

- (5) Lim, K. C.; Kapitulnik, A.; Zacker, R.; Heeger, A. J. *J. Chem. Phys.* 1986, 84, 1058.
- (6) Cadenhead, D. A. *Ind. Eng. Chem.* 1969, 81, 22.
- (7) Malcolm, B. R. *Proc. R. Soc. London, Ser. A* 1968, A305, 363.
- (8) Kellner, B. M. J.; Müller-Landau, F.; Cadenhead, D. A. *J. Colloid Interface Sci.* 1978, 66, 597.
- (9) Matuo, H.; Rice, D. K.; Balthasar, D. M.; Cadenhead, D. A. *Chem. Phys. Lipids* 1982, 30, 367.

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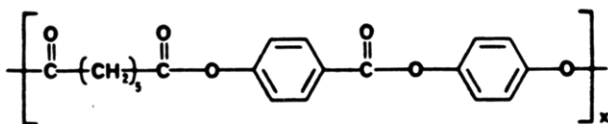
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## Surface-Enhanced Rate of Molecular Alignment in a Liquid Crystal Polymer

The orienting effect of surfaces on liquid crystals formed by small molecules is a well-known phenomenon.<sup>1-5</sup> It has been explained theoretically on the basis that orientation avoids high-energy elastic distortions in mesophases that are in contact with specific types of surfaces.<sup>6,7</sup> The types of surfaces that are known to have this "guiding" effect on the liquid crystal's orientation include chemically modified surfaces and also those containing topographical features such as uniaxial grooves or cavities. Should it be possible to extend these effects to macromolecular liquid crystals, many possibilities would exist for the study of solid-state properties in highly ordered thin films formed at interfaces. However, recent findings suggest that little if any orientation can be induced in high molecular weight thermotropic polymers by conventional surface treatments. Krigbaum and Lader,<sup>8</sup> for example, were reportedly unable to orient 10- $\mu\text{m}$ -thick samples of a thermotropic polyester by standard surface-rubbing techniques. Another example is the work by Meurisse et al.,<sup>9</sup> in which they reported difficulties in the surface alignment of a liquid crystal polyester. In our own experience over the past 2 years we find that polymeric liquid crystals respond very slowly if at all to surface forces as revealed by optical microscopy. On the other hand, small-molecule thermotropics become completely aligned in response to surface forces in times well under 1 s.<sup>10</sup> In light of these observations, it has been our objective to understand the principles and limitations of surface forces affecting molecular organization in polymeric systems. We report here on the alignment kinetics that result as a consequence of coupling both magnetic and surface forces. The effect such coupling has on alignment dynamics can help us understand the equilibrium structure of polymer liquid crystals.

The material investigated here is a main-chain thermotropic polyester synthesized in our laboratory and having the ideal chemical structure shown below.



Its synthesis was first reported by van Luyen and Strzelecki.<sup>11</sup> The structure is termed ideal since we believe this polymer transesterifies to a random chemical microstructure.<sup>12</sup> The material undergoes a solid-to-liquid crystal phase transition near 150 °C and can be oriented in magnetic fields under certain conditions. In our recent studies on magnetic field orientation dynamics of this

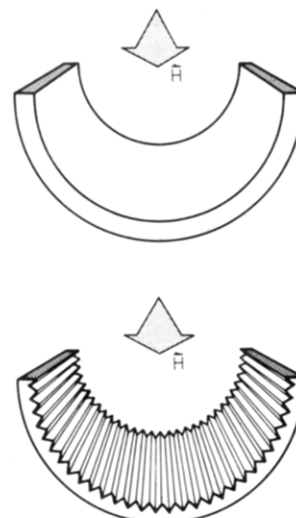


Figure 1. Schematic diagram of ungrooved (top) and grooved (bottom) NMR tubes used in orientation experiments. Note that the direction of the grooves is parallel to the external magnetic field.

