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The Contrasting Behavior of Chemically Ordered versus Chemically Disordered Liquid Crystal Polymers

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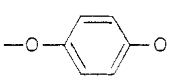
ABSTRACT: We report here on the contrasts observed betweeen a terpolymer with ordered chemical sequences and its chemically disordered isomer. The chemically ordered terpolymer and its disordered analogue were both liquid crystal polymers synthesized in our laboratory. Optical microscopy reveals that the disordered isomer exhibits a biphasic region spanning 120 °C where both birefringent and isotropic fluid coexist. In great contrast, the chemically ordered terpolymer exhibits a distinct transition from the liquid crystalline to the isotropic phase over the very narrow range of 5 °C. Furthermore, the ordered isomer responds more readily than the disordered polymer to the guiding effect of grooved surfaces toward long-range backbone alignment. The ordered-sequence polymer also reveals a clearly defined crystallization from the birefringent fluid whereas the disordered isomer exhibits an optically indistinct "crystallization".

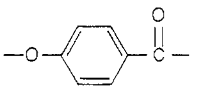
Introduction

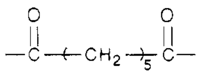
Polymers that melt into orientationally ordered fluids can exhibit more complex behavior than classical liquid crystals formed by small molecules. One example of this complexity is the gradual appearance of an isotropic phase which coexists with the anisotropic fluid over a broad temperature range.[1,2] This biphasic behavior has been observed mostly but not exclusively in mesogens which have various degrees of chemical disorder, e.g., they are aregic or lack order in their chemical sequence structure. So far, the role of chemical inhomogeneity versus that of molar mass dispersion has not been clearly identified. Another characteristic of liquid-crystal polymers is the slow formation of macroscopic orientational monodomains under the influence of external guiding forces. Molecular size is undoubtedly a factor but the role of chemical disorder in macroscopic ordering dynamics in these systems is not well understood at the moment.

We report here on some of the striking physical differences observed between a chemically regular liquid-crystal polymer and its constitutional isomer which is chemically random. In the previous paper of this series[3] we reported on the synthesis of the chemically regular liquid-crystal polymer and in an earlier publication on that of the chemically random mesogen.[4]

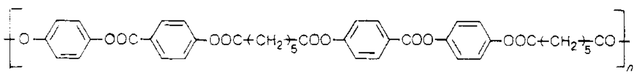
The following are the structural units in the two polymers studied:


dioxyphenyl


oxybenzoate


pimeloate

The chemically ordered polymer has the following repeating unit,



whereas the chemically disordered isomer contains random sequences of the three structural units shown above. The differences between the isomeric mesogens relate to their phase structure, their crystallization behavior, the kinetics of monodomain organization among the self-ordering chains, and the ability of the solid polymer to recover its original fluid state texture after melting. The experiments have involved optical microscopy and differential scanning calorimetry to demonstrate the contrasting behavior in the ordered–disordered isomeric pair.

Experimental Section

The materials utilized in this investigation are main-chain thermotropic polyesters synthesized in our laboratory. The syntheses of the chemically ordered and chemically disordered polymers have been previously reported by Moore and Stupp.[3,4] The as-polymerized materials were placed between two specially cleaned glass surfaces for examination in a Leitz Laborlux 12 pol polarizing microscope equipped with a Leitz hot stage controlled by a Research, Inc., thermocontroller. Quantitative microscopic data were obtained from a Mettler FP5 photodetector coupled with a Keithley 169 multimeter used in conjunction with a Pentax ME Super 35 mm SLR camera. Thermal properties were characterized with a Perkin-Elmer DSC-4 differential scanning calorimeter. A heating and cooling rate of 10 °C/min was used on samples weighing between 5.0 and 9.0 mg. A constant flow of helium was maintained throughout the course of the thermal experiment.

Viscosities were measured with a Ubbelohde-type viscometer at 30 ± 0.01 °C using solutions of the polyester in tetrachloroethane filtered through E2μ paper. Slow times at four different concentrations were obtained with dilutions made directly in the viscometer bulb. Limiting viscosity at infinite dilution, $[\eta]$, was taken as the average value of the least-squares intercept of η_{sp}/c versus c and ln (η_r/c) versus c curves.

