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Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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# Structure of Thermotropic Polyesters

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# STRUCTURE OF THERMOTROPIC POLYESTERS WITH LARGE SUBSTITUENTS*

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Abstract. Thermotropic aromatic polyesters were aligned by drawing from nematic melts and by quenching in a magnetic field of 15 tesla and subsequently examined by x-ray diffraction. The degree of alignment obtained depended slightly on the substituent (H, F, Cl, Br, $CH_3$, $NO_2$) present with the highest degree of alignment observed when the arylsulfonyl substituted group contained in the *para*-position H or F and the lowest when it contained Br or $CH_3$.

## INTRODUCTION

Substituent groups in extended linear polymers serve to reduce their melting points as do flexible spacer groups and other modifications introduced along the main chain. Lenz[1] has suggested that lateral substituents may have steric and polar effects: they may decrease the molecular anisotropy common to all liquid crystalline compounds and polymers,[2] destabilizing the mesophase thereby, or they may stabilize the mesophase through dipolar intermolecular interactions.[3] In some cases, however, it has been suggested that steric effects may increase the thermal stability of a mesophase by interlocking effects.[4]

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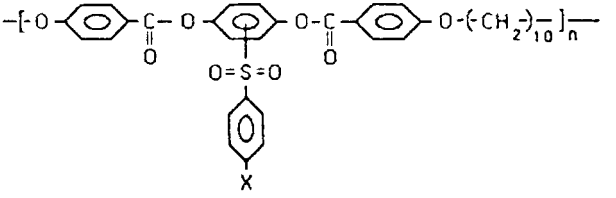
The present study was undertaken to determine the effect of different lateral substituents on the molecular packing in the nematic mesophase of thermotropic polyesters based on a triad ester mesogenic unit containing an arylsulfonyl substituted hydroquinone group and a decamethylene spacer group of the following structure:



X = H, $CH_3$, Cl, F, Br, $NO_2$

The arylsulfonyl groups were expected to show large steric and polar effects.

## EXPERIMENTAL PROCEDURE

All six polymers in this study were first examined by DSC to determine their thermal transition points (Table I) which agreed, within experimental error, with those reported previously.[3] The molecular weight averages of these polymers were determined next. All GPC curves, Fig. 1, except that for the $NO_2$ substituent, which did not dissolve fully in dichloromethane, contained a large peak corresponding to the polymer present and subsidiary peaks for the oligomers present. The latter were calibrated using a polystyrene standard and the molecular weight average of the polymer was determined by subsequent extrapolation from these values, Table II.

The polymers were packed inside glass and quartz capillaries having circular and square cross sections (1mm diam.) to detect surface-induced alignments, if present.

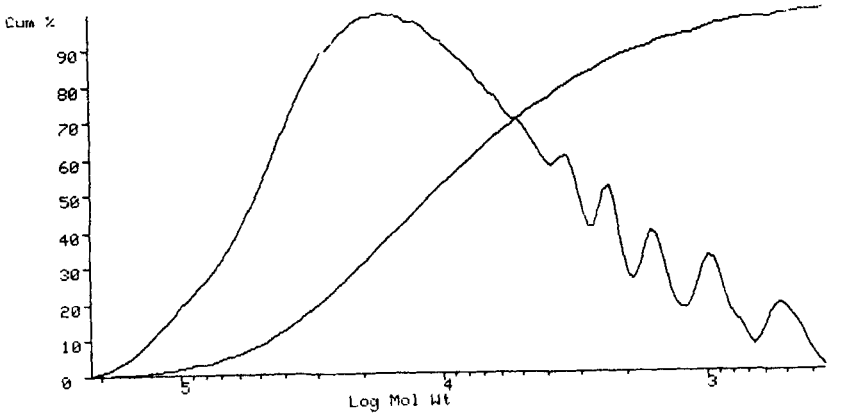



FIGURE 1. Gel-permeation chromatogram for Cl substituent.

X-ray diffraction showed that the final samples were amorphous as were the original polymers. Several capillaries containing the same polymer were placed inside a special furnace and heated to about 10-20°C above the melting point ($T_M$ in Table I) in a superconducting magnet (field strength 15 tesla) at the Francis Bitter National Magnet Laboratory at M.I.T. and, following several hours at that temperature, quenched by cooling in air. In addition,

TABLE I. Thermal transition points (°C).

| Substituent at X | $T_g$ | $T_m$ | $T_i$ |
|---|---|---|---|
| H | 87 | 100 | 170 |
| $CH_3$ | 83 | 102 | 142 |
| F | 79 | 95 | 161 |
| Cl | 85 | 101 | 154 |
| Br | 85 | 93 | 147 |
| $NO_2$ | 80 | 91 | 153 |

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TABLE II. Molecular weight average.

| Substituent at X | Weight average |
|---|---|
| H | 10,800 |
| $CH_3$ | 11,500 |
| F | 9,000 |
| Cl | 8,400 |
| Br | 8,300 |

fibers were drawn directly from the nematic melts. All of these samples were examined in a Buerger precession camera equipped with a bent-crystal monochromator using Co or Fe Kα radiations, before and after further annealing for several hours at temperatures slightly below their respective melting points.