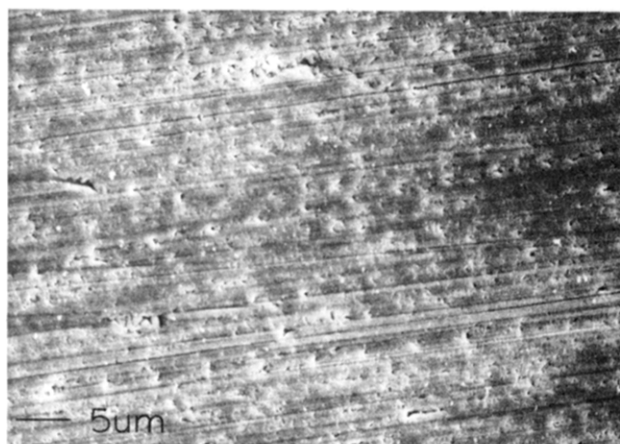
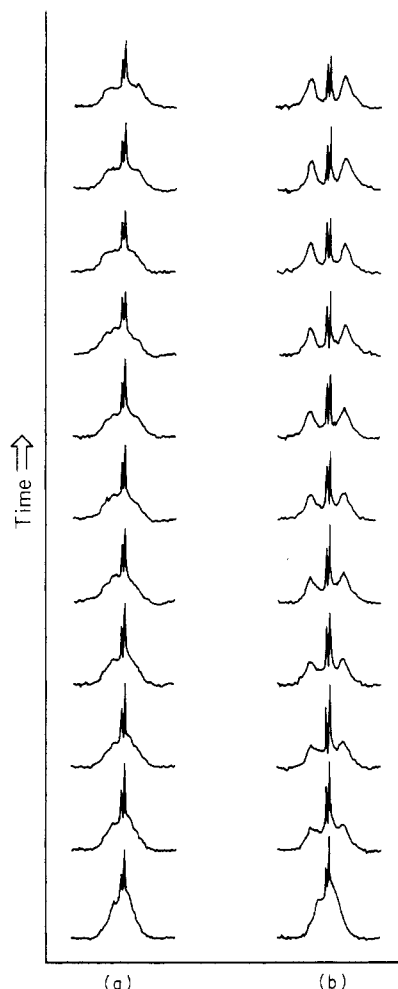


Figure 2. Scanning electron micrograph of grooved NMR tube.

polymer,<sup>13</sup> we identified one high molecular weight sample that responded sluggishly to the external field over periods of several hours at temperatures of 185 °C. We have used this specific sample in the present investigation.

Samples were placed in 4-mm-diameter glass tubes and exposed at 185 °C to the magnetic field of a superconducting magnet (4.7 T) in a Varian XL-200 NMR instrument. The control experiment utilized glass tubes with featureless surfaces. In other experiments we used featured surfaces containing uniaxial grooves prepared on the inner walls of similar tubes. The grooves were produced by abrasion with 1- $\mu\text{m}$  diamond paste and a glass plunger over a period of 10 min. This procedure was followed by ultrasonic cleaning of the surface with water, ultrasonic cleaning solution, and then a series of reagent grade solvents (30 min with each). The solvents used were isopropyl alcohol, acetone, and methyl ethyl ketone. Finally, the surfaces were immersed in a concentrated chromic acid-sulfuric acid solution for 30 h, rinsed with distilled water, and dried at 300 °C for 3 h. As shown schematically in Figure 1, the grooving direction was parallel to the cylindrical axis of the tube and scanning electron microscopy of the inner walls revealed a groove size ranging from 0.4 to 1.25  $\mu\text{m}$  in width (see Figure 2). All tubes were filled with 0.250 g of polymer, added in four equal-mass portions. After the addition of each portion, the tube was heated to 170 °C for 1 min and packed lightly with a solid glass



**Figure 3.** Broad-line proton NMR spectra of experimental polymer at 185 °C in (a) ungrooved tube and (b) grooved tube. Spectra in column a were recorded at times identical with those in column b.

rod. Once all tubes were filled, they were simultaneously subjected to thermal treatment at 200 °C for 1 h under a nitrogen atmosphere in a cell constructed in our laboratory.

