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Oscillatory Shear Alignment of a Liquid Crystalline Polymer

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ABSTRACT: The alignment of a semiflexible main-chain liquid crystalline polymer by oscillatory and steady shear is investigated in the nematic and smectic states by rheometry and X-ray scattering. Steady shear of the nematic produces alignment in the flow direction, whereas dynamic shear produces planar alignment parallel to the flow and neutral directions. In the smectic state, alignment of the layer normal along the neutral direction was predominant—the result of various frequencies and strain amplitudes. The predominance of this alignment arises from the high degree of interlayer connectivity characteristic of main-chain liquid crystals. More surprisingly, for certain alignment procedures (those with strain amplitude *less than 5%* and moderate to low frequency), alignment of the layer normal is approximately *parallel* to the flow direction. Alignment parallel to the velocity-gradient direction was found only when another smectic form, having less interlayer connectivity, was induced by the deformation process. This study demonstrates a rich relationship between applied shear flow, phase behavior, and the molecular orientation.

Introduction

Complex fluids possess unique and interesting interrelationships between molecular order and applied flow. Several significant studies[1−5] have been made with 4-cyano-4′-octylbiphenyl (8CB), a liquid crystal that, depending on temperature, may be isotropic, nematic, smectic-A, or crystalline. The mesophases are of interest, and during shear flow, the nematic molecular director or the smectic layer normal may assume a particular orientation with respect to the principal directions defined by the flow: "A" alignment when parallel to the neutral (or vorticity) direction, "B" when parallel to the flow, and "C" when parallel to the velocity gradient. Simple arguments would predict A alignment in the nematic phase (since the viscosity for this orientation is minimal) and C alignment in the smectic phase (so that layers may slide past one another undeformed). In reality, the observed orientation depends on both shear rate and temperature. B alignment indeed is documented at the highest temperatures in the nematic phase. As the temperature approaches the (second-order) smectic transition, however, fluctuations significantly affect the viscoelastic properties of the fluid, and the molecules (and transient layer normals) align in the neutral direction.[4] This A alignment is a compromise of both the nematic, B, and the smectic, C, alignments, so that the distortion of the nematic director and the transient layer fluctuations are minimized.[4] The A alignment is also found in the smectic phase.[2] At lower temperatures (where the layered structure is more conspicuous) and lower flow rates, a mixture of A and C results.

That more pronounced smectic ordering (or greater independence between layers) favors C alignment is borne out by experiments on surfactant systems. In a lamellar L_α phase, formed in a mixture of water, dodecane, and surfactant, the neighboring membrane interfaces can more freely slide past one another and align in the C orientation at high shear rates; the layers are isotropically arranged at low rates.[2] *Polymeric* surfactant systems (PEP−PEE diblock copolymers) have also been investigated.[6−9] These studies are of dynamically sheared polymers that exhibit only two phases, isotropic and smectic. As in the case of 8CB, A alignment is found above the transition when smectic fluctuations are large. Two different alignments below the smectic-ordering transition have been accessed. At high rates and temperatures, A alignment is found. Under such conditions, local melting[7] and re-formation (by the fluctuation mechanism just described) has been proposed. Alternatively, molecular entanglements may inhibit layer sliding, as is necessary in the C alignment, at high shear rates. At low rates and temperatures, C alignment is found.

Our purpose in this study was to gain some insight into the mechanisms at work during the alignment process by investigating the alignment behavior of another layer-forming liquid that posseses unique and important characteristics. Our fluid has the same four phases as 8CB, yet the *extended-chain polymeric nature* of our molecule presents a much higher degree of interlayer connectivity than has been previously studied. Moreover, we employ dynamic as well as steady shear, and we find a significant strain dependence. Surprisingly, alignment is found even at very small strain amplitudes.

