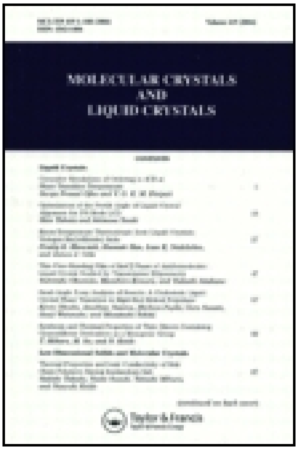

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A Pulsed NMR Study of Ionic-Conduction Induced Flow Alignment in Nematic Liquid Crystals

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A Pulsed NMR Study of Ionic-Conduction Induced Flow Alignment in Nematic Liquid Crystals†

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Nematic liquid crystals with negative dielectric anisotropies align with the nematic director approximately parallel to a low frequency electric field due to the presence of ionic impurities. The movement of these ionic impurities produces shear in the medium. Theoretical expressions for hydrodynamic flow in the presence of shear predict that the nematic director will rotate to make a small angle with respect to the direction of shear flow. Nuclear magnetic resonance techniques are used to determine both this "flow alignment angle" and to determine the molecular order and orientation as a function of time after the sudden application of an electric field.

INTRODUCTION

When nematic liquid crystals with negative dielectric anisotropies are exposed to electric fields, the resulting alignment depends upon the frequency of the applied field. At high frequencies the dielectric torque on the molecules causes them to align such that the director is perpendicular to the field. Below some cut-off frequency the movement of ionic impurities produces a shear-torque on the moelcules and the resulting alignment is such that the director makes some small angle (the flow alignment angle) with respect to the electric field.

Nuclear magnetic resonance (NMR) provides a good tool for determining the orientation of nematic liquid crystals. The proton NMR

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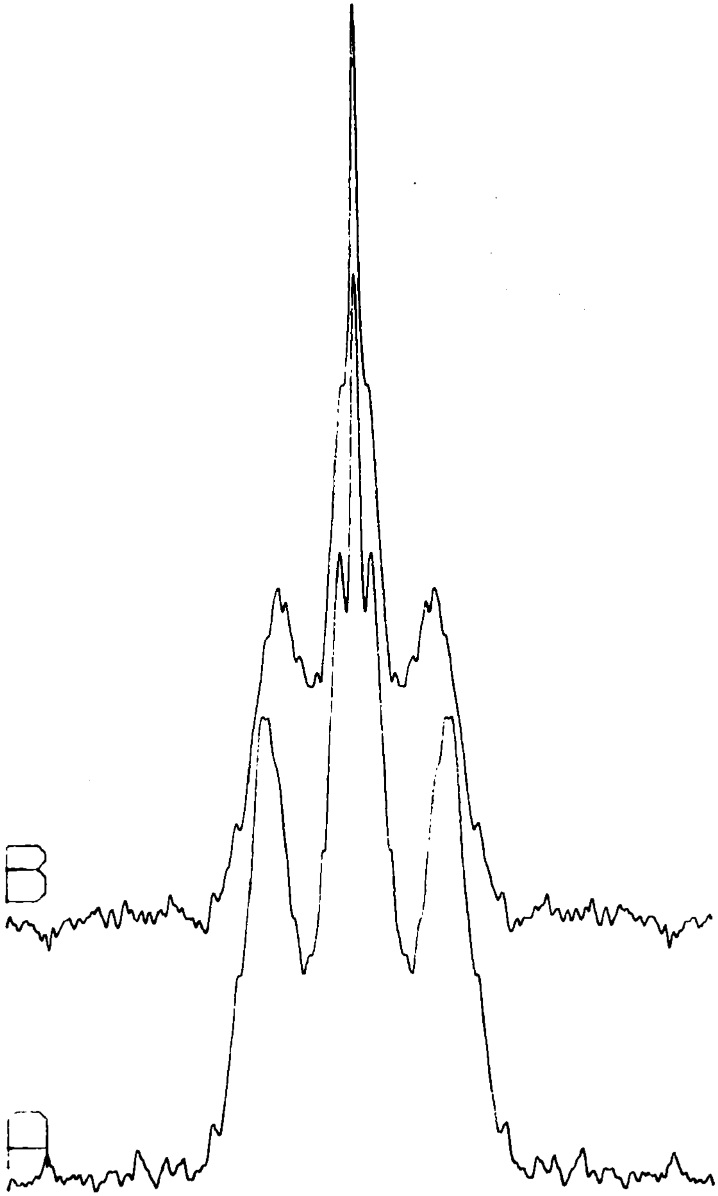