Macroscopic molecular orientation was monitored by measuring the proton NMR second moment as a function of time. We refer the reader to previous literature on the use of NMR to study small-molecule and polymer liquid crystals.<sup>14-16</sup> In Figure 3 we show a series of proton spectra at increasing times in the field corresponding to the mesophase in contact with the featureless (Figure 3a) and grooved glass (Figure 3b) surface. The second moment of these spectra is given by the relation

$$\langle \Delta\nu^2 \rangle = \frac{\int_{-\infty}^{\infty} g(\nu) [\nu - \langle \nu \rangle]^2 d\nu}{\int_{-\infty}^{\infty} g(\nu) d\nu} \quad (1)$$

where  $g(\nu)$  represents the functional form of the NMR line shape,  $\nu$  is the frequency at which resonance occurs, and  $\langle \nu \rangle$  is the average frequency of the resonance band. The second moment is related to the macroscopic order parameter  $S_{zz'}$ , which results from a quadrupolar averaging of the director orientations with respect to the laboratory frame.  $S_{zz'}$  is defined as

$$S_{zz'} = \frac{3}{2} \cos^2 \theta_0 - \frac{1}{2} \quad (2)$$

where  $\theta_0$  represents the angle between the director and the

external magnetic field. The relationship between  $S_{zz'}$  and the second moment is given by

$$\langle \Delta\nu^2 \rangle_M = \frac{1}{3} \left( \frac{\gamma^2}{2\pi} \right)^2 h^2 I(I+1) \langle S_{zz'}^2 \rangle \sum_{p,q} \frac{1}{r_{pq}^6} [s_{zz} \langle \frac{3}{2} \cos^2 \beta_{pq} - \frac{1}{2} \rangle + \frac{1}{2} (s_{xx} - s_{yy}) \langle \sin^2 \beta_{pq} \cos 2\alpha_{pq} \rangle] \quad (3)$$

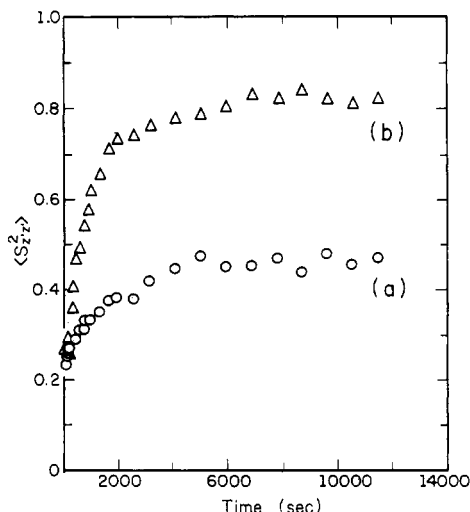
where the summation runs over all spins  $p$  and  $q$  ( $p \neq q$ ) of the same nuclei within a given molecule. The angles  $\alpha$  and  $\beta$  are the Eulerian angles relating the  $p$ - $q$  internuclear vector to the principle molecular frame,  $r_{pq}$  is the internuclear distance, and  $s_{xx}$ ,  $s_{yy}$ , and  $s_{zz}$  are microscopic order parameters. Since all time-averaged terms in eq 3 can be assumed constant at a given temperature, it is apparent that  $\langle \Delta\nu^2 \rangle_M$  is directly proportional to  $\langle S_{zz'}^2 \rangle$ . Furthermore, if one assumes that the central resonance peak results from the presence of an isotropic phase,<sup>17</sup> then the relationship between the experimentally measured second moment and  $\langle S_{zz'}^2 \rangle$  is

$$\langle S_{zz'}^2 \rangle = \frac{\langle \Delta\nu^2 \rangle - f_I \langle \Delta\nu^2 \rangle_I}{\langle \Delta\nu^2 \rangle^0 - f_I \langle \Delta\nu^2 \rangle_I} \quad (4)$$

where  $\langle \Delta\nu^2 \rangle_I$  is the value of the second moment of the pure isotropic phase,  $f_I$  is the fraction of material in the isotropic phase, and  $\langle \Delta\nu^2 \rangle^0$  is the experimentally measured second moment of a perfectly aligned specimen. As we have described elsewhere,<sup>13</sup>  $\langle \Delta\nu^2 \rangle^0$ ,  $\langle \Delta\nu^2 \rangle_I$ , and  $f_I$  can be measured from low molecular weight samples which align fully in the field. At the temperature of our experiments, the material is above its solid-to-liquid crystal transition (near 150 °C as measured by DSC) but below the broad isotropization range often reported for similar polymers.<sup>18</sup>

