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AN APPROACH TO MOLECULAR COMPOSITES

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20. Abstract (cont)

One objective was to demonstrate that a nematogen can be made to exhibit a cholesteric phase by the incorporation of chiral centers into the polymer chain. The Yamazaki reaction was used to introduce 3 mole percent of chiral L-valine into poly(p-benzamide). This was shown to form a lyotropic cholesteric phase by circular dichroism and the induced circular dichroism of an achiral dye. A disadvantage of the use of lyotropic mesomorphism was that few solvents were available and the production costs were high. The early lattice model treatment of Flory indicated that a highly extended molecular conformation was essential to the formation of this type of mesophase. It has been demonstrated that the melting point depression of a crystalline polymer by this type of mesophase will be quite small unless the polymer-solvent interaction is very favorable. This implies that the polymer solubility will only be sufficient for the formation of a lyotropic mesophase for those few polymer-solvent systems in which the interactions were very favorable. It was found that the Yamazaki phosphorylation reaction could be made to yield aromatic polyamides of higher inherent viscosity by using a monomer having pre-formed amide linkages. It is believed that this occurs due to reduction in the byproducts of the polymerization. Thermotropic mesophases offer the potential of a less expensive route to high modulus fibers and films. Theory indicates that thermotropic nematogens must be less highly chain extended than lyotropic nematogens, and the anisotropic interactions are needed to stabilize the mesophase. However, existing theory offers little guidance concerning how the chemical structure of the repeating unit will affect the range of stability of the mesophase, or whether the mesophase will be smectic or nematic. It was suggested that polymers exhibiting thermotropic mesomorphism could be prepared by incorporating a rigid and a flexible segment in the repeating unit. It was ascertained that incorporation of chiral units would transform a nematogenic polymer into one forming a thermotropic cholesteric phase. The properties of three semi-flexible polymers were investigated. These three polymers were spun, and the fiber properties were poor. Two explanations can be offered. It was found that the entropy change for the nematic-isotropic transition is small compared to that for the crystal-nematic transition. This indicates that these molecules do not adopt a rodlike conformation in a thermotropic nematic phase. Secondly, for polymers of this type, the degree of crystallinity of nematogens is notably poorer than that of smectogens. While the cause of this difference is currently unknown, the spinning results strongly suggest that good mechanical properties are related to highly extended chain conformation, and not simply to spinning from the nematic phase. To date, six publications have resulted from this research.

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AN APPROACH TO MOLECULAR COMPOSITES

OBJECTIVES: To investigate the possibility of forming a high strength film using cholesteric dopes or melts to obtain a high degree of biaxial orientation. A cholesteric phase is a chiral nematic in which the vector describing the preferred molecular orientation varies from one layer to the next, tracing out a helical path. Since the angle between the vectors in adjacent planes of molecules can be made quite small, an oriented cholesteric phase should be a true molecular composite.

I. ACCOMPLISHMENTS

Our first objective was to demonstrate that a nematogen can be made to exhibit a cholesteric phase by the incorporation of chiral centers into the polymer chain. We first utilized the Yamazaki reaction to introduce $\frac{1}{3}$ mole percent of chiral L-valine into poly(p-benzamide). This was shown¹ to form a lyotropic cholesteric phase by circular dichroism and the induced circular dichroism of an achiral dye. The concept described above under OBJECTIVE was the subject of U.S. Patent Application 179,962 which is still pending.²

A disadvantage of the use of lyotropic mesomorphism is that few solvents are available, and the production costs are high. The early lattice model treatment of Flory³ indicated that a highly extended molecular conformation is essential to the formation of this type of mesophase. We have demonstrated⁴ that the melting point depression of a crystalline polymer by this type of mesophase will be quite small unless the polymer-solvent interaction is very favorable. This implies that the polymer solubility will only be sufficient for the formation of a lyotropic mesophase for those few polymer-solvent systems in which the interactions are very favorable.

In view of this circumstance, our efforts were divided into two objectives:

A. Improving the solubility of aromatic copolyamides.

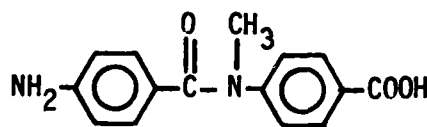
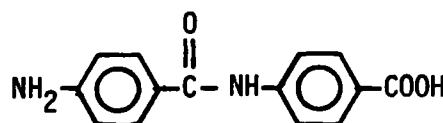
B. An investigation of thermotropic mesophases.

The results obtained will be described separately below.

A. Improving the Solubility of Aromatic Copolyamides

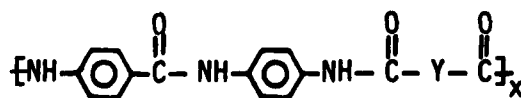
The general concept is that it should be possible to reduce the melting temperature, and improve the solubility, by copolymerization. We sought to apply to Yamazaki reaction for this purpose.

It was found⁵ that the Yamazaki phosphorylation reaction could be made to yield aromatic polyamides of higher inherent viscosity by using a monomer having pre-formed amide linkages. We believe that this occurs due to reduction in the byproducts of the polymerization. Homopolymers and copolymers were prepared⁶ from the monomers:



The first monomer yielded a poly(p-benzamide) of higher inherent viscosity, 2.4, than any previously reported from the Yamazaki reactions. The N-methyl substituent was introduced to improve polymer solubility, but the inherent viscosities of random copolymers decreased monotonically with N-methyl substitution. Since the molecular weights were nearly independent of methylation, this indicates that the chain extension is decreased by N-methylation of the amide linkage.

