

# OPTICAL AND X-RAY STUDY OF HIGH MOLECULAR WEIGHT POLYMER-POLYESTERAMIDE

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## ABSTRACT

We envision the crystallization of the high molecular weight polyesteramide as occurring by the nucleation of spherulitic centers. The outward growth of a spherulite, as has been seen in the cross-polarized optical microscope, ceases when it has impinged upon the growing surface of another spherulite. By controlling the nucleation rate through the degree of supercooling, the size of a spherulite can be varied to some extent which can be distinguished optically. The spherulite size decreases with supercooling temperature. X-ray data confirm that the structure contains two main phases, a partly crystalline and a liquid crystalline phases beside the amorphous state.

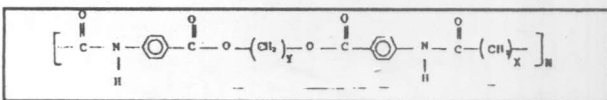
## INTRODUCTION

One of the general facts observed in many polymers is that they are usually partially crystalline. The most evidence of this fact is provided by X-ray studies. The diffraction pattern for polymers crystallized from melt, are usually in the form of rings superimposed on diffuse background, liquid-like diffraction [1].

Spherulite structure is the most common feature for most polymers which are crystallized from the melt. Most commonly, the spherulites grow to a size that can be seen in the polarizing optical microscope. Spherulites are usually little spheres with diameters in the range of  $0.5\mu\text{m}$  to about  $100\mu\text{m}$ . Accordingly, spherulitic growth may appear whenever crystallization develops, so that they are polycrystals which are radiating from common point with repeated branching.

Aharoni [2] pointed out that the polyesteramide family belongs to the main-chain polymeric liquid crystal group (MCPLC) but whose mesomorphicity is dependent on intermolecular hydrogen-bonds directed about normally to the main-chain direction. It was suggested that these polyesteramides are probably present in a smectic C liquid-crystalline form [2].

The subject of this paper deals with optical and X-ray study of an annealed and melt-crystallized high-molecular weight polyesteramide. Its molecular repeat unit is:



where  $X=12$  and  $Y=3$  are the numbers of methylene groups between the amide residues and between the ester moieties respectively and  $N$  is the number of repeat units in the molecule. The molecular weight per repeat unit is 536. The unique structural features of this polymer are its high regularity and strict alteration of two amide groups and two ester groups and substitution of each aromatic ring in the paraposition by one amide and one ester group.

Differential scanning calorimetric (DSC) study on the same polymer [3] revealed the possibility of existing one or two mesomorphic (LC) phases with a level of crystallinity estimated to be in the range of 24 to 32%. In the present paper, the results of hot-stage cross-polarized optical microscopy and of wide angle X-ray diffraction (WAXD) study are given and discussed.

## EXPERIMENTAL

The high molecular weight polyesteramide (trade name:A 1703-40), was kindly supplied by Allied-Signal Corporation Engineered Materials Morristown, N.J., U.S.A. The polymer was prepared from the acids and aromatic amines in the presence of triphenyl phosphate and pyridine according to the Yamazaki procedure. The structure was confirmed by carbon-13 NMR spectroscopy.

As received polymer in the form of granules, were compressed to thin films of about ( $50\mu\text{m}$  thickness) between glass slide and cover slip. Cross-polarized light

microscopy studies were conducted using Vickers M 72 polarizing microscope equipped with a Mettler hot-stage (max. temperature 350°C and controlled by temperature controller (Stanton Redcrest TH 600). To allow complete melting of the sample, the Mettler was first heated to ~260°C (the isotropic melt temperature [3]). During heating and cooling process (rate 1.5 °C/min...), several pictures were taken to reveal the structure. Sometimes after melting (~210°C), the temperature of hot-stage was set at different crystallization temperature for certain times. The magnification is 100 x.

Variable temperature wide angle X-ray diffraction (WAXD) patterns were generated from samples having few millimeter path length, wrapped in a very thin aluminum foils and sandwiched between two coated beryllium foils. The patterns were taken using Siemens D500 TT,  $\theta$ - $\theta$  diffractometer, with monochromatized Cu- $\alpha$  radiation ( $\lambda=1.5418$  Å). The system is equipped with a Mettler hot-stage, for variable temperatures data, automated to supply data in 5°C intervals.

