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Factors Affecting Microstructural Scale in Liquid Crystalline Materials

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Light microscopy was used to study the effects of molecular weight and chain flexibility on microstructural scale in liquid crystalline materials. Studies of poly(*p*-hydroxybenzoic acid) oligomers show that the scale exhibited by a semiflexible molecule is not sensitive to increasing molecular weight when the contour length exceeds the persistence length. For contour lengths shorter than the persistence length, the microstructural scale is significantly coarser and depends on molecular weight. In the case of linear rigid polytolan oligomers, increasing the molecular axial ratio results in coarser microstructures. Rheinberg differential color contrast is shown to provide an optimum combination of contrast and resolution for highlighting fine-scale orientational defects.

Keywords: axial ratio, domain size, flexibility, microstructural scale, molecular weight, Rheinberg

INTRODUCTION

The relationship between chemical structure and a wide range of physical properties in liquid crystalline materials has been studied in great detail. Thus, much is known about balancing the type, sequence and connectivity of rigid and flexible moieties to obtain a particular liquid crystalline phase.[1] One can predict how to tailor the temperature range over which the phase is stable, or how to ensure that the material exhibits particular optical properties. However, bulk physical properties cannot depend only on the chemical nature and conformation of individual molecules, but must also be affected by the microstructure—i.e., the scale on which different levels of molecular order occur—a fact clearly recognized in the traditional areas of materials science. For example, although polymer extruded in the liquid crystalline state may exhibit exceptionally high modulus and tensile strength, the compressive strength is generally still comparable to that of conventionally processed polymers; we expect that enhanced compressive strength would result from an

increased disclination (or orientational defect) density in the microstructure. Conversely, undesirable optical scattering by a film of liquid crystalline material may be avoided if the density of microstructural defects is reduced.

There are indications that high molecular weight liquid crystalline polymers exhibit finer scale microstructures compared to lower molecular weight liquid crystalline materials. This behavior was noted for poly(*p*-hydroxybenzoic acid)[2] and for poly(*p*-phenylene terephthalamide).[3] Monte Carlo models[4] predict that a coarser microstructural scale results from higher molecular axial ratios if molecules are perfectly rigid and experience only steric interactions.

MATERIALS

Poly(*p*-hydroxybenzoic acid) (PHBA) exhibits a thermotropic nematic phase. Also known commercially as Ekonol, it is useful for high modulus fibers.[2,5] The ester linkages in the backbone render the molecules semiflexible. Oligomers of PHBA[6] studied in this work are designated by their degrees of polymerization: DP4, DP15, DP18, DP23 and DP28. (The molecular weights range from ~500 to ~3400.)

Three oligomers based on a tolan unit were also studied. They are designated by their axial ratios: T4.3, T4.7 and T5.7 (Figure 1). These molecules are rigid and exhibit thermotropic nematic phases.[7]

EXPERIMENTAL: LIGHT MICROSCOPY

Transmitted Polarized Light Microscopy

Each polymer sample was held between two glass cover slips. No special steps were taken to modify the glass surfaces. Microstructural comparisons were always made between samples of similar thickness. Specimens were observed with a Leitz Laborlux 12 Pol microscope equipped with a Linkam 26-THM-600S heating/freezing stage and 26-PR-600 controller.

Samples of PHBA (DP15-DP28) were placed on the heating stage preheated to 1.1 times the crystalline→nematic transition, on an absolute scale. Pressure was applied by hand to the hot sample to promote formation of a thin specimen. The samples were then quenched to room temperature by transferring them onto an aluminum block. It has been previously demonstrated that microstructures typical

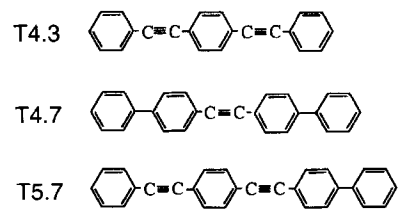

FIGURE 1 Molecular structures of linear oligomeric polytolans.

of elevated temperatures can be "quenched-in" by this technique.[2] In each case, the heating and cooling cycle was performed within 15 seconds to avoid sample polymerization or degradation. The quenched samples were examined at high resolution with a 100X oil-immersion lens.

