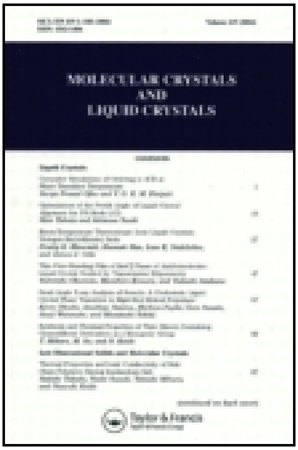

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Levels of Order in Stiff-Chain Polymers

M. Ballauff [a] , R. Rosenau-eichin [a] & E. W. Fischer [a]

[a] Max-Planck-Institut für Polymerforschung, Postfach 3148, 65, Mainz, Frg

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LEVELS OF ORDER IN STIFF-CHAIN POLYMERS

M. BALLAUFF, R. ROSENAU-EICHIN, E.W. FISCHER
Max-Planck-Institut für Polymerforschung,
Postfach 3148, 65 MAINZ, FRG

ABSTRACT

The alterations of the phase behavior and the structure of rigid rod polymers effected by bent units inserted into the main chain or alternatively by appending of flexible side chains to the main chains is considered. The present results indicate that incorporation of a small number of nonlinear units produce solids with distinct defects. Higher amounts of nonlinear moieties is followed by observation of nematic and isotropic phases. Flexible side chains of short length lead to nematic mesophases. Appending of longer side chains causes the occurence of layered structures in the solid state as well as in the mesophase.

INTRODUCTION

It is now well understood that the order observed in low-molecular-weight liquid crystals and in liquid crystal polymers is mainly caused by the anisotropy of the molecules or their constituents. The analysis of the resulting phases by wide-angle X-ray scattering (WAXS) has been proven to be indispensable to detect and to classify the various levels of ordering in l.m.w. liquid crystals[1,2]. Similar investigations of stiff-chain polyesters are severely hampered by the high temperatures necessary to convert the material into the mesophase or melt. In many cases polymers composed solely from linear, rigid units are nearly intractable and their transitions are often located at temperatures where thermal decomposition imposes serious difficulties to any structural investigation. This problem can be traced back to the small gain of entropy when transferring the rod-like polymer from the crystalline to the molten state. It may be circumvented partially by introducing rod-like moieties of different length and shape. However, the disorder thus effected only leads to moderate decrease of the transition point. In principle, a systematic lowering of the degree of crystallinity and the transition temperatures can be done in two ways:

i) Disruption of the rigid main chain by flexible or bent units which lead to a similar lowering of the degree of crystallinity and to a shift of the transition points to lower temperatures[3-5].

ii) Attached flexible side chains will disturb the crystal structure and raise the gain of entropy of the melting process; hence they may be regarded in first approximation as a solvent or a plasticiser bound to the rod-like main chain[6,7]. In this communication a survey of recent investigations mainly done in this laboratory on materials deriving from both concepts will be presented. Special emphasis will be laid on structural studies on the order present in the respective mesophases.

1. STIFF-CHAIN POLYMERS

Owing to their general intractability only a few rigid rod polymers could be studied in detail with regard to their structure. A special case is given by the aramides which may be dissolved in concentrated sulfuric acid. A WAXS analysis of fibers spun from such a solution led to the proposal for the structure of poly(1,4-phenylene terephthalamide) by Northolt[8]. Since rigid chain polyesters like the poly(p-hydroxybenzoic acid) (poly(pHBA)) do not dissolve without decomposition in any known reagent, electron diffraction is the most suitable tool for structural studies on these systems. Thus Lieser[9] succeeded to show that poly(pHBA) crystallizes at room temperature in two different orthorhombic modifications I and II. Above the endothermal transition around 300°C [9,10] forms I and II both transform into a metrically hexagonal phase III[9]. It has to be noted that in this phase the strong reflection corresponding to a Bragg spacing of 4.6Å indicates the interchain distances to be well defined. No further transition to a molten state prior to thermal decomposition can be observed in this material[9]. As indicated by a recent study of Wendorff and coworkers[11] the occurence of the highly symmetrical orthorhombic or hexagonal unit cells seems to be a general feature of crystal structures of stiff-chain polyesters.