FIGURE 1 PAA at 129°C. a. No electric field applied. b. Electric field applied, showing equilibrium flow alignment as indicated by decrease in peak splitting.

spectrum of a typical nematic consists of three well-separated peaks as shown in Figure 1a. The central peak is due to protons in positions in which the dipolar interactions with neighboring protons are motionally averaged. The two symmetric side peaks arise from a strong unaveraged dipolar interaction between adjacent protons on benzene rings whose internuclear vector lies along the molecular axis.

The para-axis of the benzene rings usually makes some small angle with respect to the molecular axis. The rapid molecular motions are such that there is cylindrical symmetry of the para-axis about the molecular axis and of the molecular axis about the director. The dipolar interaction between the phenyl protons is proportional to

$$P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$$

where θ is the angle between the director and the external magnetic field Ho, which is applied in an NMR experiment. One can thus monitor the orientation of the director by observing changes in the splitting of the side peaks. If the director makes some angle θ with respect to Ho, then the splitting can be written

$$\Delta\omega = \Delta\omega_0\left[\frac{1}{2}(3\cos^2\theta - 1)\right]$$

where $\Delta\omega_0$ is the splitting when $\theta = 0$.

According to the theory of flow-alignment developed by Helfrich,[1] when a shear-force acts upon a nematic it experiences a torque which depends upon the shear-torque coefficients K_1 and K_2 and the shear rate. At some angle α measured with respect to the direction of velocity, this torque is zero and α can be determined from

$$\tan^2\alpha = -\frac{K_1}{K_2}$$

In the case of ionic conduction-induced flow alignment, space charge accumulates in defects in the material. These charges interact with the electric field to shear the medium and macroscopic flow cells are produced.

In an NMR experiment done on MBBA by Tarr and Carr,[2] a D.C. electric field was applied parallel to the magnetic field. The results showed large well-aligned regions making some small angle with respect to the magnetic field and thus with respect to the direction of flow of ions. Using a 50 Hz A.C. electric field we have obtained similar results for PAA as shown in Figure 1.

EXPERIMENTAL DETAILS

The liquid crystal samples were contained in a glass sample cell of square cross section approximately 1 cm on a side. Within the cell were two sets of interleaved platinum plates separated by two slotted teflon spacers. The distance between plates was 1.07 mm. The cell was situated in the magnetic field so that the electric field and magnetic field were parallel. For PAA the electric field had an rms amplitude of 3000 V/cm and a frequency of 50 Hz while the magnetic field had an amplitude of approximately 2.3 kG corresponding to a proton Larmor frequency of 10 MHz. The electric field applied to MBBA had an rms amplitude of 4000 V/cm and a frequency of 30 Hz. The magnetic field applied was approximately 7 kG corresponding to a proton Larmor frequency of 30 MHz.

The object of the experiments was to monitor the orientation of the director in PAA and MBBA as a function of time after the onset of an electric field. Both materials have positive diamagnetic anisotropy and were thus initially well aligned with the director parallel to the external magnetic field.

The pulse sequence used to acquire the data is shown in Figure 2. Initially a comb of 90° pulses 50 ms apart was applied to bring the magnetization to an equilibrium value. A pulse to the electric field apparatus turned on the electric field. After an adjustable delay a set of 5 90° pulses was applied, again separated by 500 ms. After each of these 5 pulses the free induction decay (FID) of the magnetization was digitized and stored in memory. A final pulse turned off the electric field and the sample was allowed to return to its original orientation parallel to the magnetic field. This entire sequence was repeated 50 times for the purposes of signal-averaging.

The delay between the onset of the electric field and the data acquisition was varied from 31 ms up to 3 to 4 seconds. A lower limit on the delay of 6 ms was determined by the time necessary to reprogram the programmable pulser. Each signal-averaged FID was Fourier transformed to produce an NMR absorption spectrum corresponding to each time.

