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Chemical Disorder and Phase Separation: A Study of Two Liquid Crystal Polymers

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ABSTRACT: We have followed by optical microscopy the gradual phase separation that occurs with increasing temperature in the nematic phase of a liquid crystal polymer containing chemically disordered chains. A biphasic fluid is first observed above 250 °C displaying optically isotropic droplets dispersed in the anisotropic medium. We have estimated the isotropic volume fraction as a phase inversion to birefringent droplets in an isotropic continuum occurs over a broad temperature range. In an effort to understand the origin of phase separation we used a computer simulation which generated a population of 10 000 chemically disordered chains. In conjunction with this simulation we used the Landau–de Gennes theory of liquid crystals adapted to semiflexible chains by ten Bosch, Maissa, and Sixou. We introduce the concept of "polyflexibility", a distribution of persistence lengths, and calculate the nematic to isotropic transition temperature for the 10 000 hypothetical materials that would be generated if each of the chemical sequences were "cloned". These calculations produce a curve which is qualitatively similar to that obtained from optical microscopy measurements of isotropic volume fraction. One of the hypothetical clones was actually synthesized in our laboratory and as predicted by theory this "monoflexible" but polydisperse liquid crystal polymer is found to have a sharp nematic to isotropic transition. We conclude that polyflexibility, produced in this case by chemical disorder of the experimental system, leads to the observed gradual phase separation. It is recognized that the relation between molar mass polydispersity and polyflexibility is not universal, and therefore a broad molecular weight distribution may lead to polyflexibility in some cases. In the context of the previous statement it is also recognized that not all types of chemical disorder will lead to polyflexibility. Our observations could be relevant to other polymeric systems which do not form liquid crystalline phases such as multistructural unit polymers or mixtures of biopolymers with different chemical sequences.

Introduction

In two preceding papers we described the synthesis of a chemically ordered liquid crystal polymer and also the rather pronounced contrasts observed between this polymer and its chemically disordered isomer. One of the most intriguing observations was a very broad temperature range where birefringent and isotropic fluid coexist in the system of chemically disordered chains. In great contrast, the chemically ordered system exhibits a distinct and narrow transition from the liquid crystalline to the isotropic phase. There are no significant differences in viscosity-average molecular weight between the ordered and disordered isomers and since both are condensation polymers we do not expect drastic differences in polydispersity. Therefore chain length and/or chain length distribution did not appear to be the primary cause for phase separation. In this work we make use of an existing theory, computer simulation, and experimental observations to explore the origin of this behavior.

The theoretical concept that elongated rigid molecules spontaneously organize into orientationally ordered phases is nearly half a century old. The theories of Onsager[1] and Flory[2] describing the ordering of rodlike monomers and polymers, respectively, predict the critical molecular aspect ratios and volume fractions of rods at which liquid crystalline phases appear. The physical basis of self-ordering in these theories is the minimization of repulsive forces in condensed assemblies of rods. Later on Maier and Saupe[3] attempted to incorporate anisotropic attractive forces in the theory of liquid crystallinity. Modeling polymer molecules as rods is a serious misrepresentation of chains that should prefer to retain a finite degree of conformational entropy. In an effort to include effects related to semiflexibility in self-ordering chains, various modifications of original theories have been made. We cite here the efforts of Matheson and Flory,[4] Ronca and Yoon,[5] ten Bosch, Maissa, and Sixou,[6] and Khokhlov and Semenov.[7] The differences among these theories involve the device used to incorporate flexibility. Examples of these devices are chains composed of rods connected by freely jointed spacers, rotational isomeric models of polymer molecules, and wormlike chains. The models in which the semiflexible chains are not necessarily built by periodic sequences (i.e., wormlike chains) predict either a direct relationship between persistence length and the nematic to isotropic transition temperature ($T_{N\rightarrow I}$)[6] or a critical chain stiffness which leads to nematic phases at all temperatures.[5] In this work we have used a theoretical model to calculate transition temperatures for 10 000 different chemical sequences of a random terpolymer analogous to one synthesized in our laboratory. We have also analyzed by optical microscopy the phase separation of the experimental polymer into two fluids, one anisotropic and one isotropic. These experimental results are discussed in the context of the calculations.

Experimental Section

The materials studied in this work were an ordered chemical sequence liquid crystal terpolymer and its disordered isomer of a similar viscosity-average molecular weight. We reported earlier on the synthesis and characterization of the disordered[8] and ordered[9] polymers. These two materials were analyzed in a Leitz Laborlux 12 pol polarizing microscope equipped with a Leitz hot stage coupled to a Micristar thermocontroller. Thin films of the two materials were prepared between carefully cleaned glass surfaces. The films were approximately 1 μm thick and the glass surfaces were cleaned by using procedures described in one of our previous papers.[10] Optical micrographs of the samples were obtained as a function of temperature by using a Pentax ME Super 35-mm SLR camera. Two different photographs were taken for each microscopic image, one with crossed polars and the other only with the polarizer. The purpose of taking two photographs was to identify which black regions were air bubbles at temperatures where birefringent and isotropic fluid coexist. Conoscopic images of the black areas were utilized to verify that these regions were indeed isotropic and not caused by homeotropic alignment of the molecules (alignment perpendicular to the glass surface). Individual prints from the optical micrographs were

