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MAGNETIC ORIENTATION OF THERMOTROPIC LIQUID CRYSTAL POLYMERS

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INTRODUCTION

Thermotropic liquid crystal polymers (*LCPs*) typically contain large numbers of domains. These domains are regions of high local orientation, visible in a polarizing optical microscope, with a length scale of order 1 to 10 μm. The detailed microstructure "between" domains is not well-understood, but it is likely that the orientation is described by a continuous vector field; the direction of this vector field is highly correlated over a length of the scale characterizing the domains, with sub-micron regions of smooth transition, and perhaps with disclinations along isolated lines. The local order parameter can be of order 0.9 or greater, but the macroscopic order parameter is typically quite low because of the domain structure.

Orientation is typically induced by flow. Shear flow is an inefficient means of orienting the microstructure, and an extensional flow is usually required for high macroscopic orientation. The mechanics of deformation of the LCP melt, which is a multi-domain, (usually) nematic, viscoelastic continuum, are not well-understood; mechanical deformation experiments on the melt are difficult to control, since the stress is applied only at bounding surfaces, and complex textures are observed even in one-dimensional shear.

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LCPs can be oriented by magnetic fields; thus offering an alternative to mechanical testing as a means of probing the mechanics of microstructure development. The magnetic field is a body force, and hence acts directly on the microstructure; indeed, the 1 to 10 μm scale is optimum for inducing significant macroscopic orientation with commonly available magnetic field strengths. (Flexible chain polymers, for which the scale of the microstructure is of intermolecular or interatomic distance, do not orient in magnetic fields because the local torque exerted by the field is too small to overcome the entropy of configuration of the molecule.) The magnetic force is uniform, with a single component along a well-defined axis. The polymer can be exposed to the field in a manner enabling the study of the kinetics of orientation development and relaxation, thus providing a dynamic probe of microstructure response to deformation.

THEORY OF ORIENTATION AND RELAXATION

Low Molecular Weight Nematics

The theory of the response of low molecular weight liquid crystals to a magnetic field is well known (see de Gennes [1], for example). The equilibrium response can be obtained from a thermodynamic analysis. The free energy per unit volume, u, of a liquid crystal in a magnetic field is given by the following:

$$u = -\mathbf{B} \cdot \mathbf{M}, \tag{1}$$

where **B** is the magnetic induction (magnetic flux density) and **M** is the magnetization of the liquid crystal per unit volume. **M** is related to the applied field **H** by

$$\mathbf{M} = \boldsymbol{\chi} \cdot \mathbf{H}, \tag{2}$$

where $\boldsymbol{\chi}$ is the magnetic susceptibility of the medium. In an isotropic sample, $\boldsymbol{\chi} = \chi \mathbf{I}$, and the magnetization of the sample is proportional to the field. $\boldsymbol{\chi}$ of a liquid crystal in a magnetic field has cylindrical symmetry, and so the magnetic properties can be characterized by $\chi_a = \chi_{\parallel} - \chi_{\perp}$, the difference in the susceptibilities of the molecule oriented parallel and perpendicular to the field, respectively. The flux density **B** is related to the applied field through

$$\mathbf{B} = \mu_o(\mathbf{H}+\mathbf{M}), \tag{3}$$

where μ_o is the magnetic permeability of free space. In the cgs system, H has units of Oersted, B has units of Gauss, and μ_o is equal to unity. Nearly all organic materials, including liquid crystals, are diamagnetic but not paramagnetic or ferromagnetic. The susceptibility of diamagnetic materials is of order 10^{-7}, so $\mathbf{B} = \mu_o \mathbf{H}$. (B is somewhat less than H for diamagnetic materials because χ is lesss than zero. This is the consequence of the resistance of the electron clouds of the atoms to polarization by the field. The resistance is greatest for aromatic compounds, because the magnetic field induces a current in the aromatic ring which creates a magnetic field opposed to the applied field. The induction of current is greatest when the field lines pass through the ring. The magnetic susceptibility is therefore greater in absolute value (more negative) when the aromatic molecule is aligned normal to the field, so χ_a is positive. The sign of χ for paramagnetic and ferromagnetic materials is greater than zero; that is, the induced field B is greater than the applied field H.)

The equilibrium orientation of the director of the liquid crystal in the magnetic field can be determined by minimizing the free energy. When H is at an arbitrary angle Φ with the liquid crystal director **n**, the magnetization is (from Eq. 2)

$$\mathbf{M} = \chi_\perp \mathbf{H} + \chi_a (H\cos\Phi)\mathbf{n} \tag{4}$$

and the free energy becomes

$$u = -1/2\, \mu_o H^2 (\chi_\perp + \chi_a \cos^2\Phi) \tag{5}$$

Since $\chi_{||}<0$, the free energy of orientation of the director is a minimum when $\Phi=0$ or π; that is, when the director lies parallel to the field.

The dynamic response of a monomeric nematic liquid crystal to a magnetic field is given by the Leslie-Ericksen (L-E) equations (see [1], for example). For the case of a liquid crystal contained between two parallel walls, subjected to a pulsed magnetic field parallel to a wall and perpendicular to the easy axis of the wall (Fig. 1), the velocity is identically zero and the L-E equations reduce to

$$\gamma_1 \frac{\partial \Phi}{\partial t} = K_2 \frac{\partial^2 \Phi}{\partial z^2} + \chi_a H^2 \sin \Phi \cos \Phi, \tag{6}$$

where z is the direction normal to the wall, $\cos\Phi$ is the component of the director parallel to the field, and γ_1 is the difference between two viscosity coefficients of the L-E theory: $\gamma_1 = \alpha_2 - \alpha_3$. The left hand side of Eq. (6) represents the viscous resistance of the liquid crystal to orientation. The first term on the right hand side of Eq. (6) is the elastic resistance to orientation; K_2 is the Frank constant for twist. The last term is the orienting magnetic torque, which is given by $\partial u/\partial\Phi$. The boundary conditions for Eq. (6) are that the director at the wall is parallel to the easy axis of the wall: $\Phi(z=0) = \Phi(z=d) = 0$, where d is the plate spacing. When H is abruptly decreased from a constant value H_o to 0, the solution to Eq. (6) is

$$\Phi(z,t) = \Phi_o(z)e^{-t/\tau}, \tag{7}$$

where $\Phi_o(z)$ represents the spatial distribution at t=0 and where τ is a relaxation time:

$$\tau = \frac{\delta_1 d^2}{\pi^2 K_2} \tag{8}$$

For a typical low molecular weight nematic, $\gamma_1 = 0.1$ poise, $K_2 = 10^{-6}$ dynes, and so for $d = 10\ \mu m$, $\tau = 0.01$ s.

For the case in which H is abruptly *increased* from 0 to a constant value H_o at $t = 0$, an approximate solution to Eq. (6) can be obtained which is valid for H_o only slightly larger than the critical field H_c required for the transition; in this case the tilt angle of the molecules is small and the profile of Φ can be approximated by a sinusoid. This solution is of the form (see de Gennes [1], pp. 181-184)

$$\Phi(z,t) = a_o w(t) \sin(\pi z/d), \tag{9}$$

where

$$a_o = 2 \left[\frac{H_o - H_c}{H_c}\right]^{1/2} \tag{10}$$

and w is given by

$$w(t) = m(t)[1+m^2(t)]^{-1/2} \tag{11a}$$

$$m(t) = (\text{constant}) \times \exp\left[2(H_o - H_c)t/H_c\tau\right] \tag{11b}$$

Equation (11) describes the exponential growth of a small fluctuation ($m \ll 1$) followed by saturation ($m \gg 1$, $w \rightarrow 1 - 1/2m^2$). The time constant for each step is of order $H_c\tau/2(H_o - H_c)$.