## RESULTS AND DISCUSSIONS

Figure (1) shows the appearance of thin film of the polyesteramide under study using a cross-polarized optical microscope. This micrograph was taken at 241°C during cooling from the melt. The texture is composed of spherulites of small sizes separated from each other. The major endotherm was reported to appear at about 210°C [3]. This suggests that there are some portions of the material which have not been yet melted up to 241°C. We conclude that the molecules exhibit some ordering to form a new crystalline phase. This is in agreement with DSC data [3] where two minor exotherms appear at about 215 and 233°C with a heat of transition, for each, of approximately 7% of that of crystallization transition (major exotherm at ~180°C). This means that the polyesteramide exhibits thermotropic liquid crystalline state.

Figure (2) shows the textural change of the same sample below the major endotherm's temperature (at 200°C) during cooling. The appearance of the specimen reveals that the spherulitic structure fills most of the space but for some regions in between, the spherulites are still in the molten state and they can be crystallized even if the temperature is lowered than 200°C. This can be seen in Figure (3) where the micrograph was at 180°C during

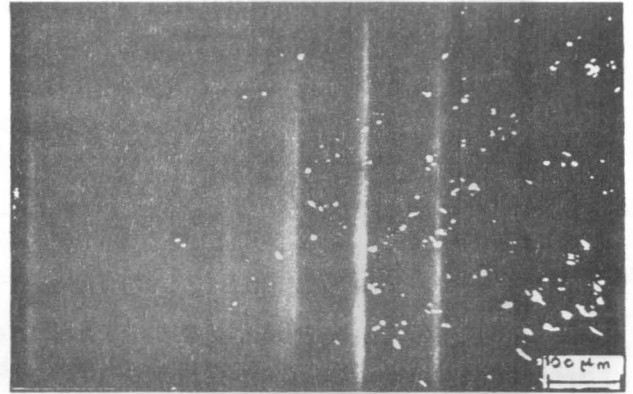


Figure 1. Optical micrograph of polyestramide spherulites at 241°C during cooling from the melt.

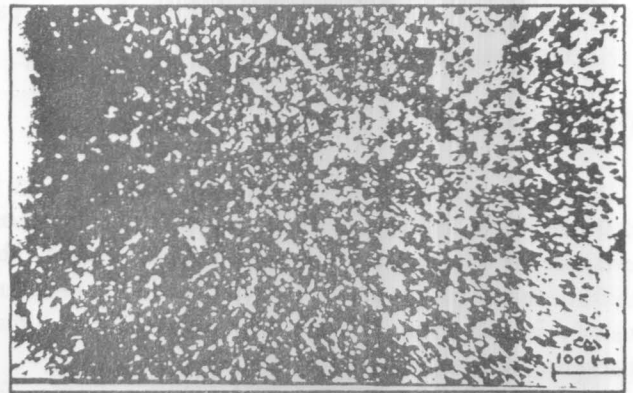


Figure 2. Optical micrograph of melt-crystallized polyestramide spherulites taken at 200 °C during cooling.

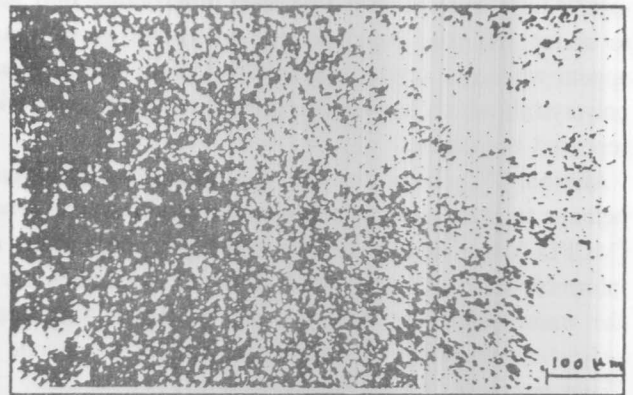
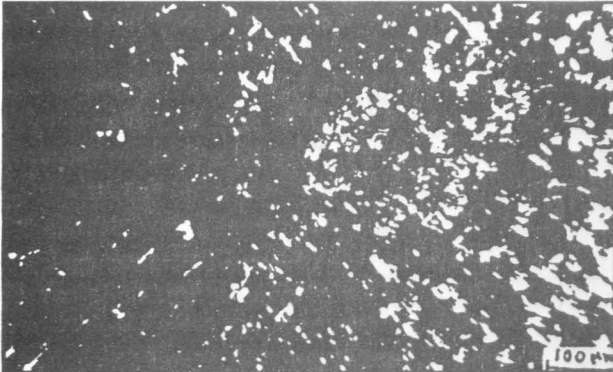


Figure 3. Optical micrograph of melt-crystallized polyestramide spherulites taken at 180 °C during cooling.

cooling. Below such a temperature these molecules constitute the major part of the specimen (~70%); the amorphous phase.

