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Recent Advances in Liquid Crystalline Polymers

Edited by
L. LAWRENCE CHAPOY

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RECENT ADVANCES IN LIQUID CRYSTALLINE POLYMERS

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PREFACE

This volume contains an eclectic collection of 22 papers on liquid crystalline polymers presented at the Sixth Polymer Workshop, in the series sponsored by the European Science Foundation, entitled: 'Liquid Crystal Polymer Systems', in Gentofte, Denmark, 12-14 September 1983. Since a contribution to this volume was strictly voluntary, and in some cases represents a considerably expanded version of that which was presented, it is strictly speaking not correct to term this a 'proceedings'. A description of the aims and purposes of the European Science Foundation with respect to the polymer area has been presented in: *Shell Polymers*, Vol. 5, No. 2, pp. 34-35, 1981.

The papers given here represent a cross-section of current research interests in liquid crystalline polymers in the areas of theory, synthesis, characterization, structure-property relationships and applications. At least some of the current interest is motivated by attempts to practically exploit the novel properties of these materials in the developing technologies of high strength fibres and advanced materials for constructional purposes, but also for functional materials in the areas of information retrieval, electronics and opto-electronics applications.

The editor wishes to thank all those involved for their courtesy and co-operation.

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PART I

**SYNTHESIS, STRUCTURE,
PROPERTIES RELATIONSHIPS**

SYNTHETIC ROUTES TO LIQUID CRYSTALLINE POLYMERS

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INTRODUCTION

This chapter is concerned with the synthesis of main chain, liquid crystal polymers, but only with the reactions used to prepare polyesters and polyamides. At the time of this review, polyesters have been of interest only as thermotropic polymers and polyamides for lyotropic behaviour, but this situation will, likely, soon change. There are undoubtedly aromatic polyesters which show liquid crystallinity in solution, and a thermotropic polyurethane has recently been reported.¹

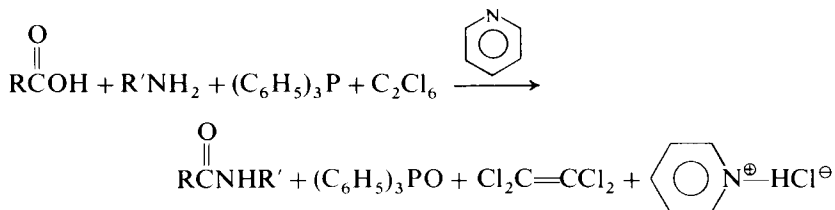
The practical application of lyotropic polyamides preceded that of thermotropic polyesters by at least ten years. Indeed, the development of the Kevlar® fibre by the du Pont Company, by the solution spinning of an aromatic polyamide in the lyotropic state, probably provided most of the early incentive for research on thermotropic polyesters.² That is, the goal of melt spinning a fibre, with comparable high strength and high modulus properties to 'Kevlar', led to the initial investigations of aromatic polyesters, which were closely related in structure to the 'Kevlar' polyamide. As yet this goal has not been realized commercially, but an aromatic copolyester containing biphenol terephthalate and *p*-oxybenzoate units which is capable of forming a thermotropic melt,³ is marketed for ceramic-like plastics, and a family of oxybenzoate-ethylene terephthalate copolyesters has been intensively studied for use in injection moulded thermoplastics.⁴

AROMATIC POLYAMIDES

Morgan has reviewed the historical development of the preparation of fibre-forming aromatic polyamides.⁵ He reported that the first polyamide of the non-peptide type, which was found to form liquid crystalline solutions, was poly(1,4-benzamide). Subsequent investigations revealed that other molecular structures, which retained the linearity and rigidity of the *p*-phenylene group, could also lead to lyotropic polyamides, including the 2,6-naphthalene, *trans*-1,4-cyclohexylene, and *p,p'*-biphenylene. In addition, *p*-phenylene units can be connected by *trans*-azo or *trans*-vinylene groups and still retain their linear, rigid conformations. The molecular structures of such units, as compiled by Morgan, are shown in Table 1.⁵

Four types of reactions have been applied to the preparation of polyamides in general, but only one of these, the reaction of an acid chloride with an amine, has been broadly used to prepare lyotropic polyamides. The direct amidation of acids and amines through a crystalline salt intermediate, as used for the preparation of aliphatic polyamides⁶ (termed a 'nylon salt'), is not applicable for aromatic amine-acid monomer pairs, but three other types of reactions have recently been developed for polyamides; these are:

(1) The oxidative amidation reaction of aromatic amines and acids with phosphorous compounds, which is generally carried out in an amine or amide solvent with organic chlorine compounds as co-reactants, as in the following reaction scheme:⁷



Lithium salts may be added to enhance the solubility of the polymer, and polymers with inherent viscosities well above 1.0 can be prepared by this route.⁸ Unlike direct amidation, this reaction is essentially irreversible, and it is capable of very high yields, so high molecular weight polymers can be readily obtained.⁹

(2) The aminolysis of an active ester, such as those of substituted phenols and hydroxytriazoles, can be used to prepare aromatic and olefinic

TABLE I
Repeating Units of Polyamides which form Lyotropic Solutions⁵