Solutions of Rigid Molecules

A theory for the orientation of liquid crystal polymers that is based in part on the theory of dilute solutions of rigid molecules in magnetic fields is discussed later in this chapter. Literature concerning the orientation of such solutions of rigid molecules has recently been reviewed by Tenforde [2]. The equilibrium orientation is again determined from thermodynamics. The free energy of orientation of a molecule in a field is given by the integration of Eq. (5) over the molecular volume V:

$$\begin{aligned} U &= - - \iiint \frac{1}{2}\, \mathbf{B} \cdot \chi \cdot \mathbf{H}\, dV \\ &= -\frac{1}{2}\mu_o\, VH^2 \left[\chi_\perp + \chi_a \cos^2\Phi\right] \end{aligned} \tag{12}$$

where Φ is the angle of orientation of the molecule with respect to the magnetic field. The population of molecules oriented parallel and perpendicular to the magnetic field is given by a Boltzmann distribution:

$$\frac{P_{\parallel} - P_{\perp}}{P_{\perp}} = \exp\left(-\Delta U / kT\right) - 1$$

For $\Delta U/kT \ll 1$, which is appropriate for small rods and small χ_a,

$$\frac{P_{\parallel} - P_{\perp}}{P_{\perp}} = \frac{\mu_o V H^2 \chi_a}{kT} \tag{13}$$

Approximating a single molecule by a cylinder with radius 5 Å and length L = 200 Å, and with $\chi_a = 10^{-7}$, Equation (13) predicts that rods of such dimensions will remain virtually unoriented at ambient temperature; the degree of orientation as defined in Eq. (13) of such a rod is 0.00038 in a 100 kG field. This prediction is confirmed by experiment. Birefringence measurements of calf thymus DNA show that the degree of orientation is only 1% in a 130 kG field [3,4]. Several examples of assemblies of macromolecules exist that do show significant orientation, however, because the anisotropic susceptibilities of the constituent molecules are additive. One example of such an assembly is the retinal rod outer segment, which shows nearly complete orientation in fields of 10 kG or less. The kinetics of orientation have been measured for the retinal rod [5,6], and it has been shown that a balance between the drag on the rod and the torque generated by the magnetic field accurately predicts the orientation time of the rods in a dilute suspension [6,7]. This balance is given by the following expression:

$$\frac{I}{2}\frac{d^2\Phi}{dt^2} + \xi\frac{d\Phi}{dt} + \frac{\partial U}{\partial \Phi} = 0 \tag{14}$$

where Φ is the angle between the rod and the magnetic field, ξ is the drag force on the molecule, I is the moment of inertia of the rod, and U is the free energy of the rod in the field (Eq. 12). Inertia is negligible for rods of molecular dimensions, so with

$$\frac{\partial U}{\partial \Phi} = \mu_o V H^2 \chi_a \sin \Phi \cos \Phi$$

Eq. (14) reduces to a first-order differential equation with solution

$$\ln \tan \Phi(t) = \ln \tan \Phi_o - \frac{\mu_o V H^2 \chi_a t}{\xi}, \qquad (15)$$

where Φ_o is the angle at t=0. For a rod, the drag force is given by the following:

$$\frac{\pi \eta L^3}{3 \ln(2L/d)} - 1. \qquad (16)$$

Here, L is the length of the rod, d is the diameter, and η is the viscosity of the fluid. From Eq. (15) and the observed rotation time of about 4 s, the susceptibility of rod outer segments from a frog was calculated to be 9×10^{-4} cgs emu [7], which is about 4 orders of magnitude larger than χ_a for individual macromolecules.

MAGNETIC SUSCEPTIBILITIES OF LCPs

There have been several investigations into the magnetic properties of liquid crystal polymers. A recent review has been written by Noël [8]; Table 1 summarizes the measurements made by several investigators of the anisotropic magnetic susceptibilities of various polymers. The measurements reported in the table are of $\Delta\chi_g$, which is the difference in the per-gram magnetic susceptibilities measured when a sample of orientation f is oriented parallel and perpendicular to the field. $\Delta\chi_g$ is proportional to χ_a and f and inversely proportional to the density ρ [9]:

$$\Delta\chi_g = \chi_a f / \rho$$

The magnitudes of the anisotropic susceptibilities measured for the polymers are comparable to that of low molecular weight liquid crystals; for example, $\chi_a = 1.21 \times 10^{-7}$ for p-azoxy anisole at 122^0 C. Except for the investigations by Sigaud et al. [10] and Moore and Denn [11,12], the measurements were made on samples with unknown order parameters. The value of $\Delta\chi_g$ reported by Sigaud et al. was calculated from vector addition of the moments of the constituent monomers, and so it is accurate for a single molecule. Moore and Denn measured orientation from wide-angle X-ray diffraction.

Noël et al. [13] measured the magnetic susceptibility at 280^0 C of a terpolymer of terephthalic acid, methyl hydroquinone, and pyrocatechol (TA/MHQ/PC; m.p.=180^0 C) with a Faraday balance equipped with resistance heating. The Faraday balance records a force due to a magnetic field gradient induced in the sample by a strong inhomogeneous magnetic field. The device that records the force on the sample is typically a microbalance with accuracy of about 1μg, so that accurate susceptibilities of diamagnetic materials can be measured with as little as 0.05 gm. It was found that the magnetic susceptibility decreased monotonically with increasing field strength, implying increasing order at higher H (Fig. 2). There was a nearly discontinuous decrease at a field strength of about 6 kG, where the sample became translucent, implying a sharp increase in orientation. The susceptibility decreased to an asymptotic value, from which $\Delta\chi_g$ was calculated to be 1.39×10^{-7} emu cgs gm^{-1}.

The abruptness of the change in $\Delta\chi_g$ and the overall shape of the curve of Fig. 2 are reminiscent of the second-order phase transition of a ferromagnet in a magnetic field below the Curie temperature, in which the domains of the magnet "condense" by aligning with the field at a critical field strength. The equilibrium distribution of the orientations of the magnetic domains is approximately described by an Ising model, in which the magnetic moments of the domains are allowed only to be normal or parallel to the field. (For a summary of Ising models and ferromagnets, see, for example, [14] or [15].) There are of course, important differences between the magnetization theory and the orientation of LCPs. The obvious difference is that the Ising model predicts that the abrupt change in magnetization occurs at H = 0, while Noël et al. observed an offset of about 6 kG in the condensation. The comparison is nevertheless useful. The Ising

model suggests that the condensation is due to cooperative interaction between the domains. A similar phenomenon involving cooperative alignment of liquid crystal domains is presumably responsible for the shape of Fig. 2.

Hardouin et al. [16] extended the measurements of Noël and coworkers to a series of copolymers of hydroxy benzoic acid (HBA), terephthalic acid (TA) and flexible hydrocarbon linkages of length C_n, with $5 \leq n \leq 12$. It was found that the anisotropic magnetic susceptibility of the samples decreased with increasing n, with $\Delta\chi_g \approx 1.1 \times 10^{-7}$ emu cgs gm^{-1} for n=5 and $\Delta\chi_g = 0$ for n=12. This decrease must reflect a decrease in the order parameter of the polymers with longer flexible spacers, since Sigaud et al. [10] calculated that χ_a for such a linkage is expected to be about 1×10^{-7}. Finally, they noted that the orientation of the samples was nearly unchanged by cooling to room temperature.