2. POLYMERS COMPOSED FROM LINEAR AND BENT UNITS

Since the unit cells of the crystal structures formed by the poly(pHBA) are well known[9] this polymer is uniquely suited to study the influence of bent units on the phase behavior. Fig.(1) displays diffractograms of a polyester containing 90% p-hydroxybenzoic acid and 10% m-hydroxybenzoic acid[12,13]. All reflections recorded at room temperature may be indexed by the unit cells of phases I and II of the poly(pHBA). This can be seen even more clearly from an electron diffraction study on these copolyesters[14]. The broadening of the reflections is due to the distortions of the orthorhombic lattice by the meta-residues.[14] Also, the WAXS analysis of the entire series of copolymers[13] indicates a raising amorphous part to be present in these materials for an increasing content of bent units. However, it is

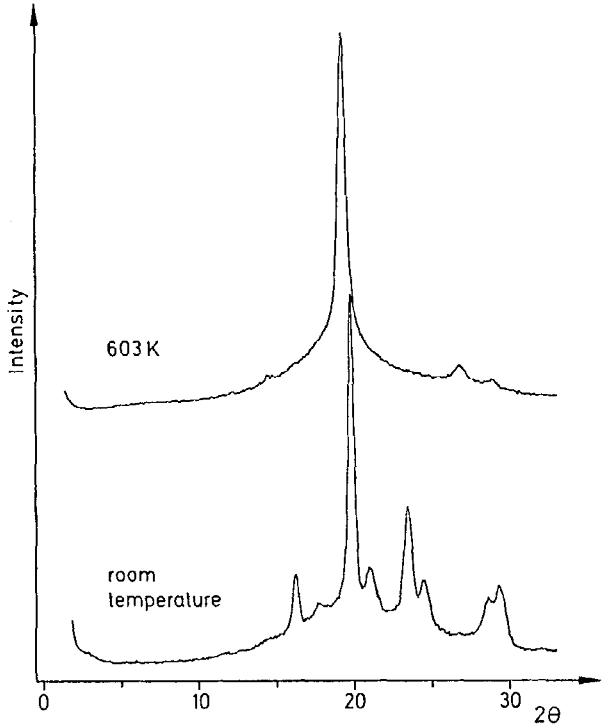

Fig.(1) X-ray diffractograms (λ=1.54Å, uncorrected) for a random copolyester composed of 90% p-hydroxybenzoic acid and 10% m-hydroxybenzoic acid at room temperature and at 603K both taken from reference /13/.

obvious from these studies that the amount of meta units being tolerated by the orthorhombic crystal lattices of form I and II is surprisingly high. Only if the content of mHBA is raised beyond 50% totally amorphous materials are formed; still higher percentages of mHBA then lead to powder patterns similar to that obtained for the semicrystalline poly(mHBA)[13].

As is the case for the homo-poly(pHBA)[9], the copolyester having 90% of pHBA is transformed into the metrically hexagonal phase III at elevated temperatures. This has been shown by electron diffraction[14] explaining the occurence of a single strong reflection in the diffractogram displayed in fig.(1). Additional experiments carried out on copolyesters containing more meta residues suggest these high temperature forms to consist of two phases: 1) form III where the interchain distances are well defined and 2) an amorphous part, probably of the nematic type[13]. Fig.(2) gives a typical example of the WAXS analysis of the high-temperature form.

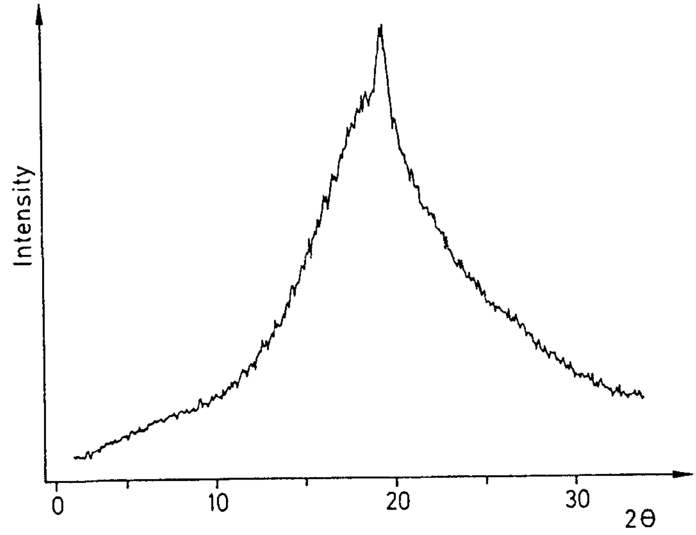

Fig.(2) High-temperature X-ray diffractogram (λ=1.54Å , uncorrected) of a polyester containing 70% p-hydroxybenzoic acid and 30% m-hydroxybenzoic acid at 603K (ref./12/).