The use of monomers having pre-formed amide linkages was extended by studying the polymerization of 4,4'-diaminobenzanilide with dibasic acids to prepare polyamides exemplified by:⁷

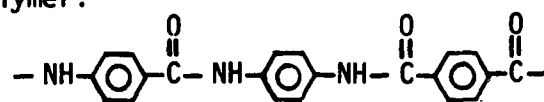


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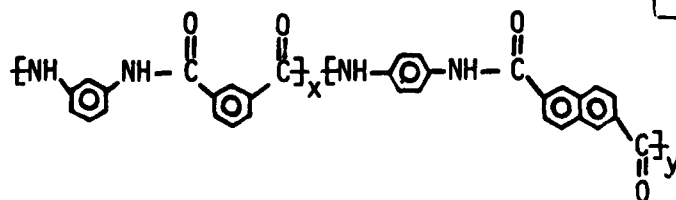
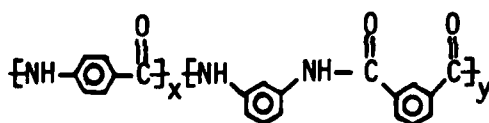
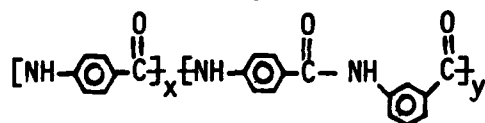
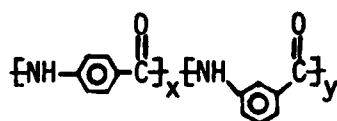
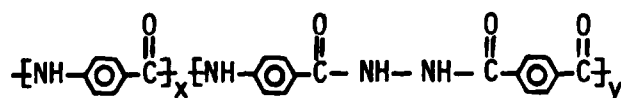
where $Y = (-CH_2)_n -$, , and 

The order of the inherent viscosities of polyamides prepared in this way using the Yamazaki reaction is isophthalic > aliphatic > terephthalic. The polyamides obtained using adipic acid formed an anisotropic solution in 100% H_2SO_4 when the polymer concentration exceeded 40%.

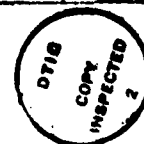
We then showed⁷ that polyamides containing p-benzamide linkages can be prepared by Higashi polymerization conditions using monomers having pre-formed amide linkages. As an example, the polymer:



had an inherent viscosity of 5.4 dL/g. This is perhaps the highest value reported to date for a polyamide synthesized by direct polycondensation, and is sufficient for the production of commercial-quality fibers. Both Yamazaki and Higashi conditions were utilized to prepare block copolyamides of the following types:⁷



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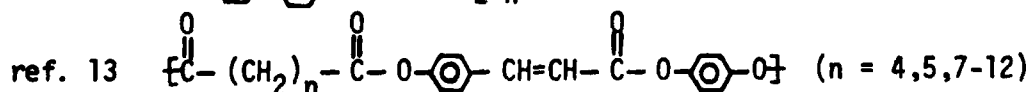
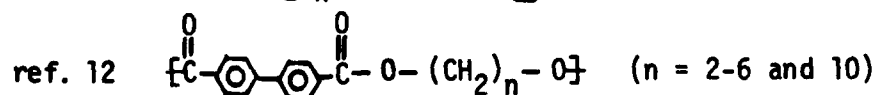
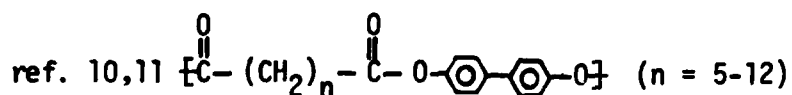


All of these block copolymers were found to form an anisotropic phase in N-methylpyrrolidone containing 4% LiCl when the fraction of meta units was less than 50 mole percent.

B. An Investigation of Thermotropic Mesophases

Thermotropic mesophases offer the potential of a less expensive route to high modulus fibers and films. Theory indicates that thermotropic nematogens must be less highly chain extended than lyotropic nematogens, and the anisotropic interactions are needed to stabilize the mesophase. However, existing theory offers little guidance concerning how the chemical structure of the repeating unit will affect the range of stability of the mesophase, or whether the mesophase will be smectic or nematic.

De Gennes⁸ suggested that polymers exhibiting thermotropic mesomorphism could be prepared by incorporating a rigid and a flexible segment in the repeating unit. This suggestion is quite attractive, since the rigid unit controls the mesomorphic character, while the length of the flexible segment affords some control of the transition temperatures. We first ascertained⁹ that incorporation of chiral units would transform a nematogenic polymer into one forming a thermotropic cholesteric phase. We then investigated the properties of the following types of semi-flexible polymers in this class:



Some of these polymers are nematogens and some are smectogens. The first example is unusual in that the polymers are nematogens when n is odd, and smectogens when n is even.

These three polymers have been spun,¹⁴ and the fiber properties were poor.

Two explanations can be offered. We find the entropy change for the nematic-isotropic transition is small compared to that for the crystal-nematic transition. This indicates that these molecules do not adopt a rodlike conformation in a thermotropic nematic phase. Secondly, for polymers of this type, the degree of crystallinity of nematogens is notably poorer than that of smectogens. While the cause of this difference is currently unknown, our spinning results strongly suggest that good mechanical properties are related to highly extended chain conformation, and not simply to spinning from the nematic phase.

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