The special glass surfaces utilized in optical microscopy experiments were either featureless (smooth) or contained uniaxial grooves. The grooves were created by rubbing 150-μm-thick glass disks on a glass substrate coated with 1-μm diamond paste for a period of 5 min. This procedure was followed by ultrasonic cleaning with detergent, water, and ultrasonic cleaning solution in preparation for treatment of the surfaces with reagent grade solvents. Both featureless and grooved glass surfaces were exposed for 30 min to each of the reagent grade solvents. The solvents utilized were 2-propanol, acetone, and methyl ethyl ketone. The surfaces were then immersed in a concentrated chromic acid–sulfuric acid solution for 30 h, rinsed with distilled water, and dried for 24 h at 183 °C. The featureless surfaces underwent one further step of firepolishing at 600 °C for at least 1 h.

Results and Discussion

Optical microscopy experiments were carried out by using thin films of the polymers on the order of 1 μm in thickness placed between two very carefully cleaned glass disks. The chemically disordered polymer gradually changes appearance upon heating and begins to flow in the vicinity of 160 °C. Due to the fact that the chemically disordered polymer has a very fine crystalline texture, the precise melting temperature is difficult to discern. Upon continued heating the chemically disordered material

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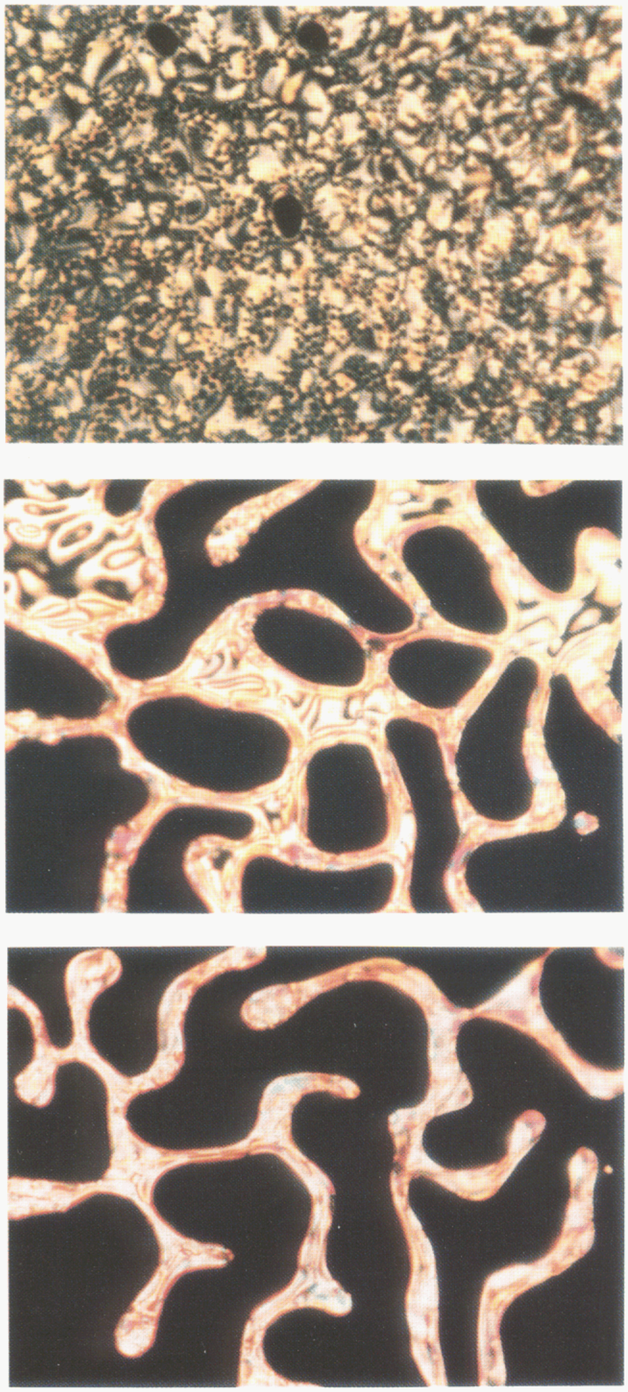

Figure 1. Optical micrographs between crossed polars of the chemically disordered polymer showing the biphasic structure at (top) 308 °C, (middle) 330 °C, and (bottom) 336 °C (magnification 215×).

eventually reveals black droplets that gradually increase in size with temperature (Figure 1). The black regions were examined during the course of the experiment under the polarizer alone in order to ascertain that these regions contained polymer and not air bubbles. An interference figure was also obtained with the optical microscope to determine whether the black areas were isotropic or contained homeotropically aligned liquid-crystalline regions (molecules parallel to the optic axis). The resulting conoscopic image revealed that black regions were in fact isotropic. Assuming a nematic phase is present, homeotropic alignment would have yielded a uniaxial interference figure. Eventually, all of the birefringent phase is consumed, leaving a completely isotropic melt at approxi-