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analyzed for isotropic versus birefringent content. From the data we generated plots of percent isotropic phase as a function of temperature. Micrographs for quantitative analysis were obtained with a 10× objective and a numerical aperture of 0.25 yielding a resolution of 1.1 μm. We also attempted to obtain similar data using calibrated readings from a photodetector connected to the optical microscope. However, photodetector measurements were found to be unreliable since the light intensity transmitted depends on the orientation of domains. Also, defects such as those associated with Schlieren textures reduce the light output even though there are no changes in the percentage of isotropic material.

Results and Discussion

Small black droplets form within the liquid crystal phase of the disordered polymer and gradually increase in size with temperature. A conoscopic image verified that black regions were associated with the isotropic phase and not with areas of homeotropic alignment. Eventually all of the birefringent phase is consumed, leaving a completely isotropic medium. This two-phase region spans a temperature range of approximately 120 °C. In great contrast, the ordered polymer remains birefringent at all temperatures up to the clearing point and only displays a very finely speckled texture of light and dark regions during its transition to the isotropic state.

Figure 1 presents experimental results of percent isotropic phase as a function of temperature for the chemically disordered and chemically ordered liquid polymers. Data for the chemically disordered polymer were generated by using area measurements from the micrographs. Comparing data for both polymers it is obvious that they differ greatly in the sharpness of the nematic to isotropic transition. In the chemically disordered polymer isotropic and birefringent fluid coexist approximately from 250 to 400 °C, whereas a biphasic range is virtually nonexistent in the chemically ordered polymer. In Figure 1 we have included photographs showing the typical appearance in the microscope of the coexisting isotropic and birefringent regions at three different temperatures. The shape and thermal range of the curve presented in Figure 1 will certainly depend on heating rate and the resolution of the microscope. Due to constraints on working distance while using the hot stage, the highest magnification objective available is 32× with a numerical aperture of 0.6. This yields a resolution of 0.45 μm which would be essentially the smallest isotropic droplet detectable when using a light wavelength of 550 nm. We used a 10× objective in order to obtain a better average of the materials' behavior, thus eliminating localized effects and yielding a more accurate picture of biphase development. One may expect that higher resolution would shift the onset of isotropization to a lower temperature and yield an even broader temperature range.

There are still many unknowns on the details of molecular organization in the temperature range where optical microscopy reveals a homogeneously birefringent liquid. In a previous publication[11] we proposed the possibility of a "liquid fringed micelle" (LFM) structure for the birefringent liquid. In the LFM structure "chain segments" rather than "entire chains" may reside, in a dynamic sense, within ordered liquid crystalline regions versus less ordered more mobile regions. Thus, the phase separation which becomes visible by optical microscopy could be preceded at lower temperatures by this type of structure. The details remain unclear as to how an LFM-type structure would transform to an optically visible biphasic fluid. However, in the context of this manuscript the important point is that the chemically disordered system displays a much broader biphasic temperature range than the ordered-sequence polymer.

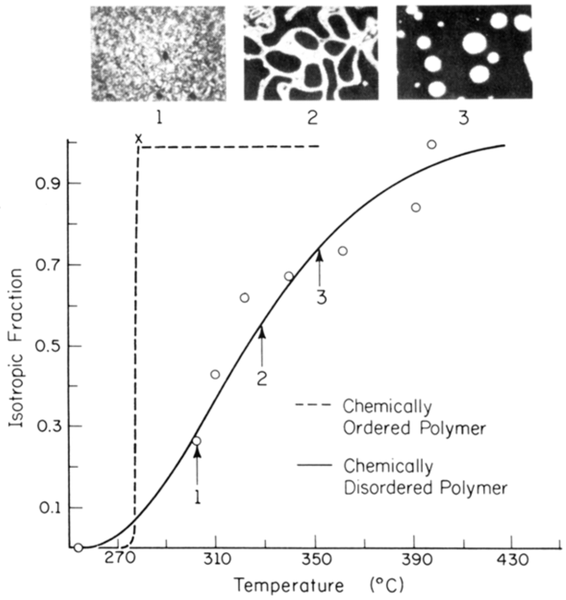


Figure 1. Fraction of isotropic phase as a function of temperature for the chemically disordered (—) and chemically ordered (- - -) liquid crystal polymers as measured by optical microscopy. The micrographs show the appearance of the biphasic fluid at three different temperatures.