Method

The semiflexible liquid crystalline polymer, ethoxy-substituted poly[(decamethylene)−(phenylene bis(4-oxybenzoate))],

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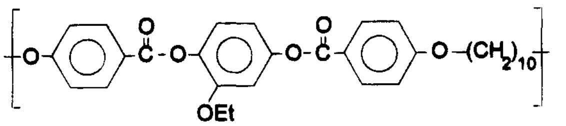
Table 1. Summary of Alignment Experiments and Results

phase	no.	M_n (kg/mol)	T (°C)	ω (rad/s)	ω_r[a]	strain ampl (%)	stress ampl (dyn/cm^2)	cycles	alignment	quality	principal variable
nematic	I	30	1450	0.2[b]		15600	1×10^3		B	v strong	steady or dynamic
	II	30	145	0.001[b]		8200	1×10^1		B	strong	
	III	5	129	1[b]		10000	5×10^2		B	v strong	
	IV	5	104	6.28	<0.06	100	1×10^4	3000	A/B		
smectic	Va	5	91.8	100	9.5	70	4×10^4	2800	A	v strong	strain amplitude
	Vb	5	91.8	100	9.5	5	3×10^4	2800	B	weak[c]	
	VI	5	73	10	10	2.5	5×10^4	2900	B	strong	
	VII	5	90	1	0.1	75	2×10^4	1900	A	strong	
	VIII	5	82	0.1	0.05	50	1×10^4	900	A (C[d])	strong	
	IX	5	73	1	1	10	2×10^4	1000	A	moderate	
	X	5	73	0.1	0.1	60	8×10^4	600	A	weak	
	XI	5	76	100	80	2.5	4×10^5	2000	A/B		ω_r
	XII	30	120	80	800	1.4	4×10^5	27500	A/B		
	XIII	5	73	10	10	7	5×10^4	2400	A/B		
	XIVa	5	74	0.8	0.8	20		700			alignment history
	XIVb	5	74	10	10	2	1×10^5	1600	A/B		

[a] Shifted frequency ($\omega_4 = \omega/\omega_x$, where ω_x is the crossover frequency). [b] Steady shear rate. [c] Very strongly A/B, but weakly B. [d] Polymorphic smectic state.

also referred to as $OQ_{OE}O10$, was identical to that used by Hudson et al.[10]



Two different molecular weights were studied: $M_n \sim 5000$ and 30 000, as determined by GPC. The number-average degrees of polymerization are approximately 10 and 60. The lower molecular weight material was used for the major portion of our study. A formal study of the phases and transition temperature for this material was done by Hudson et al.[10] The samples were compression molded at 110 °C for 5 min. The degradation was minimized by heating the material for only a short time. Later a vacuum compression mold was used to further reduce any possible degradation. No change in transition temperature was detected by DSC after several moldings and alignment operations.

Rheological experiments and alignments were conducted on a Rheometrics RMS 800 mechanical spectrometer using either parallel-plate or cone-and-plate fixtures. The plates were 25 mm in diameter and the cone had 0.1 rad angle. In each experiment, the sample was raised above the nematic-to-isotropic transition for ~2 min to produce the same disordered state at the beginning of each alignment procedure. A frequency sweep was performed first to characterize the initial state of the sample at the given experimental temperature. A maximum strain of 0.7% was used to perform all of the frequency sweeps. Alignment procedures, consisting of repeated cycles of strain at fixed frequency, are summarized in Table 1. Frequency sweeps were performed to determine the state of the aligned sample. Several frequency sweeps were performed sequentially to determine the relaxation phenomena of the aligned sample. These experiments demonstrated that the relaxation time was sufficiently long to allow cooling below T_g (38 °C) without appreciable loss of alignment. During cooling, the rheometer gap was adjusted, so that the normal force remained as small as possible. After cooling to room temperature, the solid polymer was removed from the rheometer fixture. Interfacial fracture between the polymer specimen and the stainless steel fixture was aided by use of a razor blade.