In earlier experiments[3,4] the orientation of a nematic in competing electric and magnetic fields was fit to a model in which the liquid

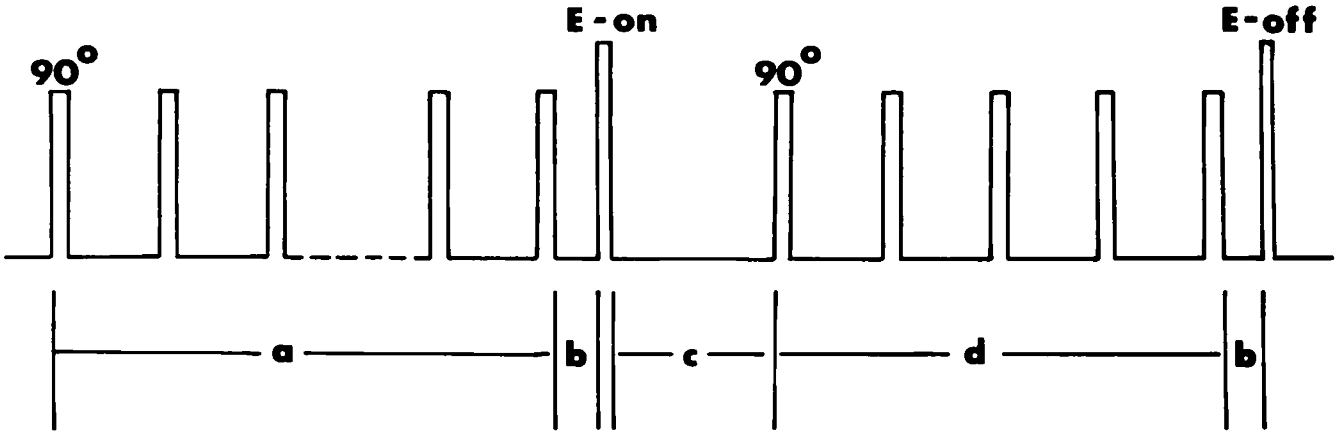

FIGURE 2 Pulse sequence for data acquisition. a. Comb of 90° pulses to bring magnetization to equilibrium value. b. Reprogramming delay. c. Initial adjustable delay of data acquisition. d. 5 90° pulses to monitor magnetization as a function of time following application of electric field.

crystal molecules were assumed to fall into one of three groups: those aligned with director parallel to the magnetic field, those aligned with director perpendicular to the magnetic field and those aligned with director at random orientations. A similar model was used to fit the data in the present experiment. In the new model a fourth possible group was added, molecules with director oriented at the flow alignment angle.

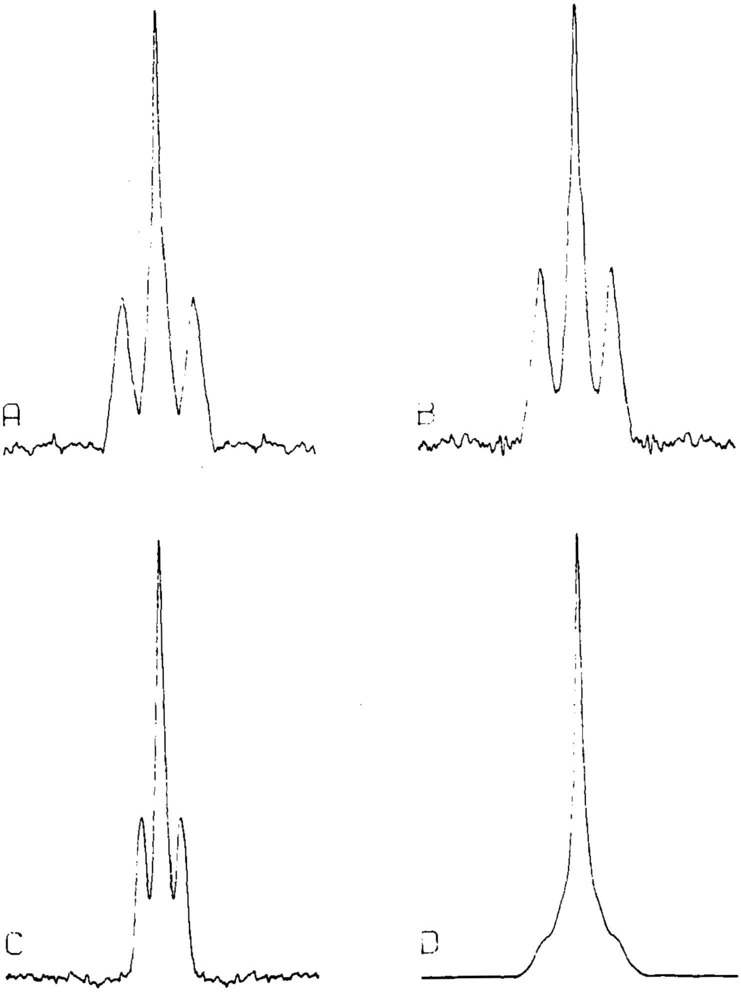

FIGURE 3 PAA at 129°C. a. Director parallel to magnetic field. b. Director at calculated flow alignment angle. c. Director perpendicular to magnetic field. d. Random orientation of director.