The tetramer of PHBA (DP4) was placed on a heating stage preheated to 288°C and observed at temperature with a 32X long working distance objective.

The polytolans also were studied under the long working distance lens while on the heating stage. Each oligomer was placed on a heating stage preheated to 50°C above the nematic→isotropic transition. The isotropic droplets coalesced and spread to form one thin drop, wetting both glass surfaces. This thin specimen was then cooled at 10°C/min into the nematic temperature range (5°C below the isotropic→nematic transition).

Rheinberg Differential Color Contrast

In the context of liquid crystals, there are advantages to considering microstructural scale as the density of orientational defects, thus avoiding the ambiguities in the definition of a "domain size".[8] Microstructures observed between crossed polars contain extinction bands that are related to molecular order between defects, and thus detract from the defects themselves. As such, this contrast cannot easily be interpreted in terms of microstructural scale.[8] To highlight the orientational defects themselves, we turn to Rheinberg differential color contrast.[9–11]

The technique is similar to dark field microscopy, which utilizes an opaque stop in the light path to block the lower diffracted orders from reaching the center of the objective back focal plane (see Figure 2). In dark field microscopy, fine detail in the specimen appears light. Coarse structure and background are not observed. Rheinberg's technique uses a filter that is comprised of a central stop and an annulus that have different colors. The coarse information is not obliterated by an opaque stop; it merely appears in a color different from that of the detail. Also, while dark field microscopy will compromise high resolution,[12] Rheinberg does not.

Rheinberg filters were cut from colored gelatin films according to descriptions

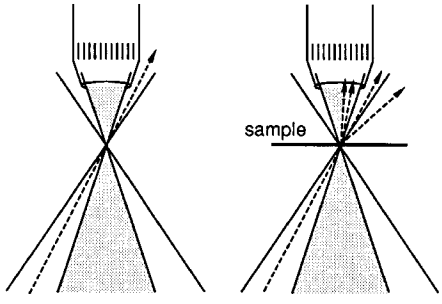

FIGURE 2 For both dark field and Rheinberg microscopy, a wide cone of light is used to illuminate the sample. The rays of light forming the outer part of the cone (unshaded) do not reach the objective except in the case that they are sufficiently scattered by the sample structure. For dark field conditions, the central part of the cone (shaded) is blocked by placing an opaque stop in or below the substage condenser. For Rheinberg conditions, the central and outer parts of the illuminating cone are given two different colors by using a colored stop and a colored annulus.

in the literature.[10–11] Blue was chosen for the annulus to obtain the highest resolution of detail. The filters were mounted onto microscope slides so that they would rest easily in the substage assembly, between the two condenser lenses. By observing the objective back focal plane, the filter could be centered accurately. The Rheinberg illumination technique was used with a 60X objective to examine the quenched PHBA samples. Images were recorded in color on slide film; black-and-white prints for this paper were made directly from the slides, so that fine detail appears dark.

RESULTS AND DISCUSSION

Molecular Weight Effects in Semiflexible PHBA

The quenched microstructures of DP15 and DP18 are shown in Figure 3. There is a marked decrease in scale between the two microstructures. The microstructures for DP23 and DP28 were not significantly different in scale from DP18. Rheinberg differential color contrast provided the same results about the relative microstructural scale of the PHBA oligomers (Figure 4). Note that, although an objective of lower numerical aperture was used in obtaining these microstructures, the degree of fine detail is comparable to that seen in Figure 3.

The tetramer (DP4) polymerized while on the heating stage. With increasing time, the microstructural scale initially coarsened, quickly became much finer (Figure 5), and then continued to decrease slowly.

The concentration of microstructural defects depends on the availability of defects in the *local* packing of molecules. For example, splay deformation, and therefore the disclinations that involve splay, cannot be constructed without the use of chain ends. So the number of defects at a micron scale will be related to the segregation of defects present at the Ångstrom scale. The disclination density can also be related to the elastic constants of the liquid crystalline material; higher elastic constants will result in coarser microstructures. We consider that, with increased polymerization of the material, there are three factors at a molecular level which might influence the microstructural scale.