A pinhole flat-film X-ray camera was used to determine lamellar orientation at room temperature. Unless otherwise noted, the portions that were exposed were taken from the very edge of the disk, for maximum strain in the parallel-plate experiments. Two exposures were necessary to characterize each aligned sample. The X-ray beam was projected along the velocity, velocity-gradient, or neutral directions. In several cases, all three tests were done. Different types of alignments are illustrated by X-ray exposures in Figure 1. Uniaxial alignment is present in the two exposures of a highly aligned A sample (Figure 1a,b). Planar alignment is illustrated in the A/B hybrid alignment exposure (Figure 1c). Both Figure 1b and Figure 1c have similar diffuse scattering associated with lateral chain packing but they can be distinguished by differences in the smectic layer points. In Figure 1b the beam was projected normal to the layers; therefore no peaks associated with smectic layers are detected. In contrast, these peaks appear strongly as rings on the planar sample (Figure 1c).

Results and Discussion

The previously determined smectic transition temperature was confirmed to be 92 °C. A series of frequency sweeps was performed at different temperatures before alignment (Figure 2). (The frequency axis is referenced with T_g; later, in Table 1 and Figure 5, a reference temperature of 73 °C is used for convenience.) Time–temperature superposition was carried out using frequency shift factors, a_T, given by the WLF equation and the same WLF parameters ($T_g = 38$ °C, $C_1^g = 13.9$, and $C_2^g = 31$) determined during the previous study.[10] In that study, it was found that the same WLF parameters could be applied to each phase: isotropic, nematic, and smectic. The empirically determined shift factors from a wide range of temperatures in the nematic mesophase could be fit by the WLF equation. The resulting equation also predicted shift factors that accurately superposed G' and G'' in both the isotropic and smectic phases. Superposition was successful, because the experimental temperatures were sufficiently far from mesophase transitions. Here, we investigate a much narrower temperature range, in the neighborhood of the smectic to nematic transition. Failure of time–temperature superposition is now detected in both the nematic and smectic mesophases. We attribute this to temperature-dependent smectic fluctuations in the nematic phase and to changing smectic order parameter in the smectic phase. Surprisingly, G' reached a maximum value at a temperature of 88.3 °C.

The above-described frequency-shifted method is suitable for comparison of rheological tests on the same material at different temperatures. However, we also desire to compare properties of materials of different molecular weights (Table 1 and Figure 5). For this purpose, we reduce the frequency by reference to the frequency that the dynamic moduli are equal, i.e., $G'(\omega_x)$