As our first effort to understand phase separation over such a broad temperature range we have focused on inhomogeneity among chains in the systems of interest. The first source of inhomogeneity that occurs to a polymer scientist is molecular weight, often identified as the culprit of unusual behavior. We therefore considered molar mass heterogeneity as a possible source of phase separation into orientationally ordered and isotropic regions. We explain later in the manuscript how we treated the problem of chain length distribution. The next possibility to consider would be chemical inhomogeneity or "chemical disorder". In this context our own experimental data from high-resolution ^{13}C NMR indicates that chains in the chemically disordered system are random "at the diad level". To a first approximation our data are compatible with the currently popular characterization of these transesterifiable liquid crystal polymers as being sequentially random. If it were possible to have analytical access to structure beyond that of diads, one might discover certain preferred longer sequences. At any rate, considering the system as a collection of chemically random chains the first fundamental confrontation in trying to explain phase separation in the liquid crystalline fluid is the violation of Gibbs' phase rule. This issue has been previously raised[12] in the context that a polymer could only be considered a one-component system provided that molecular weight distribution is quite narrow or molecular weight is very high. The other possibility is to invoke variation in chemical composition among chains in order to explain phase separation. Flory pointed out in this context that if the length of chains is very great, composition heterogeneity in liquid crystal copolymers would be insufficient to promote partitioning between two liquid phases. (See reference 13 for complete quotation.) However, we point out that chain lengths in condensation liquid crystal polyesters are generally not high enough to disregard variations in composition. Thus, the chemically disordered polymer of interest here should be described as an *n*-component system, and therefore phase separation does not violate any basic principles of heterogeneous equilibrium. Considering an equilibrated system at the very low magnification of the optical microscope,

$$\mu^{i}_{\mathrm{seq}\,1} = \mu^{b}_{\mathrm{seq}\,1}$$

$$\mu^{i}_{\mathrm{seq}\,2} = \mu^{b}_{\mathrm{seq}\,2}$$

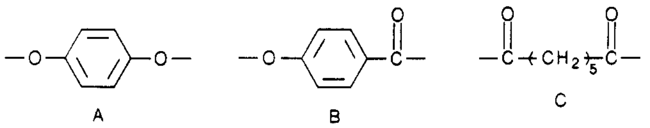
$$\mu^{i}_{\mathrm{seq}\,3} = \mu^{b}_{\mathrm{seq}\,3}$$

$$\vdots$$

$$\mu^{i}_{\mathrm{seq}\,n} = \mu^{b}_{\mathrm{seq}\,n} \qquad (1)$$

where $\mu^{i,b}$ represent the chemical potentials of n different chemical sequences in the optically visible isotropic and birefringent phases. The system might, of course, be composed of more than two phases which would add more terms to the set of equations in (1). The important point is that the n-component system has more than two degrees of freedom. Thus, in addition to molar mass polydispersity we have considered in this work the possibility that phase separation is related to the heterogeneity of terpolymer sequences. For this purpose we selected a specific model among currently available theories of liquid crystallinity in polymers. The required model was one that would relate the nematic to isotropic transition temperatures to the structure of chains in our systems. Having the model, we proceeded to calculate the predicted behavior for a system consisting of chains with aperiodic sequences and molar mass polydispersity. We point out that in the remainder of the paper we use the word polydispersity exclusively in the context of molecular weight inhomogeneity. Before describing this effort we review briefly the chemistry of the polymers studied here and the "chemical rules" that apply to their sequences.

The chemistry of the semiflexible polymers we have studied involves the structural units A, B, and C. Using



these three chemical units we have generated two macromolecular systems referred to as the ordered and disordered isomers. A schematic representation of the two isomers is shown in Figure 2. The ordered isomer system contains chains with a periodic arrangement of structural units described by the sequence $-(\mathrm{BCBACA})_n-$. As a consequence of this specific repeating sequence, the dissymmetric structural unit B has syndioregic placement within the backbone. The disordered isomer system, on the other hand, is a collection of randomly constructed chains containing the A, B, and C units connected according to the following chemical rules. These rules allow only AB, AC, BC, and BB diad combinations and sequences of B's must be enclosed by one A and one C unit (i.e., $-[\mathrm{A}-(\mathrm{B})_x-\mathrm{C}]-$. The system is therefore composed of chains having an aperiodic sequence structure and aregic placement of the oxybenzoate unit (B) within the backbone. Furthermore, a very important characteristic of the disordered system is that individual chains differ in overall chemical composition. Thus, the relative content of chemical units in these chains fluctuates about the global composition of the system. In the calculations described below we utilized a random composition distribution to "computer" generate a system of disordered chains. The only two constraints in producing this distribution are a global composition which is equimolar in A, B, and C and an equal number of A and C units in each individual chain. The purpose of this last constraint is to maintain stoichiometric balance among functional groups. Thus, using all the rules described above we have generated a representative population of 10 000 disordered chains having degree of polymerization of 50. This particular degree of polymerization was used because it represents the middle value of molecular weight in our experimental materials. We have also generated a population of chains with degree of polymerization of 150 which is a high value for these condensation polymers. The resulting populations are used to calculate the nematic–isotropic biphasic range for the disordered isomer.