Sigaud et al. [10] measured orientational order in $(C_{10}H_{20}OC_6H_4COOC_6H_4O)_x$ (polymer A) with a Faraday balance. The anisotropic magnetic susceptibility of the polymer was calculated using the procedures of Flygare [17], Jernigan and Flory [18], and Flory [19,20]. They assumed two extreme conformations of the flexible alkyl linkages in the calculation: in the first case, the linkages were assumed to have the same conformation as random coil alkane chains; in the other, they were assumed to have a completely ordered, all-trans conformation. It was found that the difference in the two calculated susceptibilities was approximately 10%, and χ_a was taken to be the average value of 1.25×10^{-7} emu cgs gm^{-1}. The order parameter of the polymer at the nematic-isotropic transition temperature was then measured to be $f \approx 0.60$ from Eq. (16).

Achard et al. [21] measured the anisotropic magnetic susceptibilities of polysiloxanes with phenyl benzoate side chains connected to the main chain with flexible methylene spacers containing four and six carbon atoms (PS/C_4 or C_6/PB) in a 15.25 kG field. The measured value of $\Delta\chi_g$ was found to depend on $T_{NI}-T$, where T_{NI} is the temperature of the nematic-isotropic transition. $\Delta\chi_g$ was smaller for the polymer with the C_6 spacer than $\Delta\chi_g$ of the copolymer with the C_4, although it was not clear from the data whether the decrease was due to a decrease in the order parameter, because of the additional flexibility of the side chains, or to the larger proportion of

aliphatic compounds, which have a lower susceptibility. The polymers were found to have a nematic-smectic transition, and the order of the polymer was essentially unchanged over the transition.

Martins et al. [22] measured the order parameter of copolymers of 2,2'-dimethyl-4,4'-azoxybenzene and dodecanedioic acid as a function of temperature with NMR. The melting point of a 4000 molecular weight copolymer was 100^0 C, and the nematic-isotropic transition was 136^0 C. Between these two temperatures, the order parameter induced by the 11.7 kG magnet of their NMR decreased monotonically with increasing temperature, with $f = 0.84$ at the solid-nematic transition and $f = 0.69$ at the nematic-isotropic transition. They concluded that the flexible spacers of the polymers align in the field with a degree of order comparable to that of the rigid moieties. Maret and Blumstein [23] oriented polymers of similar composition, some of which were cholesteric liquid crystals, in fields of up to 160 kG. The samples were cooled at various rates, and photographs of the X-ray patterns of the cooled samples were taken. Chiral samples did not orient in fields up to 160 kG; this was expected, since low molecular weight cholesterics with pitches comparable to the wavelength of light untwist only at fields in excess of 300 kG [24]. There was no apparent effect of cooling rate on the orientation of the nematic samples.

Moore and Denn [11,12] measured the magnetic susceptibilities of extruded pellets of two thermotropic LCPs, 80% hydroxy benzoic acid/20% poly ethylene terephthalate (HBA/PET 80/20) and 50% hydroxy napthoic acid/25% terephthalic acid/25% hydroquinone (HNATH). The susceptibilities of the pellets were measured with a superconducting quantum interference device ("SQUID"), with the pellet parallel and perpendicular to the field. The anisotropic magnetic susceptibilities were calculated by solution of the following two equations:

$$\chi_1 = f\,\chi_\perp + (1-f)(\chi_\parallel + 2\chi_\perp)/3\,, \tag{17a}$$

$$\chi_2 = f\,\chi_\parallel + (1-f)(\chi_\parallel + 2\chi_\perp)/3 \tag{17b}$$

where χ_1 and χ_2 are the magnetic susceptibilities of the pellet oriented perpendicular and parallel to the field, respectivey, and f is the order parameter of the sample. The order parameter was calculated from the

measured azimuthal profiles of the scattered X-ray intensity, corrected for background and absorption For the HNATH pellets, f was 0.80; f for the HBA/PET 80/20 pellets was 0.45.

The magnetic susceptibilities of HNATH and 80/20 HBA/PET reported by Moore and Denn are higher than those reported by other investigators for other LCPs. One reason for the difference is that, with the exception of the χ_a given by Sigaud et al. [10] for $(C_{10}H_{20}OC_6H_4...)_x$, which was calculated from the susceptibilities of the constituent monomers, the susceptibilities given in Table 1 are lower than the true values for the polymers because of their imperfect order, and they must be scaled by the order parameter. Sigaud et al. showed that the order parameter for their polymer was in the range $f = 0.6$ to 0.8, depending on $T_{NI} - T$, which accounts for a large part of the discrepancy. Another difference is that the polymers studied by Moore and Denn are more aromatic than the others in Table 1. The value of χ_a calculated by Sigaud et al. for the purely aromatic part of the polymer is 1.60×10^{-7} emu cgs gm^{-1}, or about 20% greater than χ_a for the complete polymer.

Orientation/Relaxation Kinetics

In most of the studies of the magnetic properties of LCPs listed above, the magnetic susceptibilities were monitored in time to ensure that the polymers were fully aligned with the field. In general, the time required to acheive complete alignment was found to depend on the field strength, on the temperature, and on the viscosity. Polymers with side-chain nematic groups orient quickly in general, but far from T_{NI} they orient no more quickly than main-chain LCPs. Achard et al [21] found, for example, that the nematic side chains of polymethylsiloxane oriented in a few seconds for $T - T_{NI} < 30^0$ C in a 15 kG field. For $T - T_{NI} = 40^0$ C, on the other hand, complete orientation required two hours. Two hours is about the time that Sigaud et al. [10] found was necessary to orient the linear $(C_{10}H_{20}...)_x$ polymer in a 16 kG field. They also found that orientation of the polymer in a 10 kG field required from two to four times as long.

Platé et al. [25] used a.c. electric fields to orient polymethacrylates with mesogenic side groups, $-(CH_2)_m-O-C_6H_4-COO-C_6H_4-R$, with $m = 2$ or 6 and $R =$ (for example) CN or $C_6H_4OCH_3$. The applied voltage was in the range 10

to 40 V; orientation was measured as percent optical transmittance of polarized light. The orientation time, which was typically a few seconds, was shown to increase with the degree of polymerization and to decrease with increasing temperature. The orientation kinetics were well described by a first-order rate process. The activation energy of the orientation process was found to vary somewhat from one polymer to another, but was in the range 80 to 200 kJ/mol for all samples and increased only slightly with molecular weight. The viscous flow activation energy of the polymers was in the range 70 to 90 kJ/mol.

Hardouin et al. [16] observed generally short time constants in the orientation of the TA-HBA polymers with flexible linkages. It was noted, however, that the time required to orient the polymers was much greater for higher n. Complete orientation was achieved for the n=5 polymer in one minute in a 15 kG field, while the n=9 polymer required about 2 hours. This increase may have been due to the reduced magnitude of $\Delta\chi_g$ (Table 1), but it may also have been due to the higher viscosity of the samples with larger n (1100 cp for n=5, and 7885 cp for n=9). The orientation time was also observed to increase when the intrinsic viscosity of the sample increased, which again may have been the result of an increased viscosity. For a one-minute orientation time, the minimum field required to achieve significant orientation was 4 kG for n=5 and 15 kG for n=9. No orientation was observed for n=12. The time required to orient the polymer with a C_5 spacer was only a few seconds; the polymer with a C_9 spacer required about 2 hours to orient.

Accurate times for the relaxation of structure cannot be obtained by monitoring the magnetic susceptibility while the sample is molten, since orientation is induced by the magnet used for the measurement. Some qualitative observations were made in some of the above investigations, nonetheless. Achard et al. [21] noted that the orientation induced in PMS/C_6/PB at 343^0 C, which is in the nematic range for this polymer, was virtually unchanged (<5% disorganization) after fifteen hours in isothermal conditions. Platé et al. [25], using an optical transmission technique, found that the time constants for relaxation of orientation were short, and of similar magnitude to the time constants for orientation: about 5 to 100 sec, with longer times corresponding to polymers with higher molecular weight.