Firstly, the increasing axial ratio of the molecules implies a decreasing *concentration of chain ends*. The fewer chain ends to be accommodated, the fewer defects will be present in the microstructure. More simply, the longer building blocks more readily form larger ordered regions. Also, the elastic constants increase.[13] Thus the scale of the tetramer initially coarsens as it polymerizes.

Secondly, because PHBA is *semiflexible*, the molecular conformation need not be linear. The molecule is only considered straight over segmental lengths corresponding to the persistence length. According to data in Reference 14 the persistence length of PHBA at 300°C is close to the contour length of the DP15 oligomer. At contour lengths greater than this, the semiflexibility of PHBA becomes apparent. These non-linear molecules cannot maintain their orientational order over as large a distance as molecules that are straight. Thus the scale is fine in Figures 3b and 4b. The increase in contour length between DP18 and DP28 does not lead to any further significant change in the conformation, so there is no significant change in the ability of these molecules to order. Because bend defor-

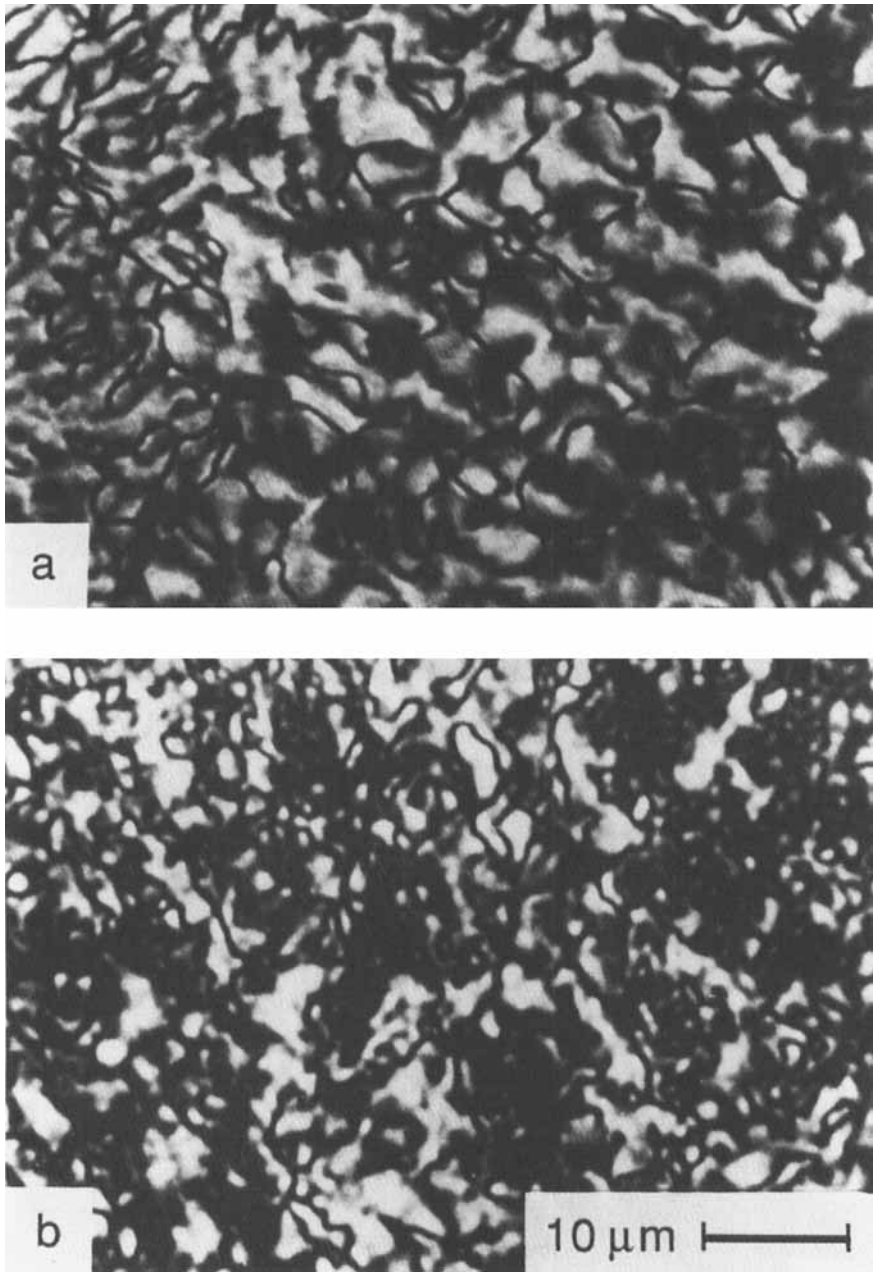

FIGURE 3 Schlieren textures observed between crossed polars for (a) DP15 quenched from 328°C and (b) DP18 quenched from 335°C. The scale of the DP15 microstructure is distinctly coarser.