A comparison of the spectra in columns a and b of Figure 3 clearly reveals that the characteristic dipolar splitting associated with macroscopic molecular orientation develops much faster for the sample in contact with the grooved tube walls. As indicated in Figure 1, the direction of the grooves is parallel to the external magnetic field,  $\vec{H}$ . Thus, both the surface geometry and the external field should induce alignment of director axes parallel to the cylindrical axis of the tube. Interestingly, it is clear from data in Figure 3 that both types of samples had essentially identical initial states of macroscopic orientation. In fact, measurements of line width at half-height on solid-state spectra prior to orientation deviated by only 2% for samples that had been thermally aged in contact with grooved vs. ungrooved tubes. These data suggest that surface-induced orientation may be initially restricted to a very thin shell near the tube wall while bulk material remains randomly oriented.

The kinetic curves shown in Figure 4 were obtained by using eq 4 and the corresponding second moment values measured from spectra in Figure 3. It is clear that both the rate and ultimate degree of macroscopic orientation are much greater for the sample in the grooved tube. This observation has been reproduced both qualitatively and quantitatively in several independent experiments. Thus, it seems apparent that surface forces can very effectively couple with external fields to enhance the alignment of polymeric liquid crystals. It is conceivable that surface effects nucleate orientation at the tube wall, which can then propagate throughout the sample driven by the magnetic field. We do not know at this point if such surface effects involve heterogeneous nucleation of a "single liquid crystal" on the preoriented surface or formation of supercritical domains under the synergistic influence of magnetic torque and elastic strain energy. We are con-



**Figure 4.** Kinetics curves plotted as the macroscopic order parameter  $\langle S_z^2 \rangle$  vs. time for samples oriented in (a) ungrooved and (b) grooved tube.

tinuing work in this area to elucidate some of these details. It is clear from the present study that surface interactions can have strong effects on the alignment of main-chain polymer liquid crystals when coupled with other force fields. The synergistic effect was manifested in this particular case by the enhancement of magnetic orientation rate.

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**Registry No.** (4,4'-HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>O(CH<sub>2</sub>)<sub>5</sub>OC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H)(4-H<sub>3</sub>CCO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OCOCH<sub>3</sub>) (copolymer), 74774-52-0; (4,4'-HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>O(CH<sub>2</sub>)<sub>5</sub>OC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H)(4-H<sub>3</sub>CCO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OCOCH<sub>3</sub>) (SRU), 74790-48-0.