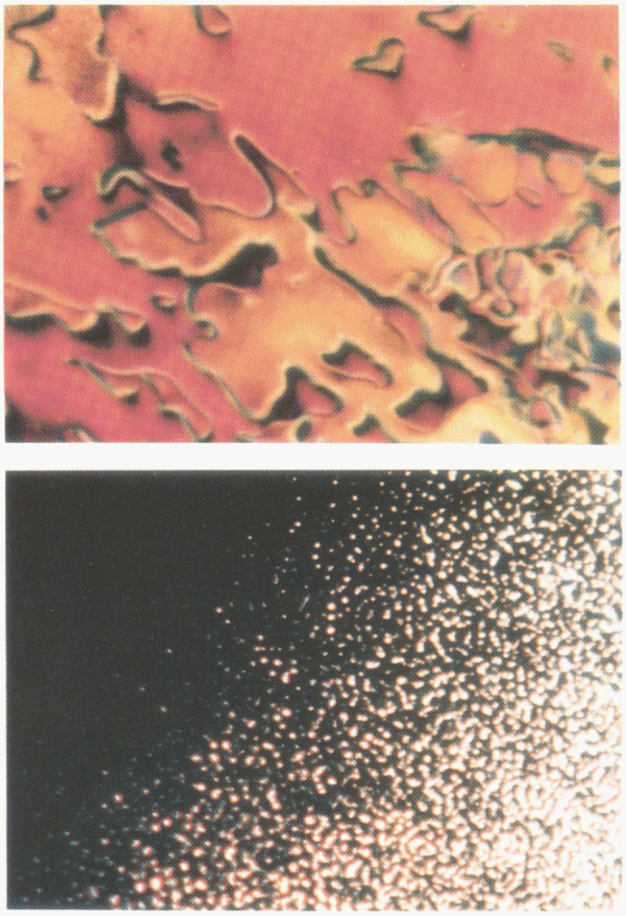

Figure 2. Optical micrographs between crossed polars of the chemically ordered polymer at (top) 272 °C and (bottom) 277 °C (magnification 215×).

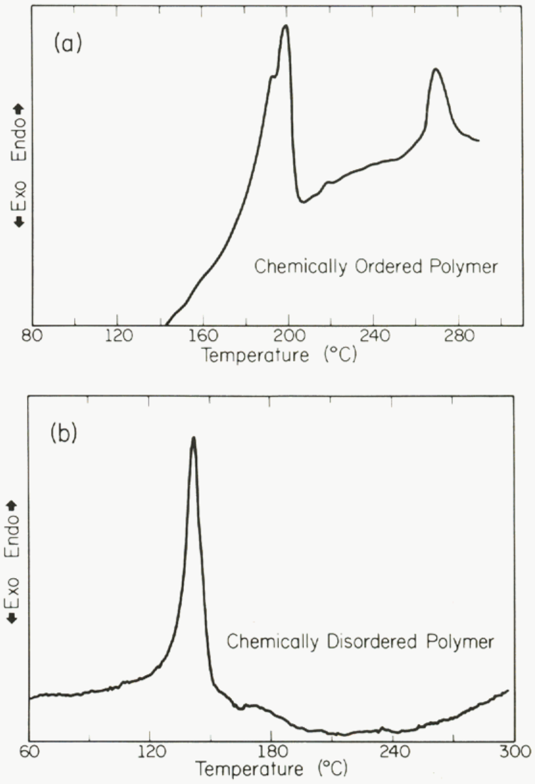

Figure 3. Differential scanning calorimetry scans during heating for the chemically ordered polymer (a) and the chemically disordered polymer (b).

Figure 4. Optical micrographs between crossed polars showing the crystallization of the chemically ordered liquid crystal polymer on smooth glass surfaces at approximately 190 °C (magnification 215×).

mately 388 °C. At heating rates on the order of 10 °C/min the biphase spans a temperature range of 120 °C.

In great contrast, the chemically ordered isomer shows a readily detectable crystal to liquid crystal transition at approximately 220 °C. Most importantly, however, the regular isomer does not display the broad biphase range and remains completely birefringent up to a temperature which is just a few degrees below its clearing point. The clearing point observed at 280 °C is preceeded by a very narrow 5 °C range where a finely dotted texture of bright and dark regions is observed (Figure 2).