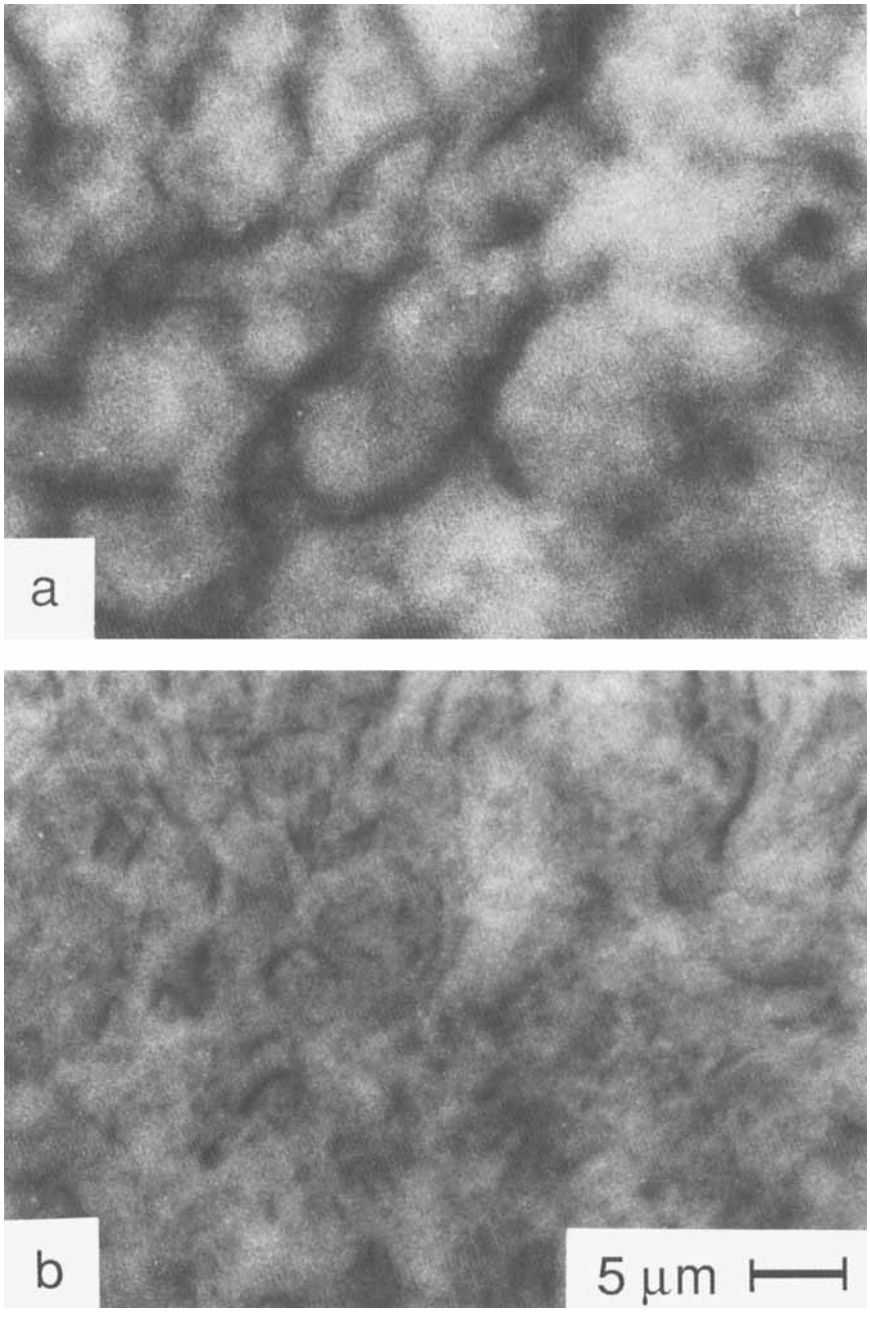

FIGURE 4 Quenched samples of (a) DP15 and (b) DP23 viewed under Rheinberg illumination conditions. Fine discontinuities in optical orientation appeared blue and coarse detail appeared red when viewed in the microscope. The black-and-white micrographs shown here were printed directly from color slides of the Rheinberg images; the fine detail therefore appears dark.

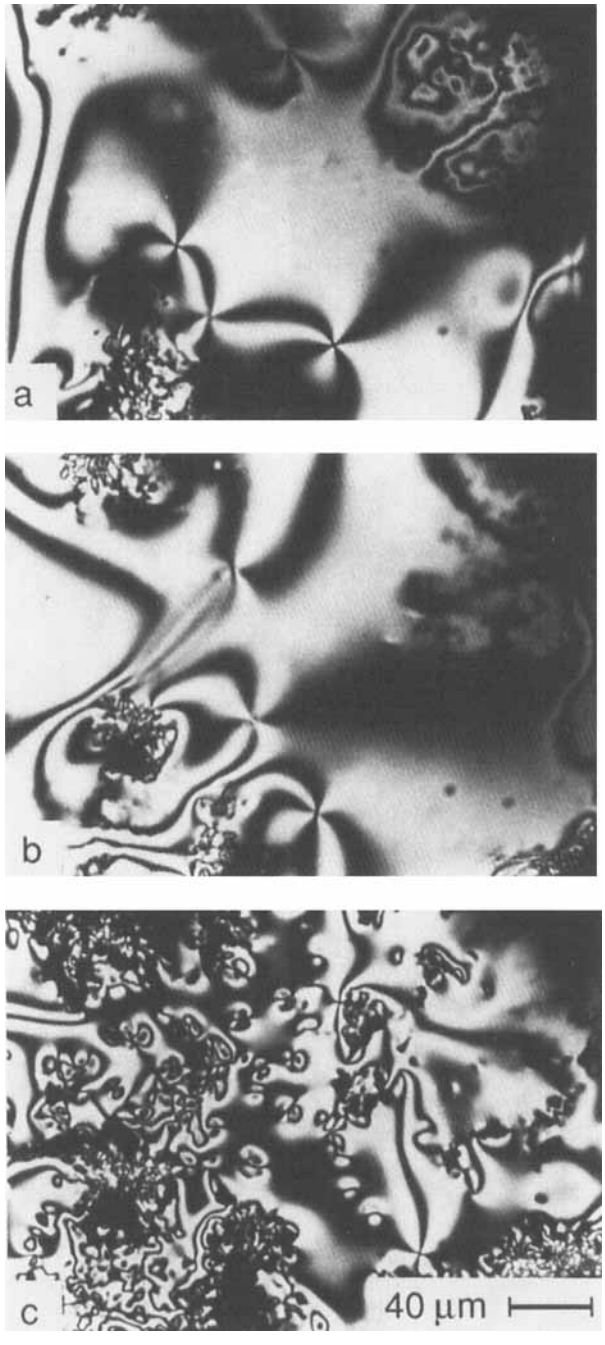

FIGURE 5 (a) Placed on the heating stage at 288°C, the tetramer of PHBA (DP4) melts and forms a schlieren texture which is initially coarse. The micrograph shows the texture after 1 minute on the stage. (b) After a further 1/2 minute, polymerization has caused the microstructure to become coarser. (c) After another 1/2 minute, further polymerization has led to an abrupt increase in the concentration of defects.