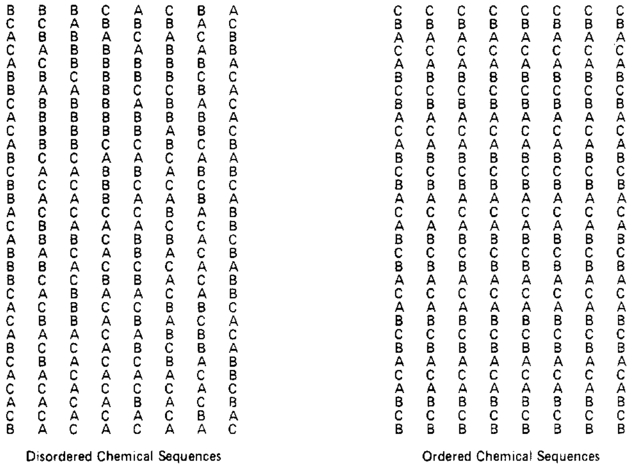


Figure 2. Chemical sequences in the ordered and disordered polymers.

Figure 3 shows a histogram indicating the fraction of chains containing various molar fractions of the oxybenzoate structural unit. The histogram reveals the spread of composition among individual chains of our computer generated population. Figure 4 corresponds to a similar histogram which reveals instead the fraction of chains containing different average lengths of oxybenzoate sequences. The histogram is a useful graphic representation of how rigidity can vary among chains in a macroscopic sample of a disordered polymer. This is suggested on the basis that oxybenzoate is the most rigid component and the only self-condensing unit in our system. Both histograms were generated by using the chemical rules described previously and a degree of polymerization of 50. As expected, distributions for degree of polymerization equal to 150 were slightly narrower than those shown in Figures 3 and 4.

As previously pointed out, current theories and recent experiments support the concept that chain length but particularly axial ratio affect the $T_{N\to I}$ transition temperature of LCP's. For example, the theoretical calculations of Ronca and Yoon produced a curve in which $T_{\mathrm{N}\to\mathrm{I}}$ transitions of semiflexible chains increase rather sharply with increasing axial ratio.[5] The qualitative aspects of these results have been verified experimentally by several research groups. The theoretical treatment of ten Bosch et al.[6] predicts that chain length affects $T_{\mathrm{N}\to\mathrm{I}}$ transition temperatures. This prediction agrees with experimental work by Blumstein et al.[14] and Asrar et al.[15] in which transition temperatures are shown to increase rapidly with chain length but reach a plateau at low degrees of polymerization. It is on this basis that we have proceeded to calculate a parameter related to the chain's axial ratio for the 10 000 different chemical sequences of our simulation. This parameter is a persistence length which we define below.

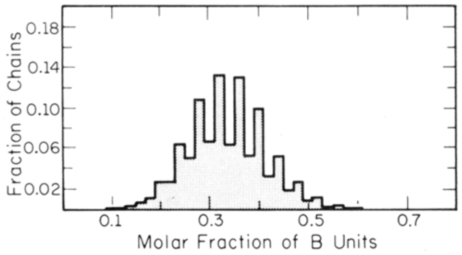


Figure 3. Distribution of oxybenzoate (B) structural units among chains of the computer-generated disordered system.

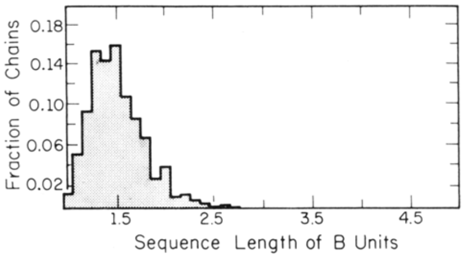


Figure 4. Fraction of chains in the computer-generated disordered system having various oxybenzoate (B) sequence lengths.

In order to calculate a persistence length for each of the 10 000 chains, we construct a set of atomic coordinates using standard bond angles and bond lengths according to the individual sequences. The mean-square end-to-end distance, $\langle R^2 \rangle$, of a particular chain is given by

$$\langle R^2 \rangle = \sum_{i=1}^{n} \langle \vec{r}_i^{\,2} \rangle + 2 \sum_{i}^{n-1} \sum_{<j}^{n} \langle \vec{r}_i \cdot \vec{r}_j \rangle \qquad (2)$$

Assuming the freely rotating chain model,

$$\sum_{i=1}^{n} \langle \vec{r}_i^{\,2} \rangle = \sum_{i=1}^{n} a_i^2 \qquad (3)$$

and

$$\sum_{i}^{n-1} \sum_{<j}^{n} \langle \vec{r}_i \cdot \vec{r}_j \rangle = \sum_{i}^{n-1} \sum_{<j}^{n} a_i a_j \prod_{k=1}^{j-1} \gamma_k \qquad (4)$$

where n in eq 2–4 represents the number of bonds in the chain, $\vec{r}_i$ is the vector representation of bond i with bond length a_i, and

$$\gamma_k = -\cos \theta_k \qquad (5)$$

where θ_k is the valence angle between bonds k and $k + 1$. The oversimplified freely rotating model is used merely as a tool to calculate the relative flexibility of the various chemical sequences in computer-generated chains. Relative flexibility is measured through persistence length, Q, which in the wormlike model is related to $\langle R^2 \rangle$ by