Parts a and b of Figure 3 show the heating DSC scans corresponding to the chemically ordered and the chemically disordered liquid crystal polymers. The scans

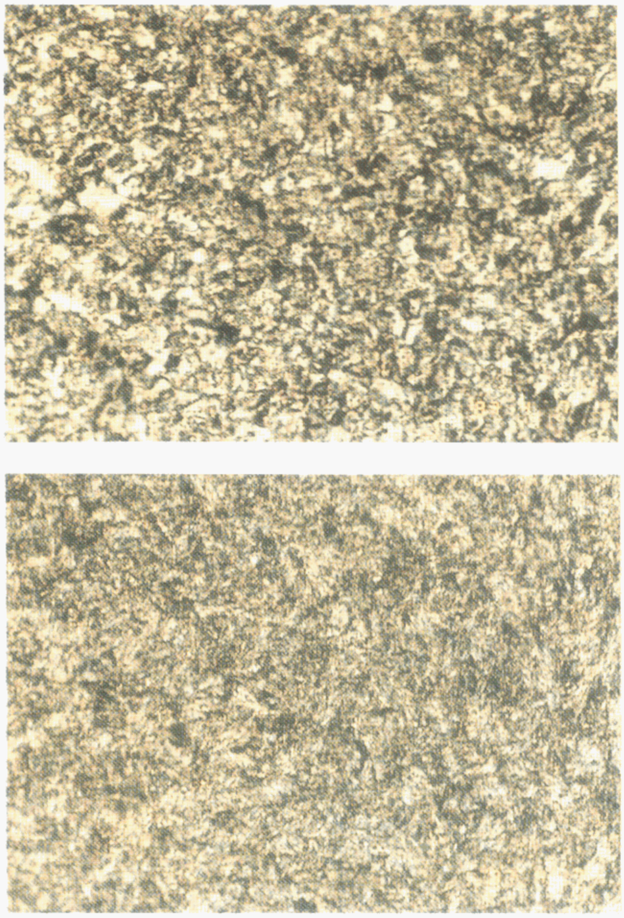

Figure 5. Optical micrographs between crossed polars of the chemically disordered polymer on smooth glass surfaces. The top micrograph corresponds to the liquid crystalline state at 213 °C and the bottom micrograph corresponds to the solid state at 77 °C (magnification 89×).

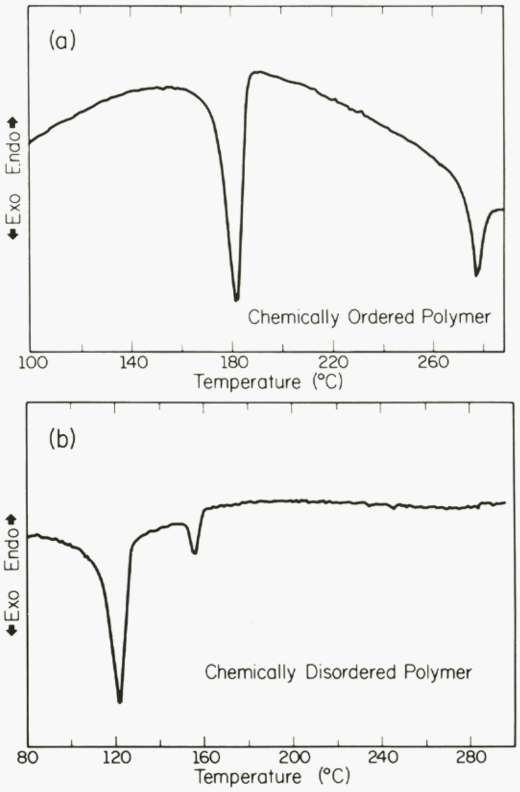

Figure 6. Differential scanning calorimetry scans during cooling for the chemically ordered polymer (a) and the chemically disordered polymer (b).