Moore and Denn [11,12] measured the orientation and relaxation kinetics of HNATH and 80/20 HBA/PET in magnetic fields ranging from 1 to 63 kG. The samples were exposed to the fields for times ranging from one minute to one hour. Some samples were quenched in the field to preserve the orientation, while other samples were allowed to relax by turning off the field for up to twenty minutes before quenching. The orientation of the quenched samples was subsequently measured with wide-angle X-ray diffraction. Some of the samples were taken from polymer that had been pre-sheared between parallel plates at 100 sec^{-1} and 300^0 C for 500 strain units. X-ray diffraction is a measure of macroscopic orientation, and does not reflect the local nematic order that exists over correlation lengths ("domains") of micron size.

In general, the macroscopic orientation of the samples increased uniformly with time, and the rate of increase was greater at higher temperature. The orientation induced in HBA/PET 80/20 by the 63 kG field is plotted against temperature in Fig. 3, with time in the field as a parameter. The maximum orientation observed near 350^0 C evidently reflects a decrease in the local order because of thermal fluctuations. Order parameter as a function of field strength for the HNATH polymer at 350^0 C is shown in Fig. 4 for samples placed in the field for one and twenty minutes, while Fig. 5 shows that the effect of preshearing is to reduce the macroscopic order at equivalent conditions. The behavior of the two polymers was generally similar, although most effects were more pronounced in HNATH than in 80/20 HBA/PET. The maximum orientation in the neighborhood of 350^0 C was not observed for the latter polymer, however. Details regarding experimental technique, interaction with the supporting glass surface, etc., are discussed by Moore [11] and Moore and Denn [12].

Moore and Denn also measured the kinetics of relaxation of orientation for HNATH and 80/20 HBA/PET by orienting the samples in 63, 20, and 10 kG fields for 1, 5, or 20 minutes, and then holding the samples at temperature for up to 20 minutes before quenching. Relaxation data for HNATH at 350^0 C after orientation in a 63 kG field are shown in Fig. 6. Several features are evident. First, relaxation is not complete, and there is significant residual macroscopic orientation. Second, the residual orientation is least for the sample that spent the shortest time in the field. The bulk of the data on both polymers are consistent with these observations, but there is considerable scatter, reflecting in part the fact that each data point

represents a separate experiment. (Indeed, the fact that the 5 minute sample shows greater residual orientation than the 20 minute sample in this series of experiments reflects the experimental scatter.)

The orientation and relaxation kinetics suggest a picture of deformations in the thermotropic LCP that differs in one important respect from the theories for monomeric liquid crystals and solutions of rigid molecules discussed above. The thermotropic melt must be viewed as consisting of locally-oriented regions having correlation lengths of micron scale ("domains"), with connecting regions of nematic fluid of submicron scale in which the director vector field undergoes changes in direction. These length scales follow both from the conventional observations in optical microscopy and from the fact that micron-scale domains are required in order to achieve a magnetic torque that is sufficient to induce orientation. Thermal motions are not strong enough at these length scales to cause relaxation when the field is removed; the relaxation must, therefore, be caused by the relaxation of the stresses associated with the Frank strains induced by the deformation of the submicron-scale fluid during the orientation of the domains.

In a classical Leslie-Ericksen nematic fluid [1] the Frank strains are elastic, and complete recovery is expected. The fact that recovery is only partial, and decreases with increasing time under strain, indicates that there is creep associated with the Frank stresses, and that these stresses are viscoelastic. Moore and Denn [12] have proposed the following one-dimensional model for the orientation of the LCPs, in analogy to Eqs. (6) and (14):

$$\xi \frac{\partial \Phi}{\partial t} + \mu_o V \chi_a H^2 \sin \Phi \cos \Phi + T_F = 0 \qquad (18)$$

The reference direction for Φ is the direction of the magnetic field. V is the volume of the "domain," and T_F is the torque from the Frank stress induced by the deformation of the sub-micron scale transition fluid. For computational purposes, ξ is taken to be equal to $\pi \eta a^3$, which is the drag coefficient for rotation of a rigid sphere in an infinite Newtonian fluid [26]; in that case $V = \pi a^3/6$. η is a characteristic viscosity. The Frank stress is assumed to be instantaneously elastic, but to relax through a first order process, and hence T_F will satisfy the equation

$$\frac{\partial T_F}{\partial t} = -\frac{T_F}{\lambda} + VK\frac{\partial}{\partial t}\left[\frac{\partial^2 \phi}{\partial z^2}\right] \tag{19}$$

K is an average Frank constant. For $\lambda \to \infty$, Eqs. (18) and (19) reduce to Eq. (6) for classical nematic liquids with $\eta = \gamma_1$ and $K = K_2$.

For computational simplicity it is assumed that $\partial^2\phi/\partial z^2$ scales with ϕ/a^2; within a scale factor, Eq. (19) is then replaced with

$$\frac{\partial T_F}{\partial t} = -\frac{T_F}{\lambda} + \frac{VK}{a^2}\frac{\partial \phi}{\partial t} \tag{20}$$

Equations (18) and (20) are therefore a pair of coupled ordinary differential equations because of the assumption of spatial uniformity. An unoriented sample at rest will have $T_F = 0$, $f = (3\cos^2\phi - 1)/2 = 0$, and these are taken as initial conditions for simulations of the experiments.

The model is crude, but it does contain the essential features observed in the experiments when λ is taken to be in the range 20 to 60 minutes. A typical simulation is shown in Fig. 7 for orientation in a 10 kG field for twenty minutes, followed by relaxation for twenty minutes prior to quenching. Each data point for HNATH and HBA/PET polymers represents a different experiment. The values of $a = 1.5$ μm, $\eta = 1000$ p, and $K = 10^{-6}$ dynes are representative of the polymers, while $\chi_a = 3.39\times10^{-7}$ emu cgs is the measured value for HNATH.

IMPLICATIONS CONCERNING CONTINUUM RHEOLOGY

The domain structure is a prominent feature of the liquid crystal polyesters. Zachariades et al. [27] found that the microstructure of 80/20 HBA/PET consists of lamellar domains 30-40 μm in diameter with thickness 200-400 Å. Viney et al. [28] observed threaded textures with length scales of about 3 μm in 60/40 HBA/PET, and Mackley et al. [29] made similar observations. The number of disclinations increases with shearing [30], and hence the correlation length ("domain size") decreases; this is consistent with the reduced magnetic orientation of sheared samples, and forms the basis of viscosity models by Marrucci [31] and Wissbrun [32]. Marrucci found that the deviatoric stress associated with a polydomain liquid crystal

is approximately given by the following:

$$\tau = K \left[\frac{1}{a^2} - \frac{1}{a_o^{\,2}}\right] \tag{21}$$

where a_o is the linear length scale of a domain before flow, a is the size during flow, and K is an average Frank elastic constant. The model explains the transition observed in lyotropic LCPs by many authors [33] from shear-thinning behavior to a Newtonian plateau at intermediate shear rates. Wissbrun [32] modified Marrucci's model to include breakdown of the domain structure during flow. The predictions of the latter model are essentially the same as those of Marrucci, except that where the Marrucci model predicts nearly perfect alignment of the LCP at the transition point, Wissbrun's model predicts a smooth transition to a Newtonian plateau and that the molecules will remain substantially unoriented. Both models predict a $1/a^2$ dependence of the stress on the domain size.

