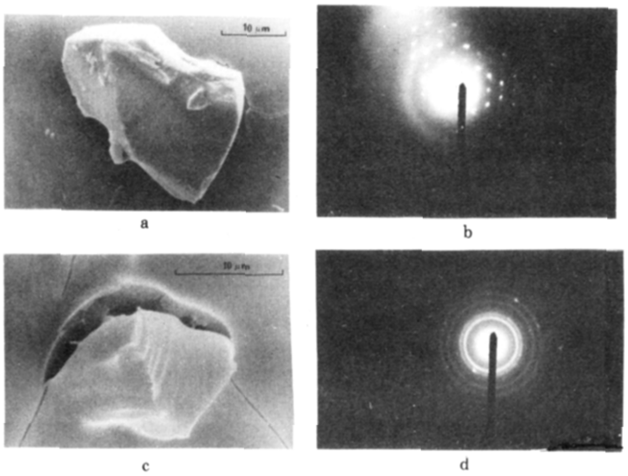

Figure 3. (a) Scanning electron micrograph of a nodule on a homopolymer film. (b) Electron diffraction pattern from an edge of the nodule. (c) Electron micrograph of a bursted copolymer nodule. (d) Electron diffraction pattern from a copolymer nodule.

electron diffraction pattern of the nodules formed from the 75% copolymer gives a much less regular pattern than diffraction from the homopolymer nodules (Figure 3d). We could not observe distinct diffraction from the nodules of a 50% copolymer.

The electron microscopic observations indicate that the homopolymer nodules have crystalline or at least some regular structure. The structure of the 75% copolymer nodules is apparently less regular.

C. X-ray Diffraction. The powder X-ray diffraction from the homopolymer, crystallized by long swelling reported earlier[1,3] contains 30 distinct sharp reflections and corresponds to three-dimensional, monoclinic crystals. The copolymer (75% of SMA) acquires a reddish-violet color after prolonged swelling in THF and gives a powder X-ray diffraction pattern containing only two diffuse rings ($d \sim 4$ and 6 Å) and one sharp reflection, corresponding to an interplanar spacing of 2.0 Å.

We could observe only a few weak sharp reflections ($d = 3.1$, 3.9, and 5.9 Å) in the powder X-ray diffraction pattern of the nodules of the homopolymer collected by picking from the film. Perhaps we picked out not only nodules but also amorphous fragments around them. However, it is also probable that the nodules are not regular crystals but rather assemblies of molecular stacks.

Discussion

Electron microscopy and X-ray diffraction of the nodules show that their formation is to be considered as the beginning of zipper crystallization, which stops after the solvent evaporation. Apparently, the number and size of the nodules is determined by the rate of initiation, propagation, and termination of the crystallization process. The size of the nodules on the homopolymer film is approximately the same (30–40 μm in length). If the propagation along the macromolecular chain goes much faster than the random stack formation, the stacking process reaching the end of a macromolecule is to be considered terminated. This means that the rate of stacking in the steady-state condition has to be higher for the fraction with the higher molecular weight. This may explain the different number of nodules formed from the low and high molecular weight homopolymers.

For the SMA-MMA copolymers only the random stack formation is feasible, however, in this case the stacking may be facilitated by the enhanced flexibility of the copolymer main chains, which promotes the segmental movement.

The results of electron microscopy and X-ray diffraction measurements of the copolymer indicate that the stacking leads to a low-order organization. The interplanar spacing of 2.0 Å relates conceivably to the intramolecular distance between equal groups of the main chain. Apparently, the macromolecules are stretched because the growth of the stacks produces much stronger pulling together of the macromolecules in the copolymer than in the homopolymer. The strain may result in rupture of the film, if a nodule exceeds a critical size (Figure 3c).

The strain of the polymer film around the nodules seems to be a cause of formation of the nonphotochromic zones surrounding the nodules (Figure 2). This explanation is consistent with the strong effect of the local free volume and segmental mobility of a polymer on the photochromic behavior of spiropyrans.[6,7] One can explain along the same lines the structural stabilization of the merocyanine form in the stacks, revealed by the high thermal stability of the nodules, which do not lose their color even above 150 °C, while the color formed on irradiation of the films disappears above 50 °C.

Conclusion

Investigation of nodules on the polymer films disclosed new important features of zipper crystallization. The stack formation in the homopolymer proceeds faster along the macromolecular chains than expected for a random process, while in the copolymer the last process becomes efficient and leads to the low-dimensional order. The possibility of random migration can explain why the zipper crystallization occurs in the atactic polymers: Apparently, the process goes predominantly along a main chain until a structural irregularity is encountered, which can be bypassed by the transfer of stacking to a neighbor macromolecule. The stack formation leads to shrinking of the material both during zipper crystallization and during the photocontraction of a "quasi-liquid".[8] Perhaps this process is to be taken into account on consideration of the photomechanical effect reported by Smets and co-workers.[9]

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Registry No. SMA homopolymer, 57981-89-2; (SMA)·(MMA) (copolymer), 51816-58-1.

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X-ray Studies of the Structure of Liquid Crystalline Copolyesters: Treatment of an Atomic Model as a One-Dimensional Paracrystal

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ABSTRACT: X-ray fiber diagrams of wholly aromatic copolyesters contain aperiodic intensity maxima on the meridian. It is shown that the positions of these maxima are predicted by calculation of the interference function for a model in which the monomers are represented as points, separated from their neighbors by the appropriate residue lengths. Subsequently these calculations were extended to an atomic model for the chain which leads to good agreement for both position and intensity of the maxima. The easiest approach for the point model is to treat the chain as a one-dimensional paracrystal with bimodal coordination statistics. This paper shows how this procedure can be used for an atomic model for the copolymer chain. This allows the prediction of the scattering by an infinite polymer chain with a distribution of residue orientations about the chain axis and, hence, the investigation of the correlation or persistence length for the stiff chain conformation.

We are using X-ray methods to investigate the physical structure of wholly aromatic copolyesters prepared, for example, from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) and from HBA, 2,6-dihydroxynaphthalene (DHN), and terephthalic acid (TPA). These copolymers form liquid crystalline melts and can be processed therefrom, e.g., as high-strength fibers and novel molded plastics. Their solid-state structure is of interest because of the sensitivity of the bulk properties to relatively small changes in monomer chemistry. In particular, there is evidence for the existence of three-dimensional order, and this order increases with thermal treatment, which is often necessary to obtain optimum mechanical properties.

In previous papers from this laboratory we have shown that the X-ray diffraction data for these copolymers are consistent with a structure made up of oriented, extended chains of completely random monomer sequence. These conclusions are based on a treatment of the copolymer chains as an aperiodic one-dimensional lattice,[1] as will be summarized below. In recent work we have begun to consider the three-dimensional packing of the random

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