$$\langle R^2 \rangle = 2QL - 2Q^2[1 - \exp(-L/Q)] \qquad (6)$$

where L is the chain contour length. Thus, knowing $\langle R^2 \rangle$ and L, it is possible to determine the characteristic persistence length of the computer-generated chains. The persistence length depends on both the chemical sequence and the overall structural unit composition in each terpolymer chain. In this context we introduce the concept of "polyflexibility" which implies a distribution of persistence lengths. We consequently refer to the chemically ordered polymer as a "monoflexible" system. The histogram of Figure 5 shows the resulting flexibility distribution or polyflexibility of our system consisting of 10 000 monodisperse chains. All computer-generated chains have a degree of polymerization of 50 and the global composition of the system is equimolar in A, B, and C structural units.

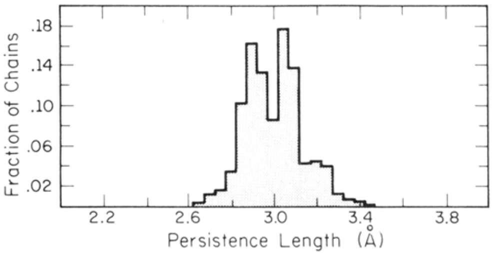


Figure 5. Polyflexibility of the computer-generated chemically disordered system. The values in this histogram are viewed as "rigidity factors" rather than actual persistence lengths (see text).

The reason why small values of persistence length are obtained is, of course, the assumption of a freely rotating chain model. We consider these values "rigidity factors" rather than actual persistence lengths. One might expect the latter to have values which are at least 1 order of magnitude higher than those obtained. The important point is, however, that a significant spread exists about the mean value of 3.10 Å (deviation ca. 20% of the average). As shown below, this polyflexibility is helpful in understanding the possible origin of phase separation.

As previously stated, the model of ten Bosch et al.[6] predicts a direct relationship between persistence length and the nematic to isotropic transition temperature ($T_{\mathrm{N}\to\mathrm{I}}$). This model adapted the Landau–de Gennes theory of liquid crystals to semiflexible wormlike chains. The free energy of a polymer chain near $T_{\mathrm{N}\to\mathrm{I}}$ is written as an expansion in the order parameter S as

$$F(S,T) = F_0(T) + A(T - T^*)S^2 - BS^3 + CS^4 \qquad (7)$$

where $F_0(T)$ is the free energy of the isotropic phase. T^* is defined by the authors as the supercooling temperature given by

$$T^* = T_{\mathrm{c}} - (B^2/4AC) \qquad (8)$$

In expression 8 T_{c} is the critical temperature for the first-order phase transition. The dependence of A, B, and C on temperature and molecular parameters can be obtained from the functional integral of the partition function for an elastic chain with orientation dependent van der Waals interactions. In the limit of long chains ($Q/L \to 0$), the coefficients of the free energy expansion are given by

$$A = \nu_\infty L/2T \qquad (9)$$

$$B = \frac{4}{945}\left(\frac{Q}{L}\right)^2 \frac{(\nu_\infty L)^3}{(KT)^2} \qquad (10)$$

$$C = \frac{1}{675}\left(\frac{Q}{L}\right)^2 \frac{(\nu_\infty L)^4}{(KT)^3} \qquad (11)$$

where ν_∞ measures the spatial average interaction energy between long chains. From eq 9–11 the supercooling temperature and T_{c} are given by

$$KT^* = (2/15)\nu_\infty Q[1 - Q/(3L)] \qquad (12)$$

$$T_{\mathrm{c}} = T_{\mathrm{N}\to\mathrm{I}} = T^*[1 + (20/441)(Q/L)] \qquad (13)$$

We have utilized eq 13 to calculate a $T_{\mathrm{N}\to\mathrm{I}}$ value for each of the "cloned" sequences. This calculation involves the use of specific values of Q and L. We treated ν_∞ as an adjustable parameter and used a single value which gave reasonable agreement with the experimental data (the value of ν_∞ does not affect the width of the biphasic spread.) We have already explained how values of Q and

Table I
Sampling of Chemical Sequences in the Disordered System

chemical sequence	calcd rigidity factor,[a] Q	calcd $T_{(N\rightarrow I)}$,[b] °C
CACACACACACACACACACABCACBABCACACBABCACACABCACBACBA	2.82	214
CACACACACBACACABCACACABCABCACACACACACACACABBCABBCB	2.86	222
ACACACACABCACACACBBACACABCBACABBCACABCABCABCACACAC	2.88	225
CABBCABCACABCACACACACABCACBABCACACBBACACABCACBBACA	2.96	239
CABCACACBBBBBBACACABCACABBCACABBCACBACACACBACACABB	3.07	257
CABCBACABCBACABCBACABCBACABCBACABCBACABCBACABCBACA[d]	3.12	266[c]
ACACACBACBBACBACACBBACACABCABCBACBBBBBBACBABCACBAC	3.16	273
BBCACACACBBBABCABBBCACBACABBCBABCBBBBABCABBCABCABC	3.33	303
ACABCABCBABBCACACBBABBBBCABBBBBCABBCACBBABCBBBBBAC	3.42	319

[a] These values are viewed as rigidity factors rather than actual persistence lengths (see text). [b] $T_{(\text{nematic}\rightarrow\text{isotropic})}$. [c] The experimental $T_{(N\rightarrow I)}$ for this sequence is 277 °C. [d] Chemical sequence of the ordered polymer.