RESULTS AND CONCLUSIONS

Time-dependent data were taken for PAA at three temperatures, one below the solid-nematic transition temperature in which there was flow alignment in a supercooled state and for MBBA at a single temperature. The data were least squares fit to four normalized spectra corresponding to the four groups. These spectra are shown in Figure 3 for PAA and in Figure 4 for MBBA. The results of the fit

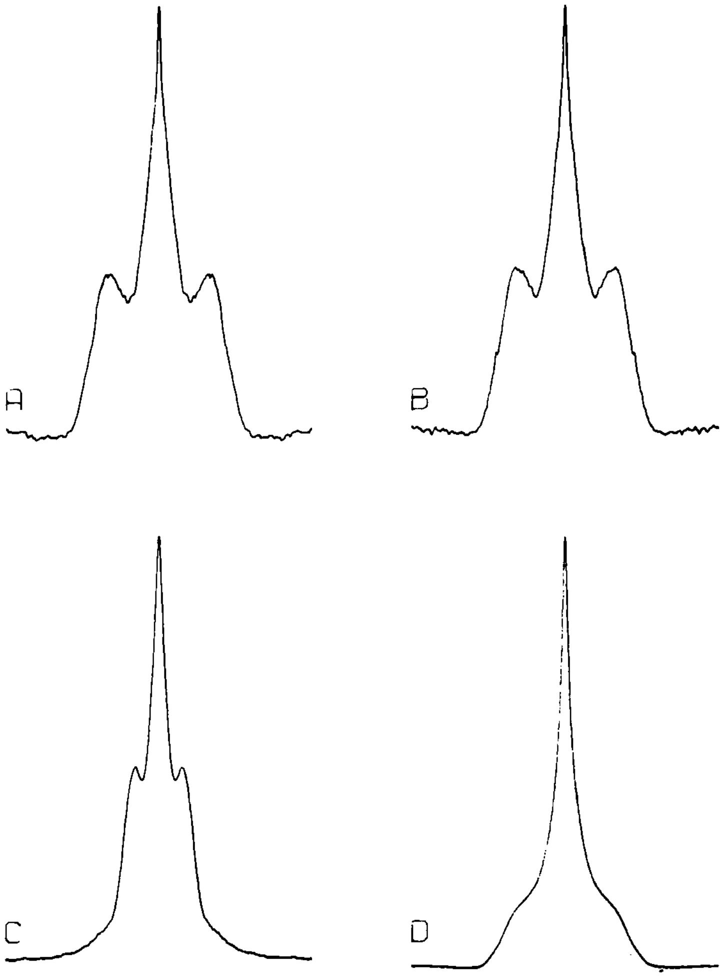

FIGURE 4 MBBA at 24°C. a. Director parallel to magnetic field. b. Director at calculated flow alignment angle. c. Director perpendicular to magnetic field. d. Random orientation of director.

yielded percentages of molecules associated with each group as a function of time after the onset of the electric field. Typical fits for PAA and MBBA are shown in Figure 5 and 6 respectively. The time evolution of each component for PAA at the three temperatures is shown in Figure 7–9 and for MBBA in Figure 10.

In the case of PAA, the flow alignment appears to be established almost immediately, and the experimental technique does not permit