## References and Notes

- Kahn, F. J. *Appl. Phys. Lett.* **1973**, *22*, 386.
- Urbach, W.; Boix, M.; Guyon, E. *Appl. Phys. Lett.* **1974**, *25*, 479.
- Goodman, L. A.; McGinn, J. T.; Anderson, C. H.; Digeronimo, F. *IEEE Trans. Electron Devices* **1977**, *24*, 795.
- Kutty, T. R. N.; Fischer, A. G. *Mol. Cryst. Liq. Cryst.* **1983**, *99*, 301.
- Creagh, L. T.; Kmetz, A. R. *Mol. Cryst. Liq. Cryst.* **1973**, *24*, 59.
- Berremann, D. W. *Mol. Cryst. Liq. Cryst.* **1973**, *23*, 215.
- Wolff, U.; Greubel, W.; Kruger, H. *Mol. Cryst. Liq. Cryst.* **1973**, *23*, 187.
- Krigbaum, W. R.; Lader, H. J.; Ciferri, A. *Macromolecules* **1980**, *13*, 554.
- Meurisse, P.; Friedrich, C.; Dvolaitzky, M.; Lauprêtre, F.; Noel, C.; Monnerie, L. *Macromolecules* **1984**, *17*, 72.
- Castellano, J. A. *Opt. Laser Technol.* **1975**, *7*, 259.
- van Luyen, D.; Strzelecki, L. *Eur. Polym. J.* **1980**, *16*, 303.
- Moore, J. S.; Stupp, S. I., submitted for publication.
- Moore, J. S.; Stupp, S. I., submitted for publication.
- Doane, J. W. In *Magnetic Resonance of Phase Transitions*; Owens, F. J., Poole, C. P., Jr., Farach, H. A., Eds.; Academic: New York, 1979; p 171.
- Mueller, K.; Hisgen, B.; Ringsdorf, H.; Lenz, R. W.; Kothe, G. *Mol. Cryst. Liq. Cryst.* **1984**, *113*, 167.
- Boeffel, C.; Hisgen, B.; Pschorn, U.; Ringsdorf, H.; Spiess, H. W. *Isr. J. Chem.* **1983**, *23*, 388.
- Bruckner, S.; Scott, J. C.; Yoon, D. Y.; Griffin, A. C. *Macromolecules* **1985**, *18*, 2709.
- Krigbaum, W. R.; Kotek, R.; Ishikawa, T.; Hakemi, H.; *Eur. Polym. J.* **1984**, *20*, 225.

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## In Situ Polymerization of Gaseous Monomers: Effect on Polymer Structure

Both the chemistry and physics of polymer blends have received considerable attention during the past 10 years. Much of this interest originated with the discovery that materials with improved mechanical properties can be obtained through blending [e.g., polystyrene/polybutadiene or polystyrene/poly(phenylene oxide)].<sup>1</sup> The extent to which these synergistic effects are realized is dependent on the miscibility or the degree to which phase separation occurs. Polymer miscibility is, however, limited by the fact that the entropy gained on mixing is very small. To minimize the phase separation that occurs in immiscible polymer pairs, interpenetrating networks (IPN) are synthesized. This is done by polymerizing the second monomer in a swollen cross-linked matrix of the first polymer. The cross-links serve to fix and limit the phase sizes. This field has been extensively examined for liquid monomers,<sup>2</sup> but very little has been done with gaseous monomers in a nonswollen, non-cross-linked matrix. It is this area of research that will be discussed here.

The goals of this work are threefold. First, the technique of polymerizing a gaseous monomer in a solid matrix could produce blends that cannot be obtained through other methods. This has been shown to be true with polyacetylene blends<sup>3</sup> and might be extended to other polymers such as poly(tetrafluoroethylene). Second, the technique has potential as a means of modifying polymer surfaces. A fundamental knowledge of the chemistry and physics of this technique is essential to its application. In the regime of chemistry, it is important to know whether the catalyst reactions are influenced by the use of a solid solvent. In the physics area, it is important to understand how the phase separation is influenced by polymerization conditions such as the difference between the polymerization temperature and the glass transition temperature of the matrix. Another issue to be addressed is whether this technique can be used to kinetically entrap chains in a nonequilibrium state and thereby provide a system with which to study the physics of phase separation.

Polybutadiene and polystyrene form an extensively studied incompatible polymer system. Since butadiene is a gas at room temperature, this system is a good choice for elucidating the important variables in solid-state in situ polymerization. This paper will deal with the synthesis of polybutadiene/polystyrene blends via in situ polymerization. An emphasis will be placed on the catalyst reactions and the structure of the polybutadiene. The morphology of these blends will be the subject of a future publication.

**Purification of Chemicals.** Butadiene (Matheson Research Grade 99.8%) was passed through two columns containing NaOH and 4A molecular sieves before collection in an evacuated flask. The monomer was then vacuum-distilled from dibutylmagnesium. For the polymerization reactions, a 2-L gas bulb was filled to 1 atm with the purified butadiene. A Ziegler-Natta catalyst consisting of