In this context it is important to note that at compositions exceeding 50% m-HBA the resulting high temperature phases are isotropic melts.

All findings derived from these copolymers with more than 50% linear units demonstrate that the phases observed at high temperatures are a rather complicated mixture of a distorted solid modification (form III) and an amorphous phase which may exhibit certain degrees of ordering[13]. An additional feature commanding attention is the high amount of bent units tolerated by modifications I–III of the poly(pHBA). A tentative explanation for this unexpected finding may be found in the fact that by combination of two meta residues a linear conformation of the chains can be realized again. The steric repulsion exerted by the neighboring chains thus may force these links into a linear arrangement to comply with the requirement of the orthorhombic or hexagonal lattice.(cf. reference /15/ for a further discussion of this point). Beyond a certain percentage of nonlinear moieties the extended parts of the chains become too short to form an ordered high-temperature modification or a mesophase melt.

3. RIGID ROD POLYMERS WIH FLEXIBLE SIDE CHAINS

As discussed above, the melting point and the crystallinity of the stiff-chain polymers may be lowered systematically by appending flexible side chains to the rigid backbone[7,16]. Investigations of poly(1,4-phenylene terephthalate)s modified by n-alkoxy side chains[7,17] and by n-alkyl side chains[18] demonstrate that the structure of the solid phases is governed by the side chains. In general it may be stated that layered structures causing a strong Bragg reflection are formed in all systems under consideration up to now[7,17,18,19]. The mesophases of the side-chain substituted poly(1,4-phenylene terephthalate)s[17-19] are nematic for short side chains; longer side chains lead to the observation of a layered structure in the mesophase. This is directly obvious from the strong Bragg reflection and its higher orders [7,17-20] (see Fig.(3)).

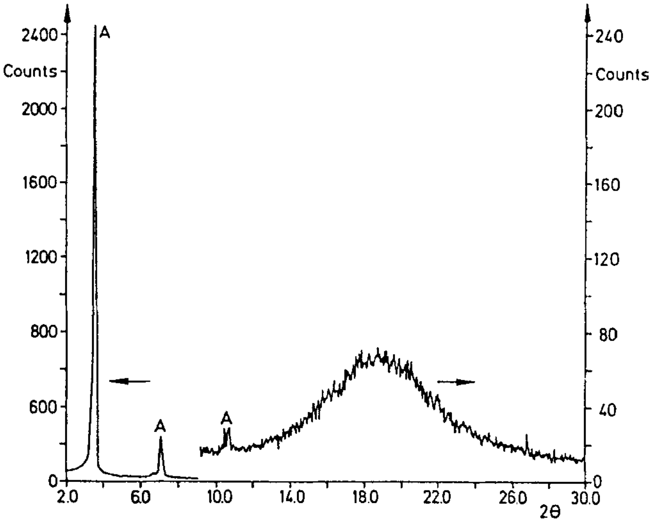

Fig.(3) X-ray diffractogram (λ=1.54Å , uncorrected) of the mesophase formed by the poly(2,5-di-n-hexadecyloxy-1,4-phenylene terephthalate) taken from reference /17/.

The WAXS analysis displayed in fig.(3) furthermore demonstrates that these mesophases have a liquid-like short range order, i.e., there is no well defined interchain distance asfound in the high-temperature modifications of the copolyesters composed of p- and m-hydroxybenzoic acid. Only if the flexible alkoxy side chains are affixed to a linear polyamide main chain, the hydrogen bonding between the amide links leads to the occurence of an additional reflection in the region of wide scattering angles which indicates a stronger correlation of the main chains[19].

CONCLUSION

The transition points of stiff-chain polymers may be lowered systematically by 1) introduction of bent units and 2) by appending of flexible side chains. As demonstrated by WAXS analysis the realization of these concepts for a number of polyesters and -amides leads to different levels of order in the respective phases: Modification of linear chains by bent units seem to produce preferentially solids with a high number of defects whereas flexible side chains induce either ordinary nematic phases or layered structures akin to a smectic A phase.

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