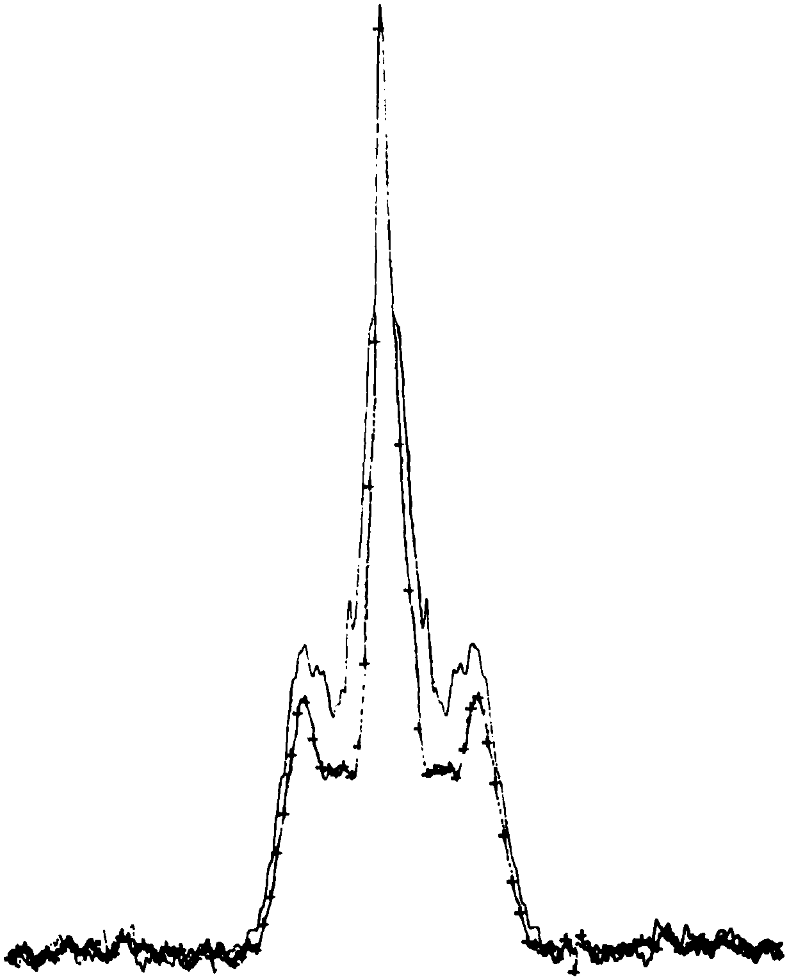

FIGURE 5 Typical fit for PAA, 129°C at 400 ms after application of electric field. Solid line is experimental data and crosses indicate fit.

observations at times less than approximately 10 ms so that the very rapid development of flow alignment can not be observed. The data for MBBA, on the other hand shows an evolution of order from an initial uniform ordering with the director parallel to the magnetic field to flow-alignment which is essentially complete after 500–600 ms. These observations are consistent with the rather large difference in viscosities of PAA and MBBA. Further, the flow-alignment ap-