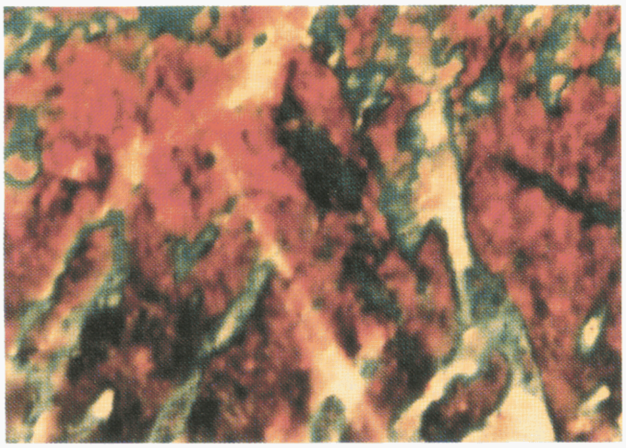

Figure 7. Optical micrograph between crossed polars of the chemically disordered liquid crystal polymer after contact with two grooved glass surfaces for 12 h. The grooves on the top and bottom surfaces were aligned parallel to each other (magnification 215×).

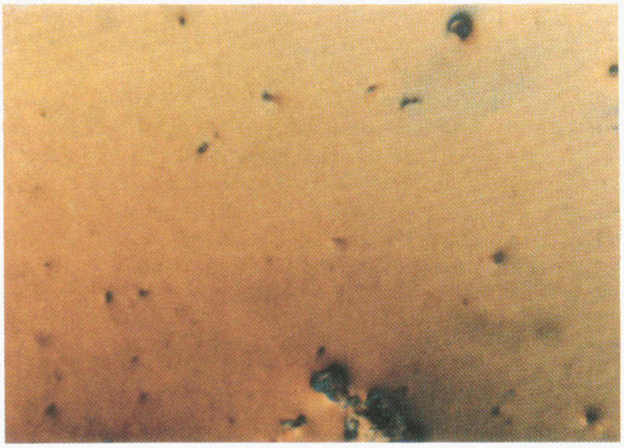

Figure 8. Optical micrograph between crossed polars of a monodomain of the chemically ordered polymer formed after 3 h between two glass surfaces with parallel grooves (magnification 215×).

Table I
DSC Data for the Ordered and Disordered Isomers

	heating, °C		cooling, °C		
isomer	T_{melt}	T_{clear}	$T_{\mathrm{lc}}{}^{a}$	$T_{\mathrm{c1}}{}^{b}$	$T_{\mathrm{c2}}{}^{c}$
disordered	140	*d*	*d*	154	120
ordered	194	276	282	189	none

[a] Temperature at which liquid crystallinity reappears. [b] First exotherm. [c] Second exotherm. [d] Not detected by the DSC.