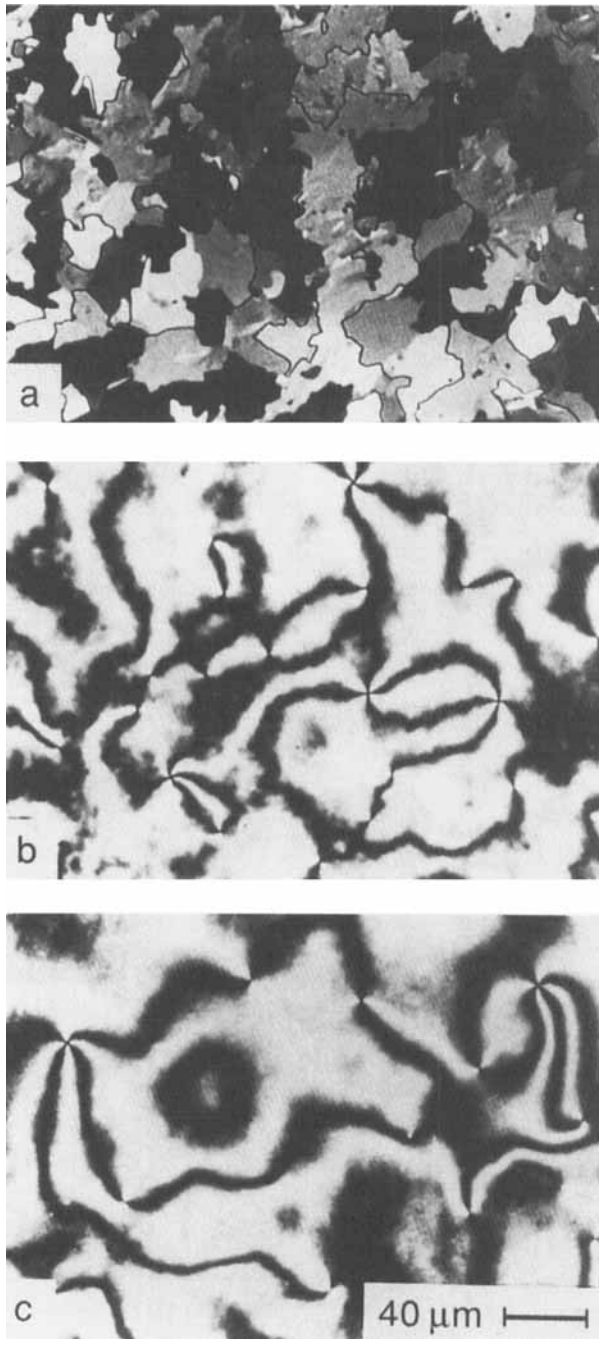

FIGURE 6 (a) Nematic marbled texture of T4.3 at 167°C. (b) Schlieren texture of T4.7 at 238°C. (c) Schlieren texture of T5.7 at 242°C. The scale of the polytolan microstructures increases with increasing molecular axial ratio.

mation is easier with flexible molecules, the bend elastic constants are lower. The fact that most disclinations in a nematic require some bend could account for the significant change in microstructural scale occurring in response to a relatively small increase in degree of polymerization.

The microstructure of the tetramer did continue to decrease in scale beyond the length at which the persistence length was exceeded. The third factor we recognize is the *polydispersity* of the sample. Polydispersity increases as polymerization proceeds. As the molecules become increasingly dissimilar their segregation patterns become more complex, leading to additional microstructural defects.

Molecular Weight Effects in Rigid Polytolans

The microstructure of T4.3 exhibited a nematic marbled texture between crossed polars (Figure 6a). Each domain varied in shade from light to dark as the polars were rotated through 90°. Samples T4.7 and T5.7 exhibited classic schlieren textures (Figure 6b, c). The scale of microstructure increases in the order T4.3 < T4.7 < T5.7. Of the three factors presented as relevant to the scale of PHBA textures, only the concentration of chain ends is relevant to the rigid, monodisperse polytolans. The observed increase in scale with increasing molecular weight is consistent with the initial behavior of the tetramer during polymerization.

CONCLUSIONS

We propose that:

1. Fine microstructures are promoted by semiflexible molecules of high molecular weights, by processing these molecules at temperatures where the contour length exceeds the persistence length, and by high polydispersity.
2. Coarse microstructures are promoted by high molecular weight rigid molecules, by processing semiflexible molecules at temperatures where persistence length exceeds contour length, and by low polydispersity.
3. Rheinberg differential color contrast provides high contrast and high resolution of orientational defects in liquid crystalline microstructures.

Acknowledgment

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