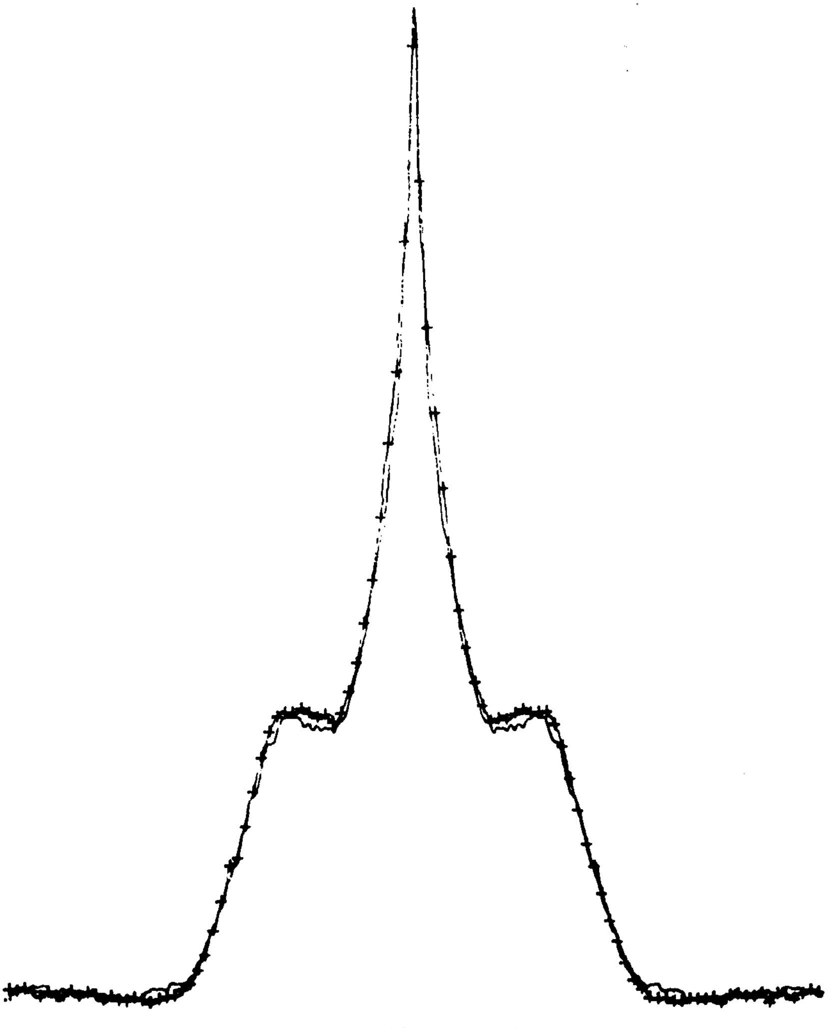

FIGURE 6 Typical fit for MBBA 24°C at 1.5 s after application of electric field. Solid line is experimental data and crosses indicate fit.

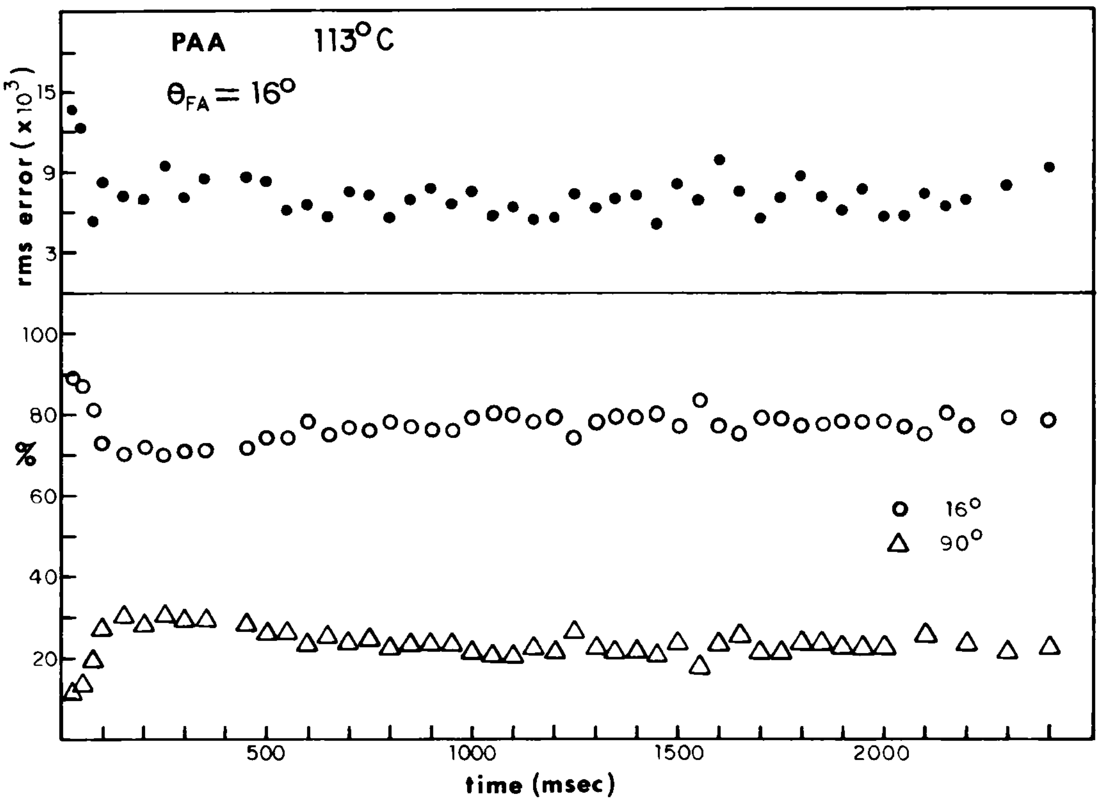

FIGURE 7 Time evolution of molecular orientation for PAA at 113°C.