L are obtained, and we now proceed to describe the calculation of chain-length distribution for a specific chemical sequence.

To a first approximation we expect a distribution in chain length that follows Flory statistics. It is also reasonable to assume that such statistics will prevail in both the chemically ordered and chemically disordered polymers. In fact, in a previous calculation of polydispersity in the disordered polymer we found a monotonic approach to the most probable distribution with increasing extent of reaction.[8] We therefore expect similar results in the more classical solution polymerization of the ordered chain. As far as the disordered system is concerned, unexpected molecular weight distributions might occur since its polymerization takes place in a rather complex biphasic state. Unfortunately, there is no formalism available now to address the effect of molecular environment on polydispersity. Keeping a simple approach, one can write the classical relation for condensation polymers,

$$w_i = ip^{(i-1)}(1-p)^2 \tag{14}$$

where w_i represents the mass fraction of chains of length i and p represents the extent of reaction. Using the value of p corresponding to $\bar{X}_n = 50$ and eq 14 we generated a distribution of chain length, L, for the ordered polymer. This distribution allowed us to model the effect that polydispersity has on the spread of $T_{N\rightarrow I}$ values.

We have calculated the nematic to isotropic transition temperature for each of the 10 000 chains in our computer-generated chemically disordered system. These calculations utilized the theoretical expression derived by ten Bosch et al. (eq 13) and values of persistence length obtained by the method described above. The calculated transition temperatures correspond to those of the 10 000 hypothetical materials which could be generated if each of the disordered chains were cloned. Table I contains a sampling of 10 specific chemical sequences from the computer-generated disordered system. The table also contains the corresponding values of the rigidity factor and transition temperatures for the selected sequences. It is clear that the transition points of the hypothetical systems produced by cloning the sequences vary over a broad temperature range. By examination of Table I it is obvious that B sequences raise rigidity factor values and transition points whereas long AC sequences increase chain flexibility and lower $T_{N\rightarrow I}$ values. One expects the self-condensation of oxybenzoate units to decrease the conformational entropy of chains. On the other hand, AC sequences containing only sporadic B units should produce segments that can explore many conformations. In a previous paper we had explained how $-(B)_n-$ and $-(AC)_n-$ sequences form through transesterification reactions.[8] Table I includes the calculations for the one chemical sequence produced experimentally in cloned form, namely, that corresponding to the chemically ordered polymer synthesized in our laboratory.[9]

It is interesting to envision possible average conformations for some of the 10 sequences described in Table I. Figure 6 shows possible conformations of four different sequences generated by using arbitrarily chosen isoenergetic conformers for the pimeloate unit. If individual sequences of a chemically disordered population of chains were cloned, one may infer that a broad range of molecular organization would be observed in the fluid state of the resulting systems. Some systems may organize as fluids with localized nematic arrays, others might have more classical liquid-crystalline structures and yet others may only form isotropic liquids. Inspecting the large number of chemical sequences produced by the computer simulation, one wonders what might be the thermodynamic logic that drives sequence formation in an actual polymerization. For example, specific chemical sequences can control entropy retention in single chains as the reaction proceeds. Also, the formation of specific chemical sequences might be controlled by the molecular environment around growing chains, i.e., the uniaxial field of neighboring segments.

Figure 7 shows the thermal dependence of the cumulative fraction of chemical sequences from the computer simulation that once cloned would form isotropic liquids at the temperatures considered in the graph. One curve in this graph is that of a monodisperse–polyflexible system and the other corresponds to a polydisperse system of chemically ordered chains (monoflexible system). The distribution of $T_{N\rightarrow I}$ values used to calculate the curve for the polyflexible system is shown in Figure 8. Data in Figures 7 and 8 were generated with chains having a degree of polymerization (DP) of 50. When DP is equal to 150 the results are qualitatively similar but with a slight narrowing of the biphasic spread (approximately 35 °C narrower). Regardless of the specific DP value in the range 50–150, it is clear from Figure 7 that the chemically ordered system with polydispersity exhibits a much sharper transition to the isotropic state than does the chemically disordered monodisperse system. In agreement with the statement quoted earlier,[13] as DP values increase, the phase transition of the chemically disordered polymer begins to resemble that expected for a single-component system. Nonetheless, given the results obtained at DP = 150, complete loss of chemical inhomogeneity is unrealistic given the current synthetic methods for this type of polymers. Therefore, the simulation suggests that chemical disorder in our experimental system gives rise to a chain flexibility distribution and consequently to a broad isotropization zone. In this particular system polydispersity does not seem to contribute significantly to the broad biphasic temperature range. In this context it is extremely important to appreciate the fact that a universal relationship does not exist between polyflexibility and poly-