The magnetic field experiments are consistent with the notion that the continuum stress in a LCP is largely a consequence of the deformation of the polymer in the transition zone between regions of high director correlation, and that these stresses can relax; the correlated regions will flow as solid bodies, though the correlation length scale will change. The stress in a Leslie-Ericksen nematic liquid is given by

$$\tau = -pI + \tau_F + \tau_D \tag{22}$$

p is an isotropic pressure. τ_F is the Frank stress; in the classical L-E theory this stress is elastic, and is given by

$$\tau_F = -\frac{\partial W}{\partial \nabla n} \cdot \nabla n \tag{23}$$

where W is a free energy function that is quadratic in the components of gradients of the director, $\nabla \mathbf{n}$, leading to the three Frank elastic coefficients. (Equation 21 is a one-dimensional approximation to this term.) The approximately first-order stress relaxation observed in magnetic field experiments suggests that τ_F in a LCP is approximately given by

$$\frac{\mathcal{D}\tau_F}{\mathcal{D}t} + \frac{1}{\lambda}\tau_F = -\frac{\mathcal{D}}{\mathcal{D}t}\frac{\partial W}{\partial \nabla \mathbf{n}} \cdot \nabla \mathbf{n} \tag{24}$$

where $\mathcal{D}/\mathcal{D}t$ is a properly-invariant derivative. The parameter λ would be expected to increase with decreasing mobility of the chain. τ_D is the contribution to the continuum stress from a uniform director field; it corresonds to the Ericksen Transversely Isotropic Fluid [34] in the L-E theory, but is probably better approximated by the Doi theory [35,36] in the case of LCPs.

These equations can be solved for a given initial director field. What is missing, even at this elementary level, is a statistical theory that can account for a non-deterministic initial director field. It is not clear to what extent a theory of disclination formation needs to be incorporated in order to account for the apparent decrease in the size of domains with increasing shear.

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CAPTIONS FOR FIGURES

Fig. 1. Orientation of a nematic by a magnetic field. Y is the easy axis of the wall.

Fig. 2. Magnetic susceptibility of TA/MHQ/PC vs. field strength (after Noël et al. [13]).

Fig. 3. Effect of temperature on the orientation kinetics of 80/20 HBA/PET for H = 63 kG (after Moore and Denn [11,12]).

Fig. 4. Order parameter vs. field strength for HNATH after one minute and 20 minutes in the field (after Moore and Denn [11,12]).

Fig. 5. Order parameter vs. field strength at 339^0 for sheared and unsheared samples of HNATH (after Moore and Denn [11,12]).

Fig. 6. Relaxation kinetics of HNATH at 350^0 C from order induced by a 63 kG magnetic field (after Moore and Denn [11,12]).

Fig. 7. Orientation and relaxation kinetics of HNATH and 80/20 HBA/PET at 339^0 C after a 20 minute exposure to a 10 kG field. Parameters for the model predictions were H = 10 kG, a = 1.5 μm, η = 1000 poise, λ = 1 hr., and $\chi_a = 3.39 \times 10^{-7}$ (after Moore and Denn [11,12]).

Table 1
Anisotropic Magnetic Susceptibilities

Polymer		$\Delta\chi_g$ (emu cgs g^{-1})	Investigator
TA/MHQ/PC		1.39×10^{-7}	Noel *et.al* [13]
$(C_{10}H_{20}OC_6H_4..)_x$		1.25×10^{-7}	Sigaud *et.al.* [10]
HBA/TA/C_n	n		Hardouin *et.al.* [16]
	5	1.10×10^{-7}	
	7	0.90×10^{-7}	
	9	0.48×10^{-7}	
	12	0	
PMS/C_6/PB	$T_{NI}-T$		Achard *et.al* [21]
	80	1.3×10^{-7}	
	40	1.0×10^{-7}	
	20	0.8×10^{-7}	
	10	0.7×10^{-7}	
HBA/PET 80/20		2.14×10^{-7}	Moore and Denn [11,12]
HNATH		2.67×10^{-7}	Moore and Denn [11,12]