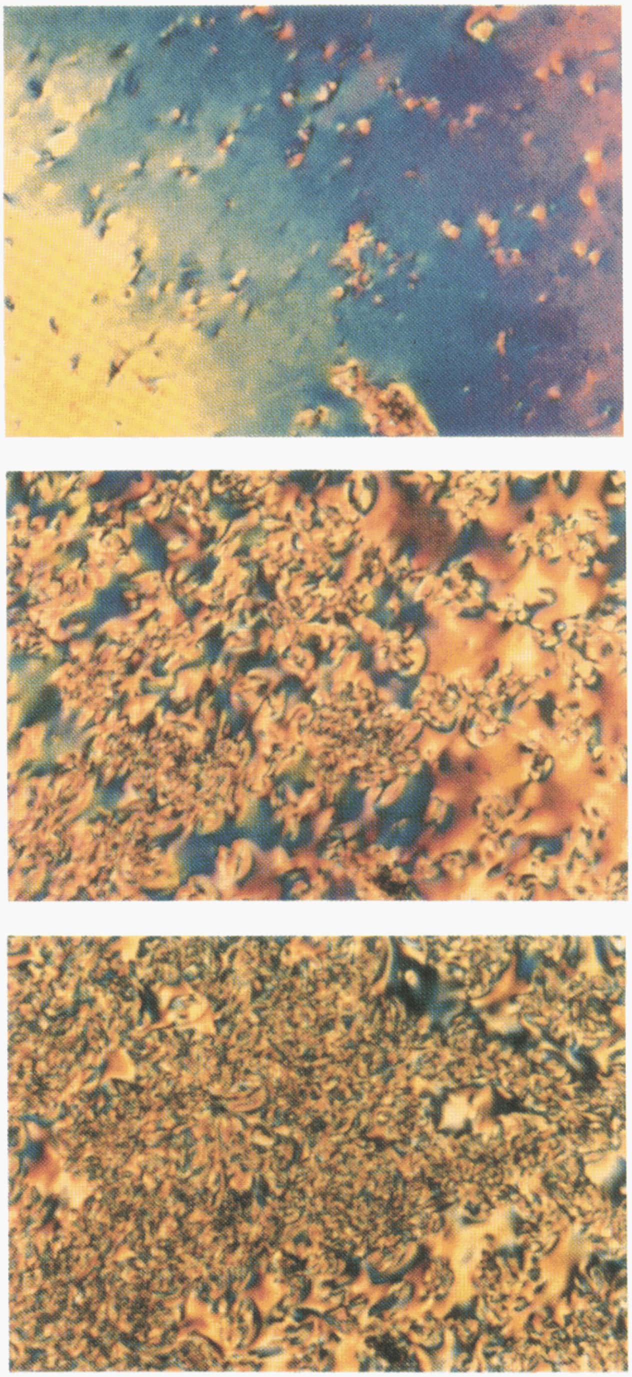

Figure 9. Optical micrographs between crossed polars showing the crystallization of the chemically ordered liquid crystal polymer between glass surfaces containing parallel grooves (the temperature was approximately 192 °C) (magnification 215×).

Table II
Optical Data for the Ordered and Disordered Isomers

	heating, °C		thermal width of biphase, °C	cooling, °C	
isomer	T_{melt}	T_{clear}		$T_{\mathrm{lc}}{}^{a}$	T_{cryst}
disordered	160	388	119	281	106
ordered	221	280	5	275	190

[a] Temperature at which liquid crystallinity reappears.

presented are those of the second heat cycle since the first cycle displays multiple peaks (endothermic and exothermic) which presumably result from the nonequilibrium structure of the as-synthesized materials. The thermal traces shown become reproducible in all scans subsequent to the first heat cycle. Consistent with our optical observations, the DSC data show that the chemically ordered liquid-crystal polymer exhibits both a crystal to liquid crystal transition at 194 °C and a liquid crystal to isotropic transition at 275 °C. The DSC of the chemically disordered polymer, on the other hand, exhibits only a crystal to liquid crystal transition near 140 °C. One must then explain the absence of a discernible liquid crystal to isotropic transition in the chemically disordered polymer by the presence of a broad biphasic range. The gradual development of this isotropic phase is effectively concealed by the baseline of the DSC scan. Tables I and II summarize the optical and DSC temperature data. The discrepancy in DSC versus microscopy data is expected on the basis of the higher temperatures required for optical resolution of the transitions.

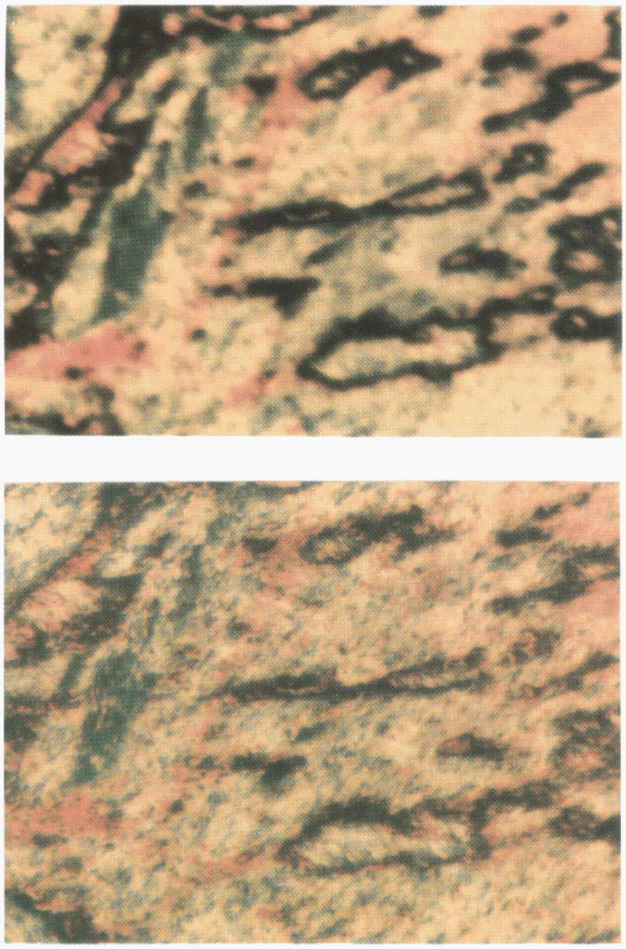

Figure 10. Optical micrographs between crossed polars of the chemically disordered polymer between glass surfaces with parallel grooves. The top micrograph corresponds to the liquid crystalline state at 199 °C and the bottom micrograph corresponds to the solid state at 105 °C (magnification 215× and 246×, respectively).