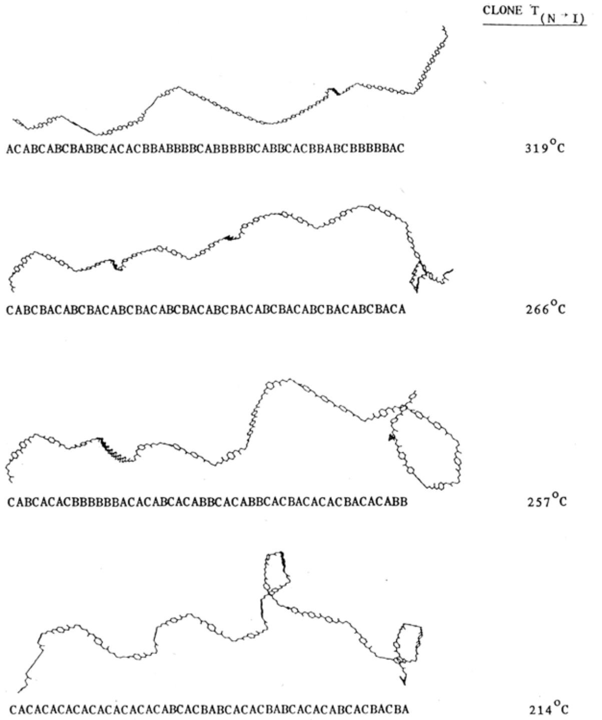


Figure 6. Schematic representations illustrate the varying flexibility of four different chemical sequences. The conformation of each pimeloate unit in all four illustrations was arbitrarily chosen from a set of isoenergetic conformational states. The second from the top corresponds to the chemically ordered sequence.

dispersity. Depending on chemical detail, polydispersity may have a profound effect on the system's polyflexibility. At the same time, chemical disorder per se may be of no consequence to polyflexibility in certain chemical sequences. An example of such sequences is that of structural units in which diads or triads make similar contributions to the conformational entropy of chains. Another example would be certain types of disordered backbone substitution by side groups. In our experimental system chemical disorder should lead to broad polyflexibility given the large differences in the number of conformers among segments of the type $-(BAC)_n-$ or $-(B)_n-$ versus $-(AC)_n-$. This concept and the simulation we have described here are consistent with our experimental observations on the chemically ordered and disordered isomers.

A number of factors need to be addressed in future work on the problem we have analyzed here. Our simulation of the disordered system involved a monodisperse but polyflexible collection of chains. Real aperiodic systems of the type we simulated are, of course, both polyflexible and polydisperse. This rather voluminous calculation would probably broaden the biphasic range even further. Another very important problem that needs to be addressed is the effect of the uniaxial molecular field in self-ordering polymers. At a given temperature the uniaxial nematic field can stabilize certain chemical sequences of the disordered system that if cloned would prefer an isotropic environment. At the same time, chemical sequences in the disordered system with high persistence length may "melt" prematurely as a result of being embedded in a molecular environment of more flexible chains. These uniaxial field effects could also contribute to the broadness of the biphasic range in chemically disordered systems and are not easily incorporated in theories of liquid crystal polymers. On the experimental side it is necessary to obtain concrete evidence that major differences in polydispersity do not exist between the chemically ordered and disordered systems. It is also important to characterize the kinetic aspects of phase separation in these systems. The curve presented in Figure 1 is most likely not an equilibrium curve and this must be considered in comparing experimental results to any simulation. One of the problems in obtaining the equilibrium curve for these high melting polymers is the possibility of chemical degradation when long isothermal time periods are required during the experiments. A similar problem is encountered in studying the behavior of the system during cooling, which is incidently quite complex. An exciting prospect for the future is the possibility of analytical chemistry on actual sequences and the possibility of chemical cloning. Finally, as far as calculations are concerned, one must keep in mind that all existing theories of liquid crystallinity in polymers still need a great deal of further development. All theories can be criticized and in carrying out calculations one inevitably stretches the limits of relatively simple models of complex problems. As a relevant example, Khokhlov and Semenov have criticized the method used by ten Bosch, Maissa, and Sixou to obtain the coefficients of the Landau–de Gennes expansion of the free energy in powers of the order parameter. In spite of current limitations, we hope that our experiments and simulation will contribute to the understanding of intriguing behavior in chemically disordered liquid crystal polymers.