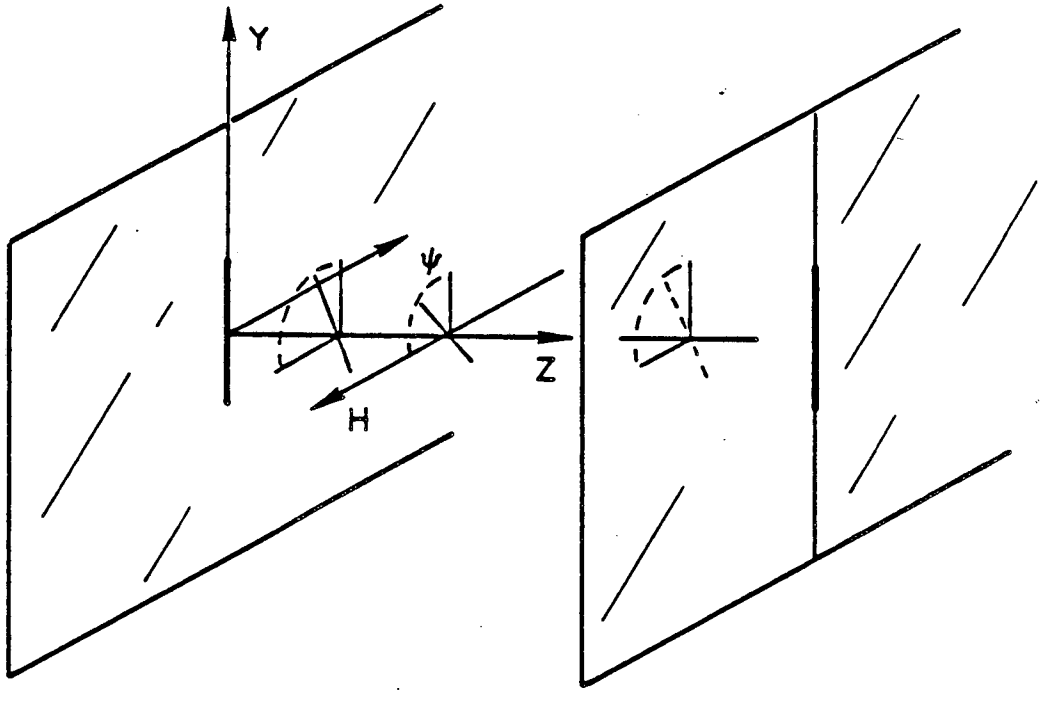

Figure 1

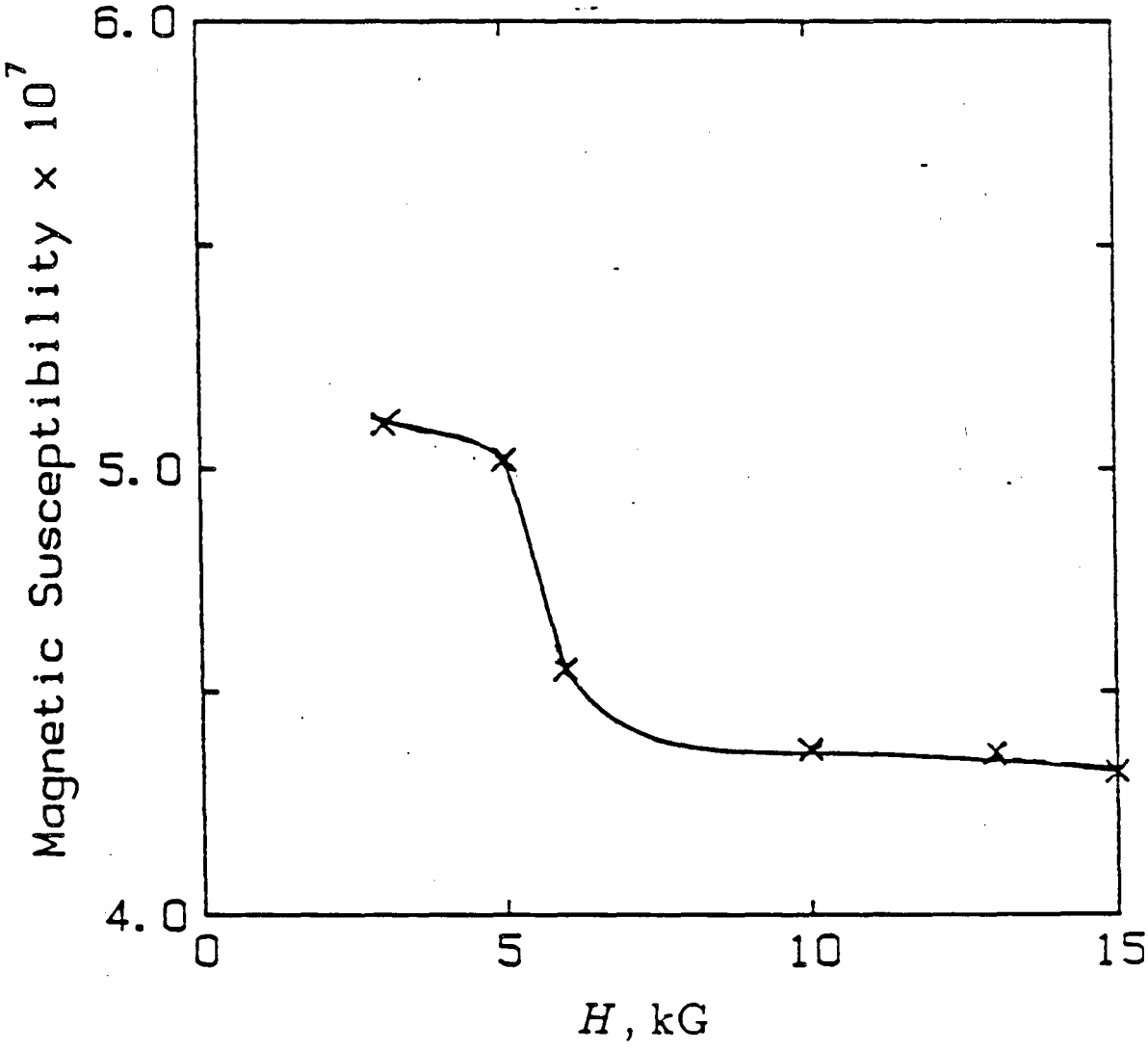

Figure 2

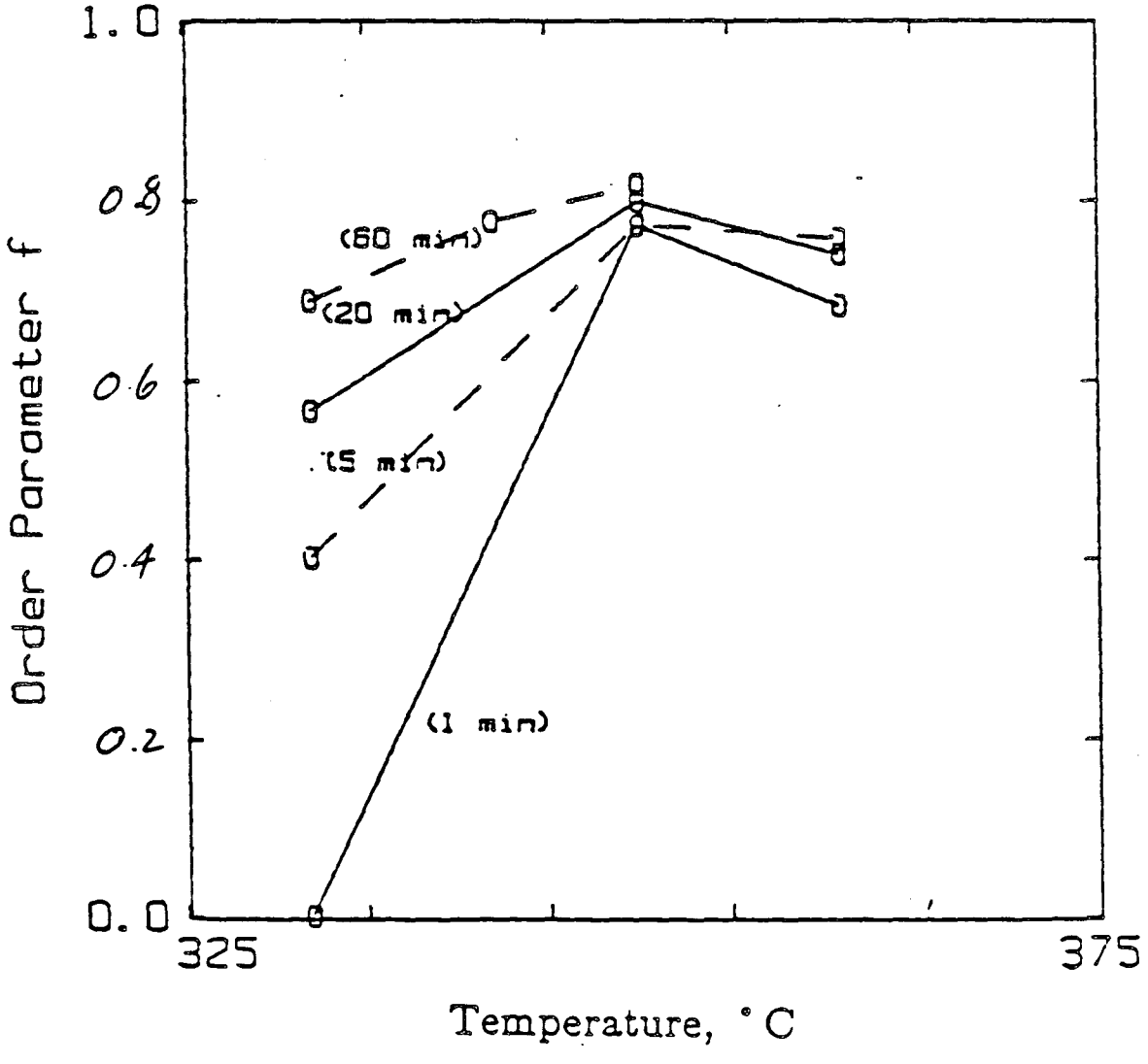
1.0
0.8
0.6
0.4
0.2
0.0
Order Parameter f
(60 min)
(20 min)
(5 min)
(1 min)
325
375
Temperature, °C