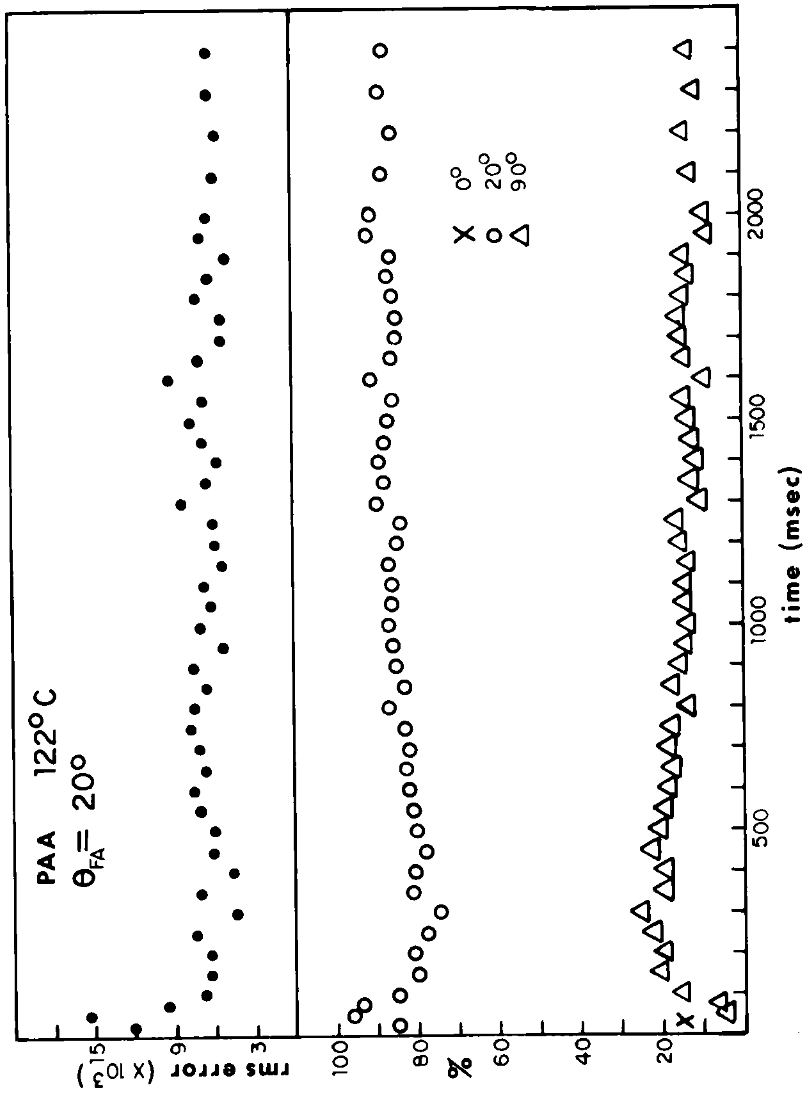

FIGURE 8 Time evolution of molecular orientation for PAA at 122°C.