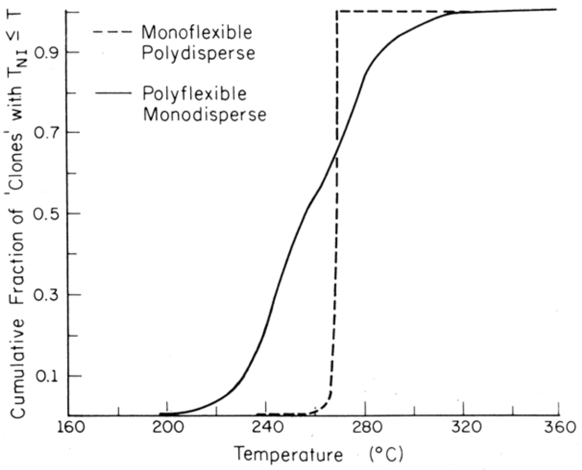


Figure 7. Cumulative fraction of hypothetical "cloned" chemical sequences above their respective nematic to isotropic transition temperature for the chemically ordered (- - -) and chemically disordered (—) systems (chemical sequences in the disordered system were generated through a computer model). Chains in the ordered system have essentially a single persistence length and a Flory distribution of molecular weight (monoflexible, polydisperse); chains in the disordered system have an identical number of structural units but a distribution of persistence lengths (polyflexible, monodisperse).

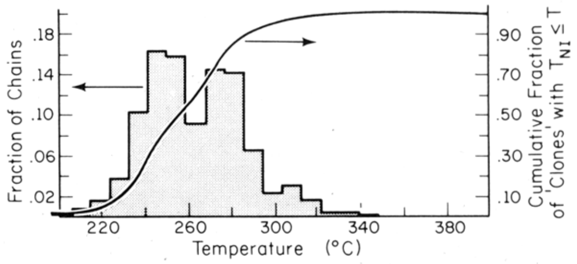


Figure 8. Histogram of the nematic to isotropic transition temperatures for 10 000 "cloned" chemical sequences generated by a computer model of the disordered system. The solid line represents the cumulative fraction of clones above their respective nematic to isotropic transition temperatures.

In closing we would like to point out the possible implications of our work in phenomena involving synthetic polymers which do not exhibit liquid crystalline order or perhaps in biopolymers such as proteins and DNA. Phase separation related to conformational characteristics of sequences in chemically disordered polymers may occur frequently but go undetected by current experimental methods. If the system does not have the molecular characteristics that lead to mesophase formation, it may fail to produce the contrast necessary for detection or may simply phase separate with exceedingly slow kinetics. Slow kinetics may occur in systems where the conformational differences produced by chemical disorder are rather small compared to those between chains in isotropic versus nematic phases. Proteins are of course very specific chemical sequences of amino acids just as DNA macromolecules have specific sequences of nucleotides. However, in biological systems proteins or polynucleotides may occur as blends of many different molecules which differ in chemical sequence but contain similar structural units. In this context, a mixture of proteins or polynucleotides becomes analogous to the chemically disordered system studied here. It is not unusual for certain amino acid or nucleotide sequences to acquire fairly extended and rigid conformations and they may therefore self-order with neighboring sequences into liquid crystalline structures. One wonders therefore if polyflexibility can be effective in phase separation among polymeric sequences in the mixtures of proteins or genes that occur in nature or biotechnological systems.

Conclusions

We conclude that the broad biphasic thermal range observed in liquid crystal polymers results from the "polyflexibility" (persistence length distribution) present in many of these systems. In the specific case of the liquid crystal polymers studied here it is postulated that polyflexibility originates from chemical disorder. Since the relation between polyflexibility and molar mass polydispersity is not universal, broad molecular weight distribution may lead directly to polyflexibility in some systems. Conversely, not all types of chemical disorder will lead to polyflexibility. The conclusions in this paper are based on synthesis and comparative analysis of ordered and disordered isomers and are supported by computer simulation and theory. This simulation allowed us to calculate the theoretical transition temperatures of 10 000 hypothetical "cloned" sequences and generated a curve which is qualitatively similar to the experimentally observed biphasic spread. We believe the concepts studied here could be useful in understanding the behavior of multistructural unit polymers and mixtures of biopolymers with specific chemical sequences.

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Registry No. (A)(B)(C) (copolymer), 102127-78-6.

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Synthesis and Characterization of a Series of Polyimides Derived from 4,4′-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]-bis[1,3-isobenzofurandione]

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ABSTRACT: The dianhydride 4,4′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis[1,3-isobenzofurandione] (6FDA)[2a] was reacted with a series of diamines, viz., 4,4′-oxybis[benzeneamine] (ODA),[2b] 4,4′-methylenebis[benzeneamine] (MDA),[2c] 4,4′-(2-propylidene)bis[benzeneamine] (IPDA),[2d] 2,7-diaminofluorene (DAF),[2e] 3,3′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis[aniline] (6FmDA),[2f] and 1,5-diaminonaphthalene (NDA),[2g] to form clear, tough, thermally stable polyimides which could be cast into clear, tough films. Characterization of these films by infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry, viscometry, density, and birefringence studies is reported.

Introduction

A wide variety of polyimides have been prepared via the general reaction of a diamine with a dianhydride with final imidization effected either thermally or chemically (Figure 1).

These durable materials exhibit high strength and thermal stability,[3] e.g., they retain usable properties at 300 °C for months and even withstand temperatures >500 °C for a few minutes. During the past decade interest in these polymers has increased in response to an increasing variety