Figure 3

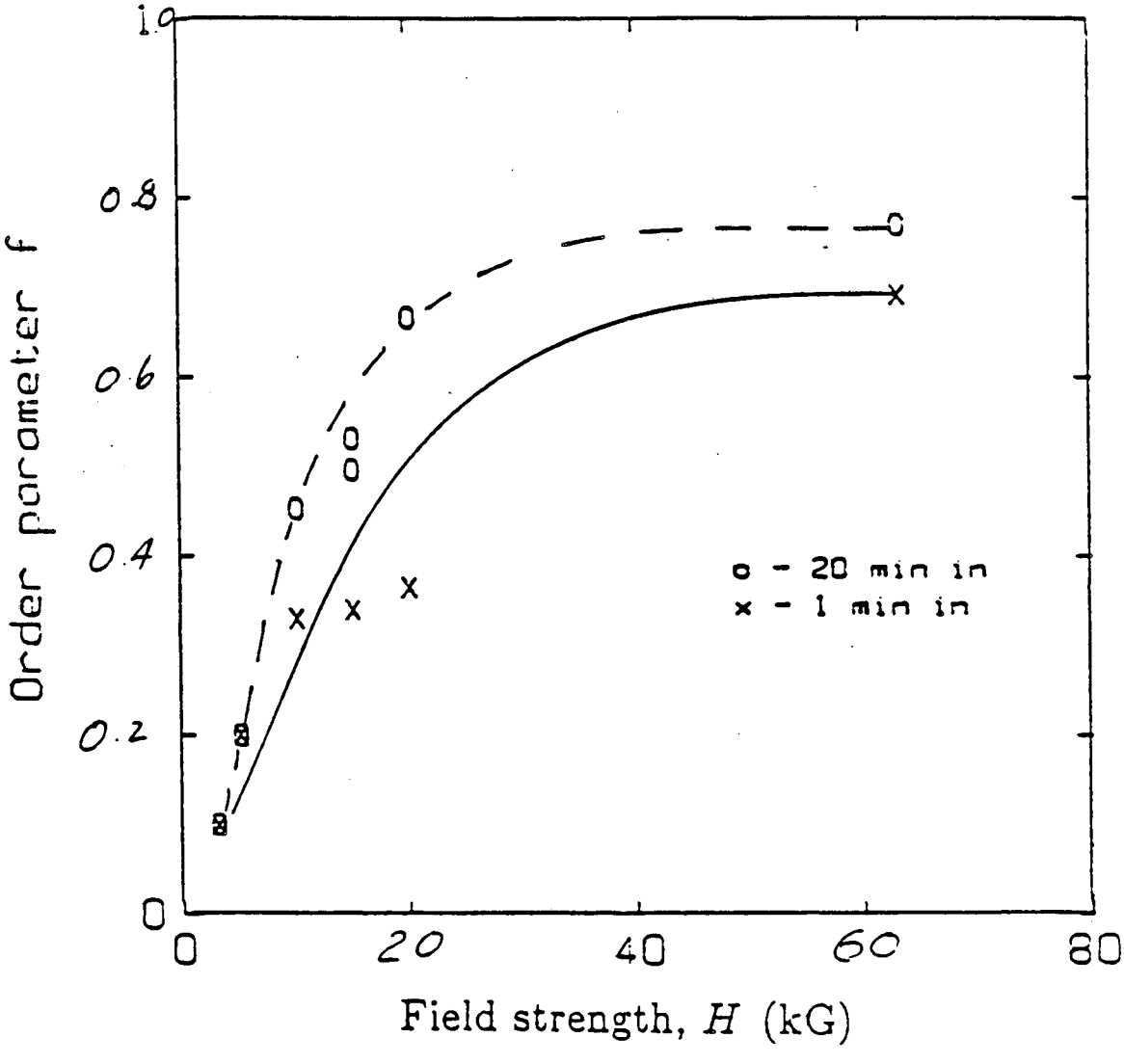
1.0
0.8
0.6
0.4
0.2
0
Order parameter f
0
20
40
60
80
Field strength, H (kG)
o - 20 min in
x - 1 min in

Figure 4

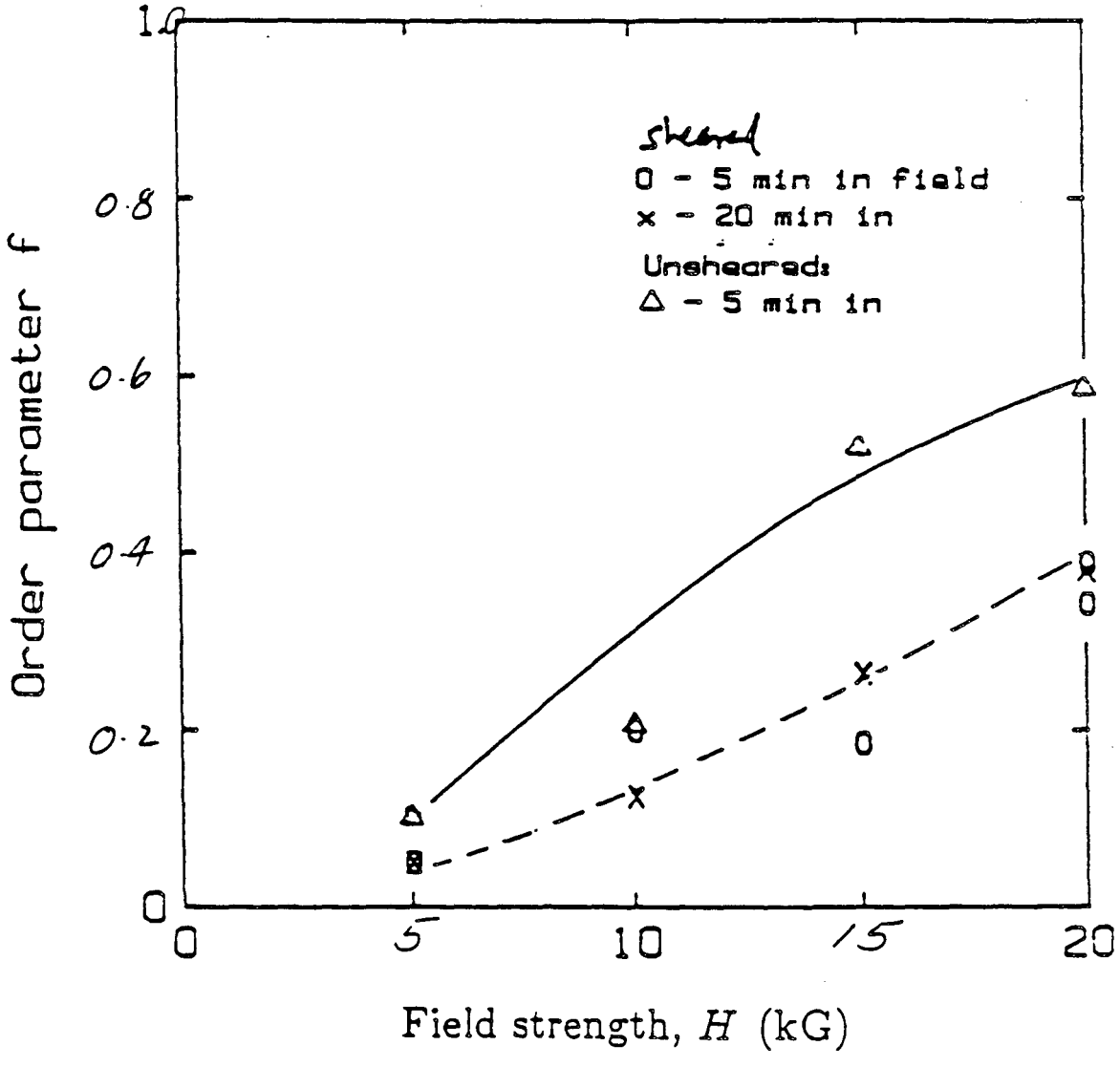
sheared
0 - 5 min in field
x - 20 min in
Unsheared:
Δ - 5 min in
Order parameter f
Field strength, H (kG)
0
0.2
0.4
0.6
0.8
1.0
0
5
10
15
20