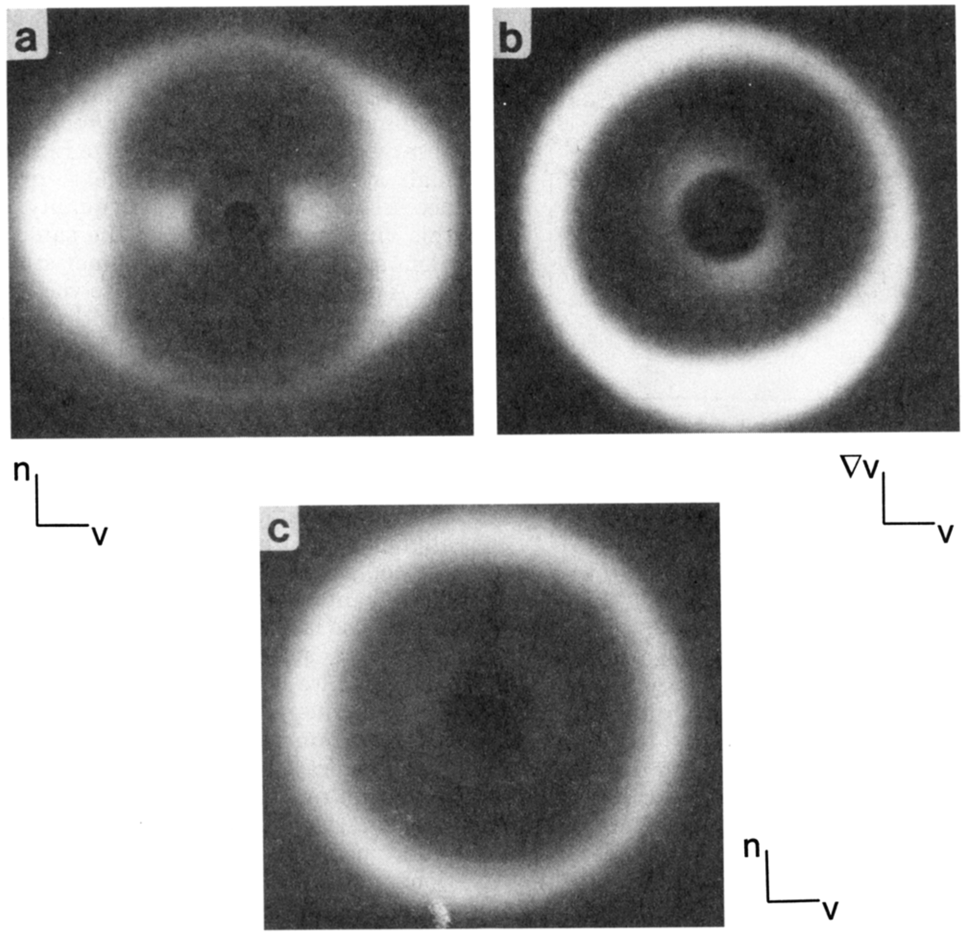


Figure 1. X-ray diffraction of two samples aligned in different orientational states. (a) For this exposure of specimen V (A alignment), the neutral direction, *n*, is vertical and the flow direction, *v*, is horizontal. The sharp streaks along the vertical axis correspond to the 003 and 006 reflections that are parallel to the lamellar normal.[10] The broad, diffuse reflections on the horizontal axis arise from liquid-like packing within the layers. (b) The same specimen V with the X-ray beam projected down the neutral axis, an axis of approximately uniaxial symmetry. The velocity-gradient direction, ∇*v*, is vertical and the flow direction is horizontal. (c) Sample XI has planar alignment, because the diffuse and sharp reflections (described in parts a and b) are both present as uniform circular arcs. The neutral direction is vertical and the flow direction is horizontal. That molecules are not also aligned along the velocity gradient is verified by other exposures.

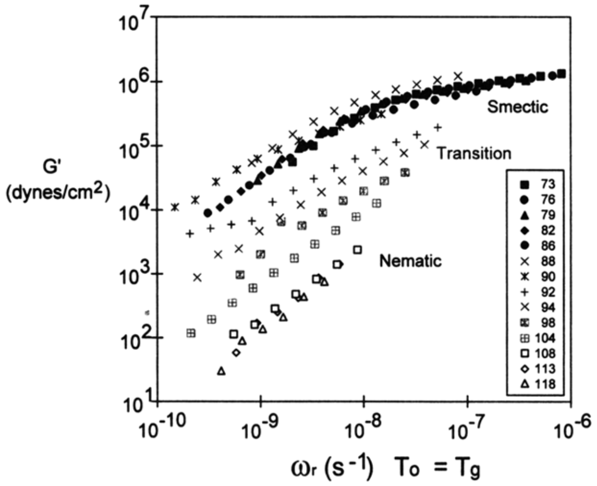


Figure 2. Elastic modulus as a function of frequency and temperature near the smectic to nematic transition. The temperature (°C) legend for each of the symbols is inset.

$= G''(\omega_x)$; $\omega_r = \omega/\omega_x$. In principle, the two methods of frequency shifting should produce identical results, and the crossover frequencies reduced by the WLF should be equal. We found $(\omega_x)_{\text{reduced}} = (0.4-1.0) \times 10^{-8}$ s^{-1}, for experimental temperatures ranging from 73 to 90 °C. The imprecision of this value is consistent with corresponding failures of time–temperature superposition in the same temperature range (Figure 2), as discussed above.