## RESULTS AND DISCUSSION

Well aligned monodomain samples were obtained both by quenching the nematic mesophase in the magnet and by forming a nematic glass by drawing a fiber directly from the nematic melt, Figs. 2 and 3. The stronger x-ray exposure in Fig. 3 shows the meridional reflections more clearly but, as can be seen in Table III, several orders were recorded for most the polymers examined with only minor variations relatable to the different substituents. Annealing the samples below their melting points did not enhance significantly the alignments of magnetically ordered samples. On the other hand, annealing the nematic-glass fibers did increase the alignment in all polymers except those containing $NO_2$ and Br substituents which remained unaltered. These differences cannot be considered

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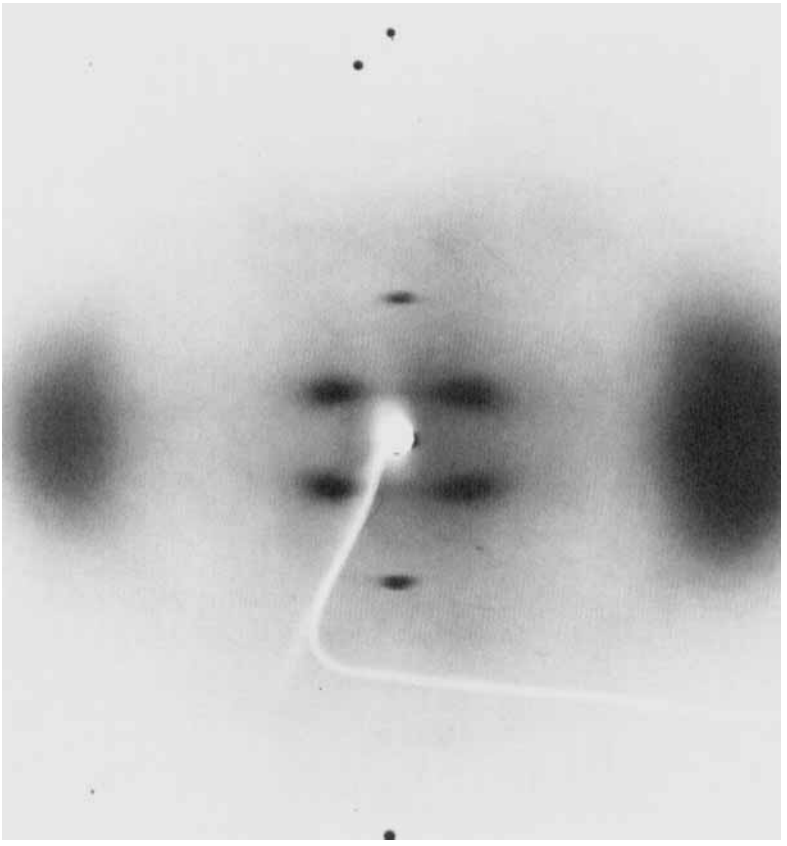

FIGURE 2. Normal-beam photograph of quenched F-substituted polymer (Fe Kα).

to be very significant, however, because the 'absence' of a reflection may be caused by the relative length of the effective x-ray exposures which were affected by the exposure time and the relative thickness (absorption) of the nematic glass fibers.

On the whole, no significant alignment effect can be attributed to the wall effect of the capillaries although,

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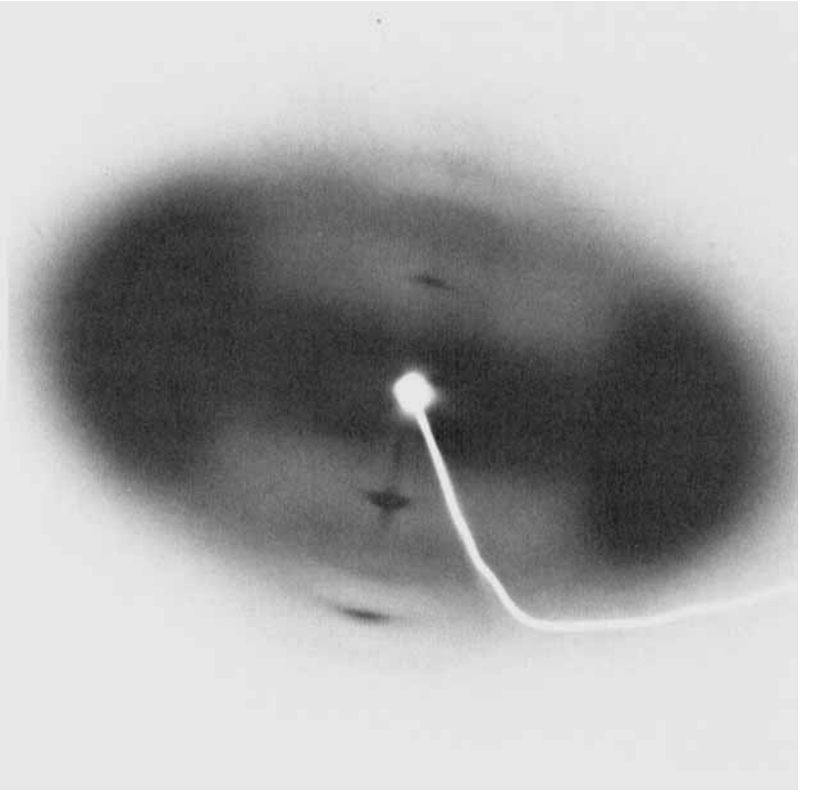