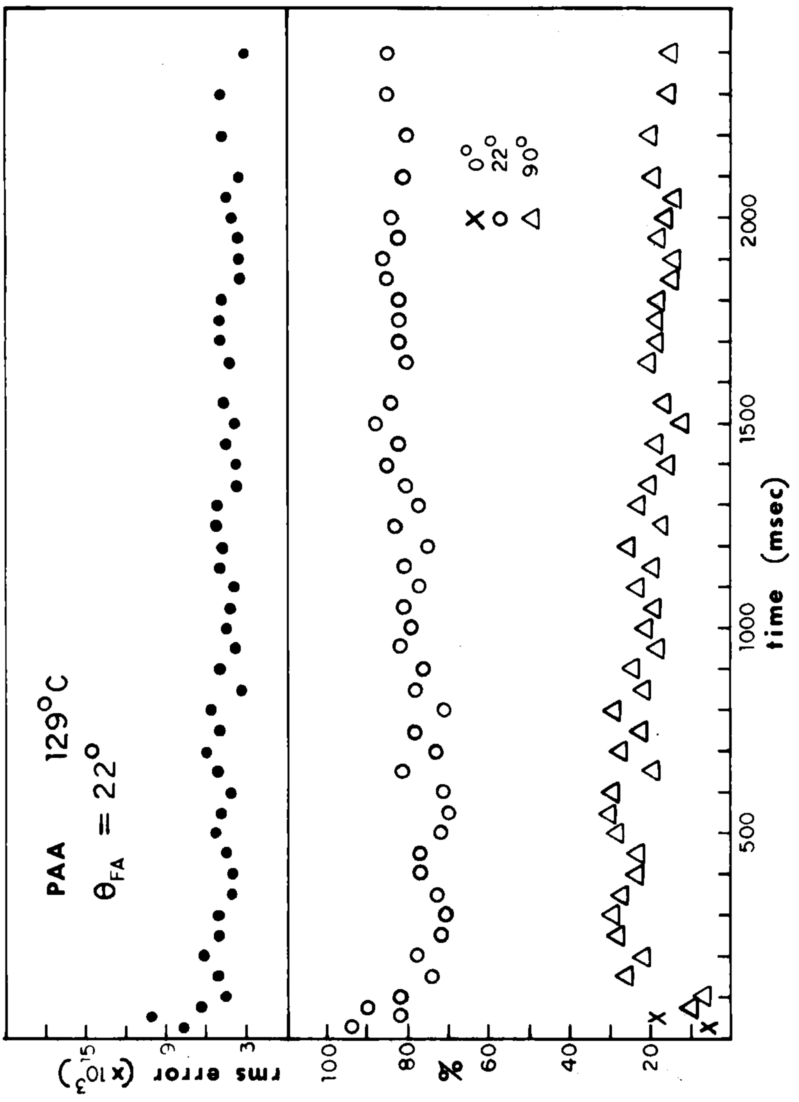

FIGURE 9 Time evolution of molecular orientation for PAA at 129°C.

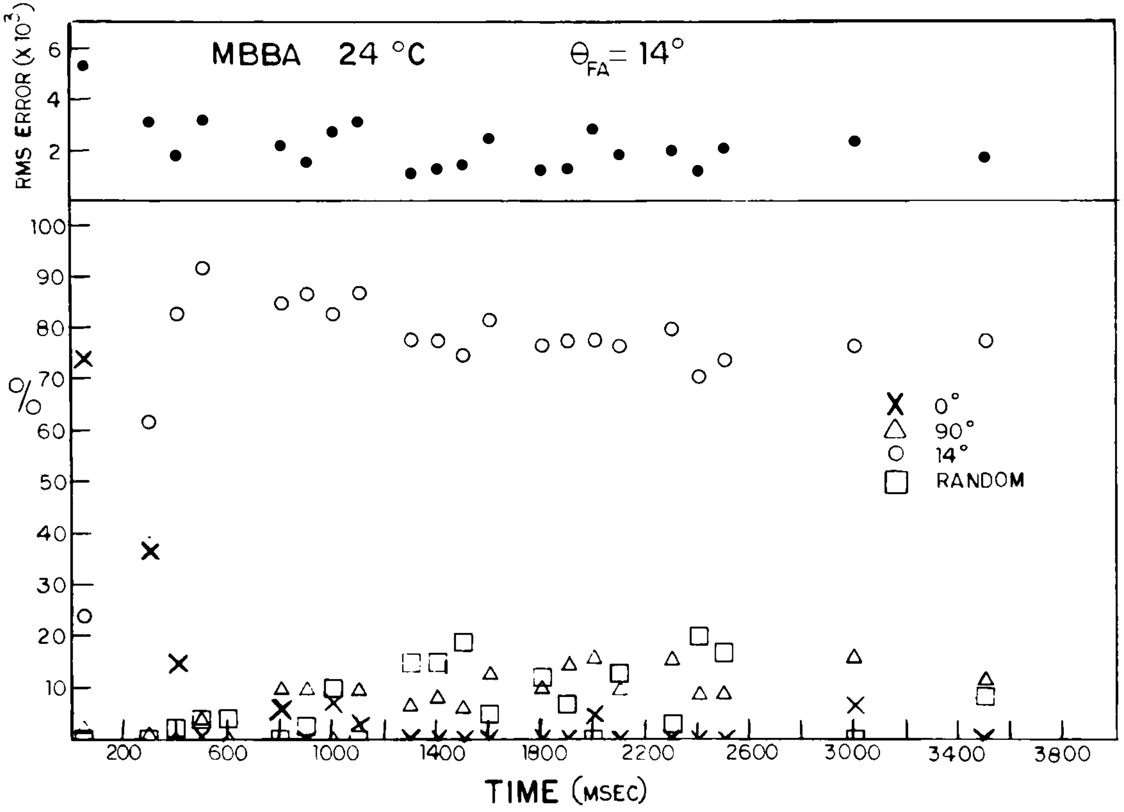

FIGURE 10 Time evolution of molecular orientation for MBBA at 24°C.

pears to be stable after the initial transient build up, which is consistent with optical observation of flow cells.

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