Figure 5

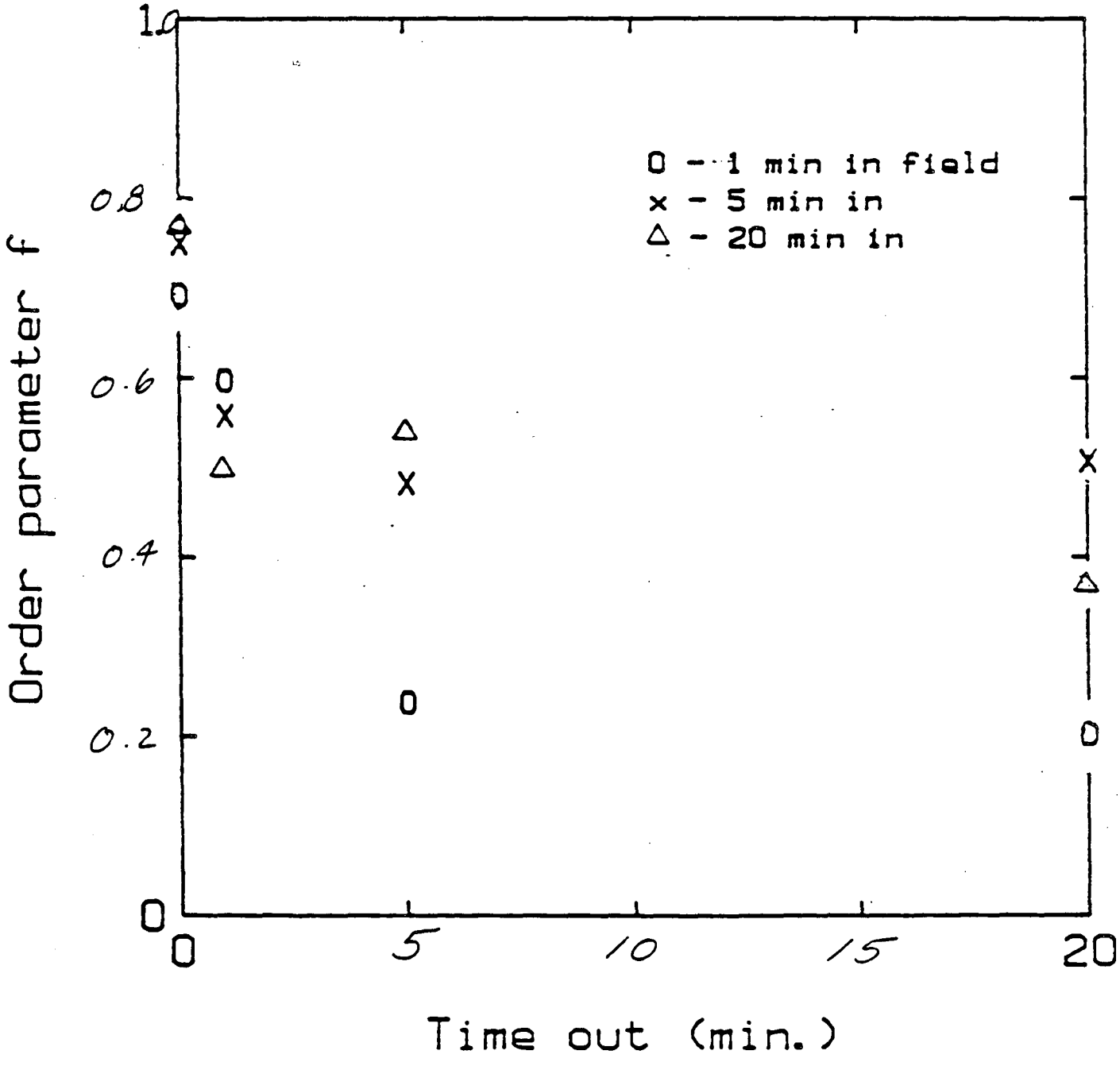
1.0
0.8
0.6
0.4
0.2
0
Order parameter f
0 - 1 min in field
x - 5 min in
Δ - 20 min in
0
5
10
15
20
Time out (min.)

Figure 6

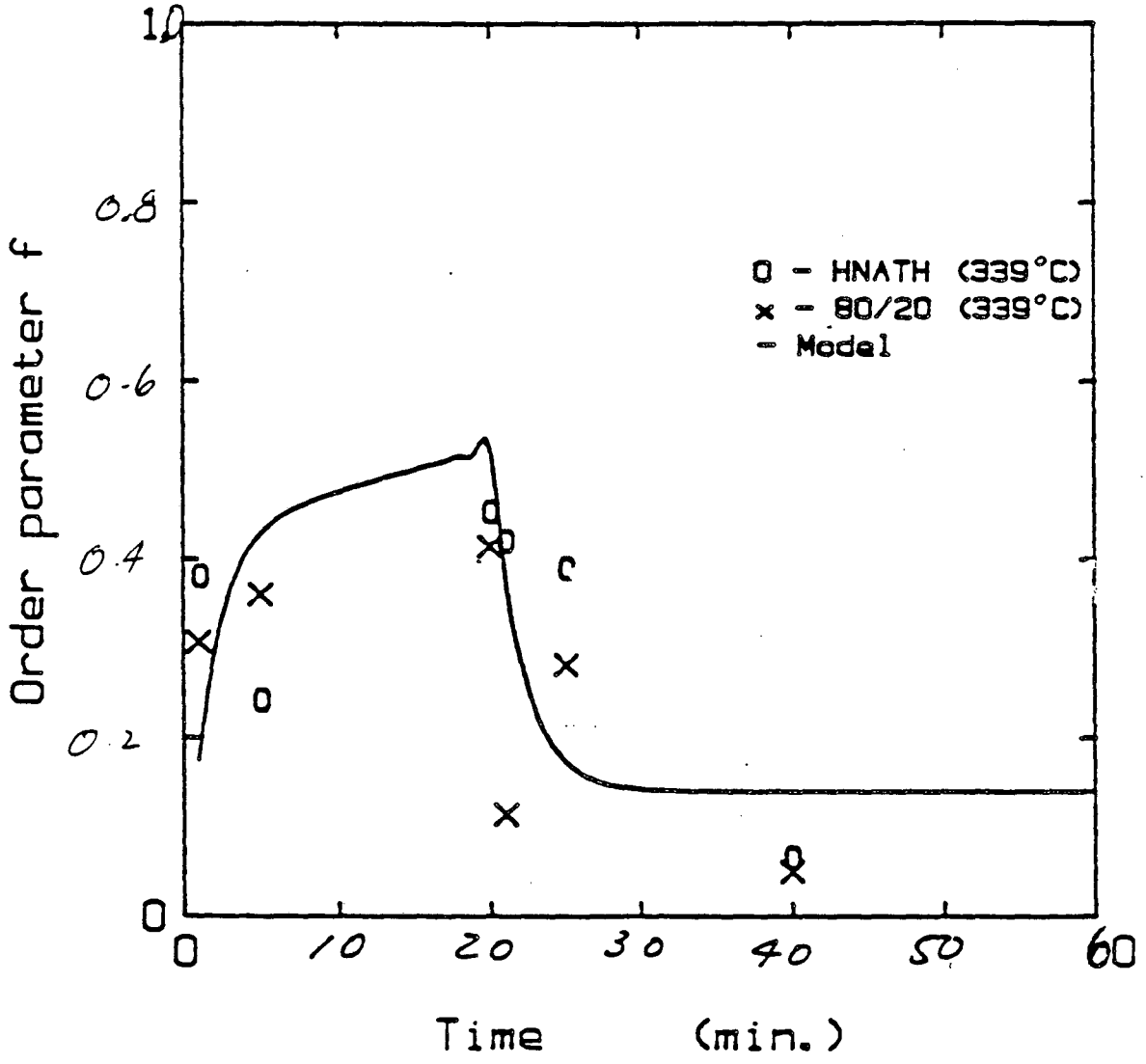
1.0
0.8
0.6
0.4
0.2
0
Order parameter f
0 - HNATH (339°C)
x - 80/20 (339°C)
- Model
0
10
20
30
40
50
60
Time (min.)

Figure 7

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