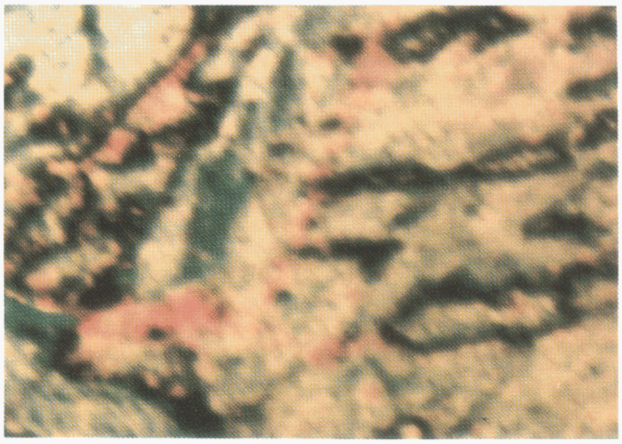

Figure 11. Optical micrograph between crossed polars of the remelted chemically disordered liquid crystal polymer shown in the bottom micrograph of Figure 10. The micrograph was obtained at 170 °C (magnification 215×).

As indicated by data in Table II, the chemically disordered polymer undergoes the crystal to liquid crystal transition at a temperature which is significantly lower than that of the ordered isomer. At the same time we know from optical data that the final clearing point temperature is significantly higher in the chemically disordered polymer. We infer from these observations that "crystals" formed by "disordered" chains are both small and highly imperfect due to the chemical heterogeneity of chains. Presumably it is possible for chains to register such that crystallization is possible. Thus, on the basis of small size and entrapment of defects, we expect lower crystal to liquid crystal transitions in random chains relative to ordered chains. Near 200 °C both isomers exhibit nematic textures but the gradual development of a biphase with temperature in the random isomer is most intriguing. We cannot attribute this contrasting behavior to differences in molecular weight or polydispersity. Measurements of viscosity tell us that significant differences in molecular weight do not exist. Specifically, the chemically ordered isomer was found to have an intrinsic viscosity of 0.55 dL/g[3] and the disordered isomer used in our experiments had an intrinsic viscosity of 0.46 dL/g (both values were obtained in tetrachloroethane at 30 °C). On the basis of the similarity of polymerization chemistry involved in synthesizing both isomers, there is no reason to suspect large differences in polydispersity. We therefore consider the possibility that chemical disorder is indeed the origin of this contrasting behavior. In the following paper in this issue we address this problem in a more rigorous way. Another interesting difference between the isomers is the fact that in the random polymer birefringent fluid is still observed within a range of temperature which is 100 °C higher than the clearing point of the ordered mesogen. This fact suggests that such regions contain the highest persistence length chains in the chemically disordered system. The important implication is that an "active" segregation of molecules must occur during the biphasic regime. We do not know at the present time what the mechanism(s) of this segregation is. We infer that diffusion must be important and other factors such as transesterification might play a role. For example, transesterification could create a more heterogeneous melt containing a population of chains which are largely flexible or largely rigid.

Upon cooling the chemically random polymer from the isotropic phase one observes a significant degree of supercooling before the appearance of birefringent fluid. This is in marked contrast to the behavior observed when cooling the chemically ordered liquid-crystal polymer. The ordered mesogen reforms the liquid-crystalline phase from the isotropic phase with minimum supercooling (approximately 5 °C). This may be due to the chemical homogeneity in this isomer. Further cooling of the ordered polymer leads to the formation of crystals which grow radially from a small number of nuclei, strongly resembling in appearance the spherulitic growth of flexible polymers (see Figure 4). Whether or not these entities are structurally related to classical polymer spherulites is unknown at the moment. A crystallization temperature of 190 °C observed by means of optical microscopy correlates well with the single exotherm observed at 189 °C by DSC (see Tables I and II).

Optical observations of the "crystallization" of the chemically disordered isomer from a homogeneously birefringent fluid reveals a gradual increase in viscosity followed by solidification into a very fine textured solid with strong resemblance to the parent fluid state (see Figure 5). Due to the gradual development of this fine textured solid, it is difficult to ascertain optically the precise temperature at which the material "crystallizes". Cooling of the chemically disordered polymer reveals two DSC exotherms (Figure 6b). The second exotherm at 120 °C is associated with crystallization but it is not clear at the moment what the origin of the first exotherm is. The second exotherm is always observed but the first one is only observed when cooling is carried out from any temperature above 180 °C. From previous work in our laboratory[5] we know that samples cannot be magnetically aligned below 180 °C and this may be related to the molecular origin of the first exotherm. A possibility is that interactions between chains increase in two stages as samples are cooled. In contrast, the ordered isomer only shows two exotherms, one corresponding to the isotropic to liquid crystal transition and the second to crystallization (see Figure 6a). It is clear that the more complicated thermal behavior is associated with chemical disorder in one of the isomers.