After characterization of the dynamic properties of the unaligned state, the material was subjected to various alignment procedures (Table 1). The steady-state stress of dynamic stress amplitude ranged from $\sim 10^1$ to 10^5 dyn/cm^2, depending on alignment conditions. After each alignment procedure, a change in the characteristic dynamic moduli was detected (Figure 3). The decreased values of the dynamic moduli seemed to be very stable, with little or no appreciable relaxation as determined by successive frequency sweeps after an alignment procedure was complete. We were unable to relate the exact change in the rheological data with the alignment that was produced, because such measurements will depend on both type and degree of alignment independently. We did notice some appreciable trends, however. After alignment, G' and G'' are both reduced at all frequencies. The reduction is greatest for highly aligned A-oriented samples, for which G' and G'' are shifted down by a factor of approximately 4. Similar, but smaller shifts occurred with the B and A/B alignments. We also observed that G' shifted more than G'' at the lowest frequencies (lower than those reported in Figure 3).

The type and quality of alignment were measured by X-ray scattering. We present results from the nematic state first, followed by those from the smectic state.

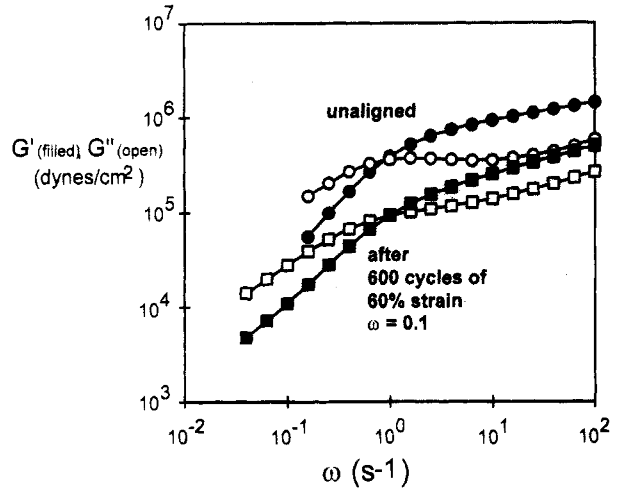


Figure 3. Comparison of the dynamic moduli before and after alignment experiment X.

Although polarized light microscopy suggests that this polymer tumbles during moderate rates of shear at temperatures below 145 °C (for example, 6 s^{-1} at 130 °C),[11,12] appreciable alignment occurs, consistent with the notion, as predicted by molecular theory,[13] that the director does not tumble at a uniform rate. Steady shear procedures I–III (Table 1) produced the B alignment, with degree of alignment related to the steady-state stress and the total strain. This is the same alignment that Safinya et al. found in the nematic phase of 8 CB.[3] On the other hand, *dynamic* shear (IV) produced planar alignment, i.e., coplanar with the velocity (v) and neutral (n) directions. We describe this as a hybrid between A and B alignments. The less specific type of alignment was produced in spite of higher applied stress (Table 1). We believe that the hybrid alignment relates to director tumbling within the sample. Molecules oriented along the velocity gradient experienced a high viscosity. These would then rotate away from this orientation to be parallel with the (v,n) plane. This process would not allow for the molecules to return to the high-viscosity state and therefore induce a hysteresis in the procedure. A similar difference in alignment between dynamic and steady shear was studied by Kambara for fiber-filled fluids.[14]

In the smectic state we observed three different alignments: A, B, and A/B hybrid. At a temperature below the smectic/nematic transition of 92 °C (and 132 °C for M_n = 30 K), we chose a variety of alignment conditions to determine what influenced the orientation of the molecules. We have found that the alignment depends on the shearing frequency. This dependence is also seen with the diblock copolymer studied by Koppi et al.[7] The other major variable in our study was percent strain. Its investigation was facilitated by using parallel plates, since the strain amplitude is a linear function of the distance from the center of the fixture. In experiment V (Table 1), two different positions within the sample were analyzed by X-ray diffraction. The portion that experienced 70% strain was found to be very highly aligned in the A orientation. On the other hand, the sample that experienced 5% strain was found to be in the B orientation! Although the B orientation in specimen Vb was not strong, a high degree of alignment resulted for specimen VI, which was aligned in a cone-and-plate fixture at 2.5% for 2900 cycles (Figure 4). The alignment in this case is better described by quasi-B alignment, because an inclination angle of approximately 20° is detected. The degree of alignment may be very sensitive to the magnitude of strain. Since experiments Va and Vb came from the same specimen, there can be little question of the strain dependence of the alignment.

