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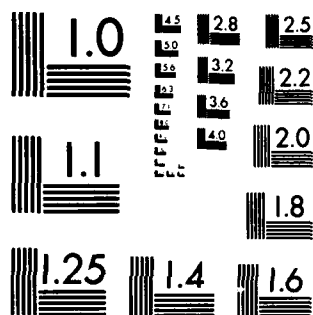
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MESOGENIC RODLIKE AROMATIC POLYESTERS

FINAL REPORT P-87

William R. Krigbaum

December 5, 1987

U. S. ARMY RESEARCH OFFICE

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The effect of substituents on poly(p-phenylene terephthalate) were investigated, as well as the spinning behavior of the thermotropic polyesters X-7G from Te messee Eastman and three compositions of the "Vectra" polyesters from Hoechst-Cellanese.		

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## SUMMARY OF RESULTS\*

## I. EFFECT OF SUBSTITUENTS ON THE RINGS OF POLY (P-PHENYLENE TEREPHTHALATE)

## b. Summary of Results

We<sup>A2</sup> have explored the effect of substituents on the crystal-nematic and nematic-isotropic transition temperatures of poly (p-phenylene terephthalate). The substituents halogen, phenyl, and hexyl replaced hydrogen on the ring of hydroquinone or terephthalic acid. One gets a much larger reduction of the transition temperatures if a phenyl substituent is on terephthalic acid. We believe this substituent forces the carbonyl group out of the ring plane, and creates a more flexible link.

## II. SPINNING THERMOTROPIC COPOLYESTERS

## b. Summary of Results

We have investigated the spinning of thermotropic copolyesters. In order to have enough polymer for these studies, we have used two types of commercial polymers. One is the Tennessee Eastman X-7G,<sup>A3,A5,A6</sup> a copolyester of 60 mole percent hydroxybenzoic acid (HBA) and polyethylene terephthalate, while the second is the "Vectra" copolymers of Hoechst-Cellanese composed of HBA and 2-hydroxy-6-naphthoic acid (HNA).<sup>A4,A7-A9</sup> Although both of these copolyesters were developed for injection molding applications, we have investigated the fiber spinning properties of these copolymers.

Conventional polymers are spun with minimal orientation, and then orientation is introduced in a later cold drawing operation. Thermotropic polyesters cannot be cold drawn, so orientation is introduced by shear in the capillary, or by spin drawing the molten fiber just below the spinneret. One can increase the shear in the capillary by increasing the L/D ratio of the capillary. Fibers with modest properties can be obtained in this way, but some spin draw is required. Better properties are obtained

\* References beginning with the letter A are found on page 6.

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by reducing L/D and increasing the spin draw ratio. A long relaxation time is essential if the orientation introduced during spinning is not to be lost before the fiber crystallizes. Jackson<sup>1</sup> has shown that a highly extended chain is necessary if the relaxation time is to be long. However, this implies a low entropy of fusion and a high melting temperature. Randomness is introduced by copolymerization in order to lower the transition temperatures so the polymer can be processed without decomposition. Lenz and coworkers<sup>2</sup> have demonstrated that melt interchange of a copolymer in a two phase system can lead to the development of longer blocks. The second phase can be either a crystalline or a nematic phase. Blockiness significantly affects the rheology of the melt, and hinders orientation of the thermotropic polyester by spin drawing. We were fortunate enough to obtain both a blocky and a random sample of X-7G. The melt of the former was shear thinning, while that of the random sample was Newtonian. This indicates the blocky sample is crystalline. Cogswell,<sup>3</sup> and Wissbrun and Ide,<sup>4</sup> have reported an interesting effect of thermal history. If the melt is heated to a higher temperature,  $T_H$ , and then cooled to the test temperature,  $T$ , the melt viscosity may be reduced and the fiber properties improved. This proved to be a very sensitive way to detect crystallites present in such a small amount that no differential scanning calorimeter exotherm could be found when they melted. The random sample, which has no blocky units, did not exhibit a thermal history effect. Fibers spun from the random sample had better mechanical properties. It should be noted that the random sample has the same copolymer composition and inherent viscosity. We also investigated three Hoechst-Cellanese copolyesters. All exhibited a flow instability, which could be overcome at high shear stress, indicating that the unstable flow occurs in the capillary. The 58HBA/42HNA copolymer gave the best fiber properties. The 75HBA/25HNA and the 30HBA/70HNA copolymers appeared to contain crystallites arising from blocky units, and gave poorer properties. We believe this is due to the presence of crystallites which seed crystallization in the thread line before the polymer is completely oriented. The highest initial modulus is found at a relatively low spin draw ratio. However, x-ray diffraction indicates that the crystallite orientation improves at still higher spin draw ratios. Evidently, at higher spin draw ratios defects are pulled into the fibers, which reduces the modulus.

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A8. D.-K. Yang and W. R. Krigbaum, "Rheological Studies of Thermotropic Liquid Crystal Copolyesters: p-Hydroxybenzoic Acid/2-Hydroxy-6-Napthoic Acid" (to be submitted to J. Polym. Sci. Polym. Phys. Ed.)

A9. D.-K. Yang and W. R. Krigbaum, "Fiber Spinning from the Nematic Melt. VI. Flow Instabilities in the 30:70 Copolyester of p-Hydroxybenzoic Acid and 2-Hydroxy-6-napthoic Acid", (to be submitted to J. Polym. Sci. Polym. Phys. Ed.)

d. LIST OF PARTICIPATING PERSONNEL

1. Dr. H. Hakemi -- has accepted a position with Johnson Wax.
2. Dr. H. Muramatsu -- has returned to Idemitsu in Japan.
3. Dr. C. K. Liu -- has accepted a position with U. S. Surgical Supply Co.
4. Dr. D.-K. Yang -- seeking an industrial position.