All of the optical data presented up to now were obtained on featureless glass surfaces. However, it is well-known that grooved surfaces guide the orientation of small molecule liquid crystals.[6-9] They can also influence macromolecular liquid crystals significantly under certain conditions as shown in our previous papers.[10,11] A more homogeneous molecular orientation over macroscopic distances develops in the chemically disordered polymer when heated to the liquid-crystalline state and held isothermally at 190 °C in contact with two surfaces containing grooves in parallel alignment. However, within time scales in the order of 12 h, the disordered isomer never forms what one may identify as a monodomain liquid crystal by optical microscopy (Figure 7). In great contrast the chemically ordered isomer forms macroscopic monodomains in approximately 3 h at a temperature just above the crystal to liquid crystal transition (Figure 8). It appears as though chemical order along the chain facilitates directional confinement of molecules on the surface. This could be caused by a more homogeneous rigidity or more interactive segments in ordered as opposed to disordered chains. Cooling of monodomains formed by the ordered isomer leads to rapid crystallization with a large number of nucleation sites (see Figure 9). This should be compared to the radial growth with a small number of nuclei observed on smooth surfaces (see Figure 4). The large number of nuclei must originate from heterogeneous nucleation on grooved surfaces. The entire film between grooved surfaces becomes crystalline in a much shorter time than comparable films on smooth surfaces. However, it is not known if the actual crystal growth rate is faster on grooved surfaces or if the difference can be explained by the density of nucleation sites. It is important to note that monodomain orientation is destroyed upon crystallization of the ordered isomer. In contrast, when the disordered isomer acquires a limited degree of homogeneous alignment it is possible to preserve it in the solid state (see Figure 10). Optical observations reveal that the disordered isomer solidified "indistinctly" into a fine-textured solid regardless of the surface with which it is in contact. Remelting the solidified disordered polymer leads to a melt that bears a strong optical resemblance to its former liquid-crystalline state (see Figure 11). Relative to the ordered isomer, phase transitions in the disordered polymer must therefore involve less disruption of molecular organization.

Conclusions

The chemical sequence structure of liquid crystal polymers containing several structural units has a strong influence on their phase transitions and molecular segregation phenomena. In this work we examined two polymers synthesized in our laboratory, a chemically regular polymer and its disordered analogue composed of identical structural units. The disordered isomer exhibits a 120 °C broad biphasic temperature range over which optically visible isotropic and birefringent fluid regions coexist. This is in great contrast to the very distinct transition from the liquid crystalline to the isotropic state over the very narrow temperature range of 5 °C observed in the ordered-sequence polymer. Both isomers are synthesized by condensation reactions and it is therefore difficult to attribute the pronounced difference in behavior to molecular weight polydispersity. Optical microscopy revealed that the ordered polymer can more readily form a monodomain by contact with grooved surfaces than its disordered analogue. Furthermore, the ordered-sequence isomer exhibits a well-defined crystallization from the mesophase whereas the disordered polymer exhibits an optically indistinct "crystallization" (solidification) from the liquid crystalline melt. On the basis of measurements of dilute solution viscosity we cannot attribute all the observed contrasts to differences in molecular weight.

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Registry No. $(HO_2C(CH_2)_5CO_2H)(H_3CCO_2$-*p*-$C_6H_4CO_2C_6H_4$-*p*-$O_2CCH_3)$ (copolymer), 74774-70-2; $(ClCO(CH_2)_5COCl)(HO$-*p*-$C_6H_4OCOC_6H_4$-*p*-$OCO(CH_2)_5CO_2C_6H_4$-*p*-$CO_2C_6H_4$-*p*-$OH)$ (copolymer), 113380-59-9; $(ClCO(CH_2)_5COCl)(HO$-*p*-$C_6H_4OCOC_6H_4$-*p*-$OCO(CH_2)_5CO_2C_6H_4$-*p*-$CO_2C_6H_4$-*p*-$OH)$ (SRU), 113380-58-8.

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