In Figure 5, the results for A, B, or A/B hybrid alignments are presented in a reduced chart. We have observed that at low to moderate reduced frequency and high strain (above 10%) the A orientation can be accessed in varying degrees of quality. We can attribute this alignment behavior to the same vorticity mechanism as in the diblock copolymer study, in which only the A orientation is immune to vorticity.[7] In our case, the greater interconnectivity of the layers increases this effect. We feel that this is the reason we have not generally observed the C orientation. Extended chains are particularly destructive for the C orientation where bridged layers would need to slide across one another. Similar alignment behavior had previously been found for steady shearing of main-chain polymeric smectics.[15] In one experiment (VIII), C alignment coexisted with A alignment, but only as a minor population. Moreover, the component aligned in the C direction was transformed into a different smectic phase. In this polymorph, the layer repeat is equal to the molecular repeat. In such a smectic phase, the rigid portions of the molecule are probably segregated from the flexible spacers, thus allowing a small degree of layer sliding and thus promoting the C alignment.

At moderate to low reduced frequencies and only at low strain rates are we able to align the material in the B orientation. Although this same alignment has been found in the nematic state under steady shear conditions, there is only one other report of this type of alignment in smectic fluids. In that case, steady shear produced B alignment when the specimen thickness was less than 1 μm.[16] The present study is the first time this type of alignment has been reported in the smectic state under bulk (dynamic) shearing conditions. Generally, the B alignment is considered forbidden in the smectic state, because the lamellae are susceptible to layer compression. Therefore, there is an upward limit to the amount of strain that can be applied to the layers before they are destroyed. At moderate frequencies, we could only access the B alignment below 5% and even this was not highly aligned. The compressional strain of the lamellae would be proportional to the square of the shear strain and thus is negligible at an amplitude of a few percent. At such small amplitudes, the fact that the material is layered ceases to be most important. Therefore, as in the nematic, the lowest energy orientation is such that the molecules slide along their axis. However, if the frequency of shear is sufficiently high (experiments XI and XII), molecular relaxation within the layer is inhibited and the penalty for layer compression is amplified. The stress amplitude (Table 1) is correspondingly higher. These procedures resulted in A/B hybrid alignments—even though the strains were low, 1.4 and 2.5%. This supports the concept of the shear deformation as the destructive force that does not allow the B formation at high strain or at high reduced frequency.

The experiments that resulted in the hybrid A/B orientation create a boundary where both A and B orientations are competing against one another but no one alignment mechanism is dominant. In the high-strain case, we feel that the B-oriented lamellae are broken down by the large amount of shear deformation. In experiment XV, the sample was sheared to produce A alignment, after which it was sheared at small amplitude as an attempt to transform the orientation to the B direction. Instead, this resulted in the A/B