FIGURE 3. Normal-beam photograph of nematic glass fiber of F-substituted polymer (filtered Co Kα).

qualitatively, magnetically aligned samples tended to give sharper photographs than corresponding unannealed fibers. This may be due to the synergistic effect of the capillary walls and the magnetic field.[5] A definite wall effect was observed, however, in the case of a fluorine-substituted polymer which was cooled from the nematic melt inside a

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round glass capillary without an external magnetic field. When it was cooled rapidly from the nematic temperature range, the normal-beam photograph showed two diffuse halos typical of an unaligned nematic. When the same sample was cooled slowly to room temperature, an aligned monodomain developed yielding a diffraction photograph only somewhat less "sharp" than that shown in Fig. 2. Whether similar alignments can be induced in the other polymer samples, by the wall effect of a capillary in the absence of an external magnetic field, was not investigated at this time.

The x-ray diffraction results reported above indicate a high degree of alignment for all polymers examined. The only variations attributable to the different substituents (Table III) are the much higher degree of alignment for H, F, Cl than for Br and $CH_3$. This may be a consequence of the decreasing polarizability of the Br and $CH_3$ substituents. The effective length of the repeat unit parallel to the polymer main chain is 2.91 nm as deduced from the sharp 003 spacing. This compares to 2.96 nm for the extended molecule calculated from known bond distances. The relative constancy of this x-ray spacing and the small amount of arcing of the equatorial reflection for all samples except that containing $CH_3$ strongly suggests that the polymers align parallel to each other in the monodomain samples with a relative splay of less than 19°. Somewhat more surprisingly, the equatorial arcs yield $d$ values in the range 0.426 to 0.431 nm, without any apparent correlation to the particular substituent in the *para*-position of the arylsulfonyl group. Thus if there is any effect of the substituents on the liquid-crystal polymers, it is primarily steric.

TABLE III. $d$ values of meridional reflections ($10^{-9}$ m)

| ℓ | H | F | Cl | Br | $NO_2$ | $CH_3$ |
|---|---|---|---|---|---|---|
| **Magnetically aligned and quenched** | | | | | | |
| 003 | 9.71 | 9.71 | 9.71 | | 9.71 | 9.71 |
| 005 | 5.68 | 5.68 | 5.88 | 5.88 | 5.68 | |
| 006 | 4.72 | 4.85 | 4.72 | 4.85 | 4.85 | |
| 007 | 4.12 | | | | 4.12 | |
| **Magnetically aligned and annealed** | | | | | | |
| 003 | 9.71 | 9.71 | 9.71 | | 9.71 | 9.71 |
| 005 | 5.88 | 5.88 | | 5.88 | | |
| 006 | 4.85 | 4.85 | 4.85 | 4.72 | 4.85 | |
| 007 | 4.22 | | | | 4.22 | |
| **Nematic-glass fibers** | | | | | | |
| 003 | 9.71 | 9.43 | 9.43 | | 9.43 | 9.43 |
| 005 | 5.88 | 5.78 | | 5.92 | | |
| 006 | 4.85 | 4.83 | 4.83 | 4.81 | | |
| 007 | 4.12 | 4.17 | 4.26 | | | |
| **Annealed nematic-glass fibers** | | | | | | |
| 003 | 9.43 | 9.90 | 9.43 | | 9.43 | 9.43 |
| 005 | 5.78 | 5.95 | 5.78 | 5.92 | | 5.78 |
| 006 | 4.83 | 4.83 | 4.83 | 4.81 | | 4.83 |
| 007 | 4.17 | 4.17 | 4.26 | | | 4.17 |

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It should be noted that the reheating of a magnetically aligned polymer with a hydrogen substituent to a temperature 10° below the isotropization temperature ($T_i$ in Table I) yielded an x-ray diffraction photograph containing several sharp arcs along the equator superimposed on the broad arc in Fig. 2 as well as an increased 'arcing' of the relatively sharp meridional and off-meridian reflections suggestive of the formation of multiple crystalline regions in the polymer. This effect and the role of the oligomers present in all samples examined is currently under investigation and will be reported separately.

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