Figure (4) shows a micrograph of a sample annealed at

210°C. There appears larger spherulites. This is because the number of nucleation centers, at that annealing temperature, have been reduced so that they are more separated. As during the growing process, the spherulites have more space to become larger. Accordingly, the spherulite size can be controlled by controlling the nucleation agents.

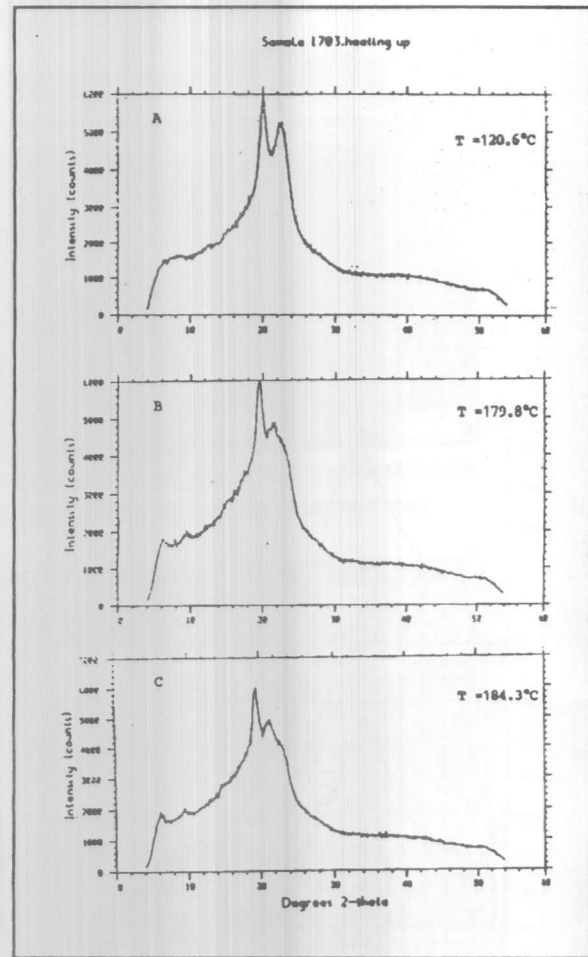


**Figure 4.** Optical micrographics shows the structure of polyestramidespherulites. The specimen was annealed at 210°C for 20 min, and then lead to 20°C.

From the present optical microscopy study one may suggest that there are three types of molecules: The first type: molecules which can not crystallize at any temperature and this type of molecules constitute the amorphous state and they were found in polystyrene and polyethylene to be short molecules [4,5]. The second type: molecules can crystallize above 180°C during heating and these represent most of the material that can be crystallized. Such molecules should have medium length and constitute the branching units of the polymer in the spherulitic structure. Thirdly, molecules that can be crystallized above the melting point which form the liquid crystalline phase and these are the longest ones. This is to be considered the major part of spherulitic structure with those of the second types (branching units) filling in between these long molecules.

Wide angle X-ray patterns taken during a heating cycle are shown in Figure (5). As can be seen, the main features are:

- (1) a smooth Gaussian shape of amorphous halo of the isotropic melt at 257.1°C (panel F),
- (2) an intense reflection doublet with  $2\theta$  between 19° and 21° with a little change of peak values on going from panel A to panel E,
- (3) development of multiple weak reflections at low



**Figure 5.** WAXD intensity vs.  $2\theta$  (scattering angle) for polyesteramide at different temperatures.

angles ( $2\theta \sim 10^\circ$ ) upon heating (panels B through E).

The d-spacings associated with these reflections can be obtained using a modified Bragg's equation which is valid for extended chain molecules [6]:

$$d = 1.11 d_{\text{Bragg}}, \quad 2 d_{\text{Bragg}} \sin \theta = \lambda.$$

The inner (intense) reflection appeared in most of the panels, corresponds to 5.2 Å distance and outer one corresponds to 4.7 Å. According to Aharoni's recent work on polyesteramide family [2], the large distance is taken to represent the average distance between the H-bonded polyamide chains which form flat or pleated sheets. The other distance 4.7 Å is the distance between such sheets which are assumed to be controlled by van der Waals