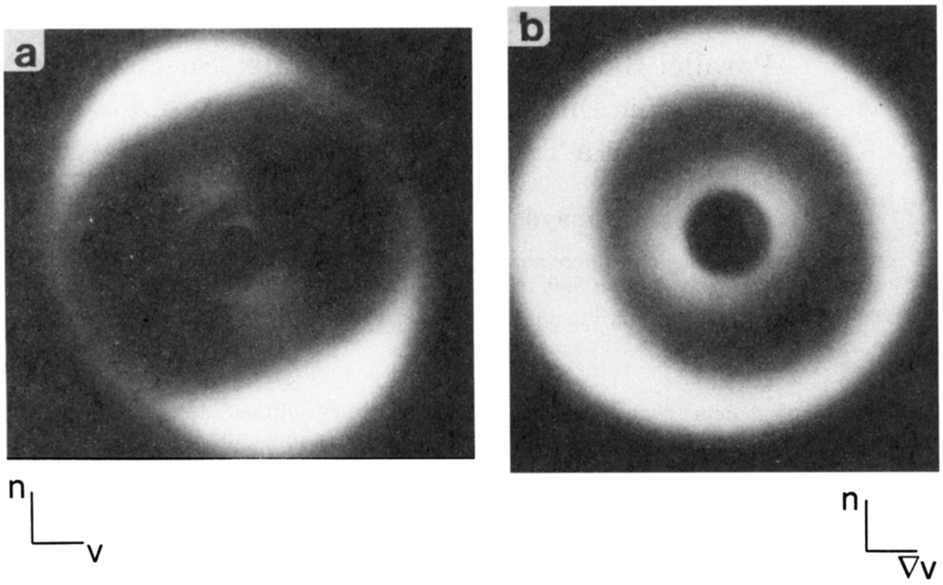


Figure 4. X-ray diffraction patterns of the quasi-B alignment of specimen VI. (a) The neutral direction is vertical and the flow direction is horizontal. Compare with Figure 1a. (b) The neutral direction is vertical and the velocity-gradient is horizontal. In this exposure, only the diffuse reflections associated with liquid-like packing are detected, because the X-ray beam (projected down the flow direction) is perpendicular to the smectic layers.

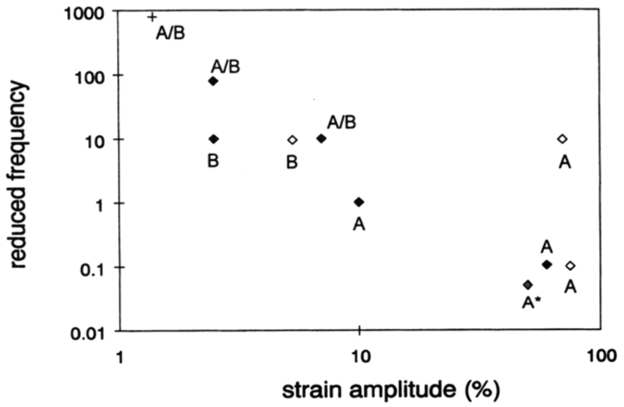


Figure 5. Alignment state as a function of applied strain amplitude and reduced frequency. The cross symbol represents the higher molecular weight material at 120 °C. The diamonds represent the lower molecular weight material: open symbols, 91 °C; shaded, 85 °C; filled, 73 °C. The asterisk denotes that a polymorphic smectic form was also present, in minor concentration and having type C alignment.

hybrid alignment. The number of cycles in the second treatment may have been insufficient to effectively complete the transformation to the A state. However, we have demonstrated that the B alignment is sufficiently strong to compete with A in producing A/B.

Conclusions

We find a wide variety of alignment behavior depending on the mesophase structure and on the frequency and amplitude of shear deformation. Comparison of the alignment attained in the nematic and smectic states proved that the smectic layering strongly affects the alignment behavior and mechanism. In the nematic state, little orientation was accomplished unless a large amount of steady shear was applied. Dynamically sheared samples were found to possess planar alignment parallel to the flow and neutral directions. On the other hand, dynamic shear produced highly aligned structures in the smectic state, even at very small strain amplitudes. At appreciable strain amplitudes and moderate rates, the A alignment was achieved. This type of alignment had been previously observed at temperatures close to the smectic transition and is said to result from minimizing the distortion of both the molecular director and layered structure. Distortion of these in other alignment states is enhanced for main-chain liquid crystals, because polymeric chains extend across the layers. Alignment parallel to the velocity gradient direction (C) was found only when another smectic form, having less interlayer connectivity, was induced by the deformation process. Most surprisingly, we find a new type of alignment in the smectic state—alignment of the layer normal nearly *parallel* to the flow direction, resulting from applied strain amplitudes of *less than 5%*.

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