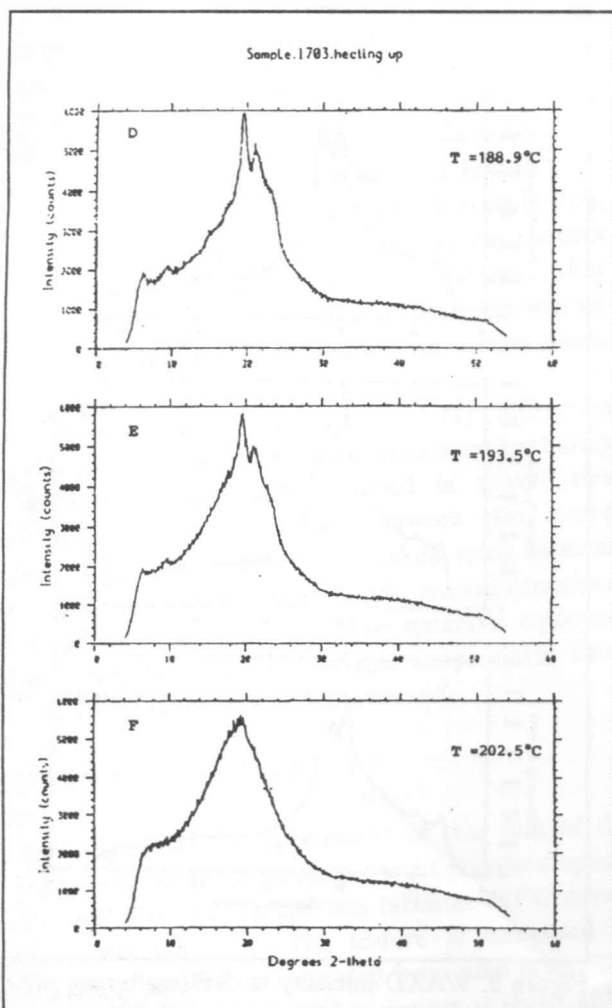


Figure 5. Continued.

interactions. The weak reflections correspond to a spacing of about 10.2 Å.

In order to correlate between optical and X-ray data, we introduce the following model for spherulitic structure in polyesteramide as shown in Figure (6): Region 1 represents the dominant lamellae which determine the framework of spherulite and these are composed of the long molecules. Regions 2 and 3 are branched and subsidiary lamellae, respectively, which fill the space between dominant lamellae. One may suggest that these lamellae are composed of medium-length molecules. The subsidiary lamellae are probably thin which grow above 170°C and melt just below 202°C. These correspond to weak reflections in X-ray data (panels B through E). Region 4 constitutes the major part of the structure, the amorphous region, which is composed of short molecules that can not crystallize at any temperature.

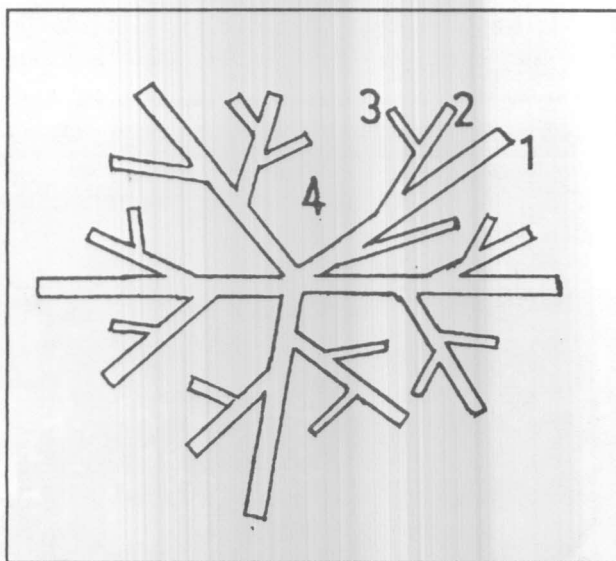


Figure 6. Schematic illustration of spherulitic growth of polyesteramide showing the four regions explained in the text.

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#### REFERENCES

- [1] Bassett, D.C., *Principles of Polymer Morphology*, Solid State Science series, Cambridge University Press, Great Britain, pp. 16-36, 1981.
- [2] Shaul M. Aharoni, "Hydrogen-Bonded Highly Regular Strictly Alternating Aliphatic-Aromatic Crystalline Polyesteramides", *Macromolecules*, Vol. 21, no. 7, pp. 1941-1960, 1988.
- [3] Okaz, Ali M., "First-Order Phase Transition in Thermotropic Liquid Crystalline Polymers; Polyesteramides", *Alexandria Engineering Journal*, Vol. 28, no. 1, pp. 251-267, 1989.
- [4] Vaghan, A.S. and Bassett, D.C., "Early Stage of Spherulite growth in Melt-Crystallized Polystyrene", *Polymers*, Vol. 12, no. 6, pp. 1397-1401, 1988.
- [5] Bassett, D.C., "Electron Microscopy and Spherulitic Organization in Polymers", *CRC Crit. Rev. Solid State Mater. Sci.*, Vol. 12, no. 8, pp. 1397-1401, 1988.
- [6] Afzana Anwer, M.Sc. Dissertation (unpublished), Dept. Materials Science and Metallurgy, Cambridge University, Cambridge, Great Britain, (1987).