# Spherulite Crystallization in Bisphenol-A-Polycarbonate of Varying Molecular Weight Distribution

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## Synopsis

The spherulitic structure of films of fractionated bisphenol-A-polycarbonate having a range of different average molecular weight and molecular weight distributions has been studied using the polarization microscope. Spherulitic crystallization was induced in specimens by the action of solvent or solvent vapor at room temperature or by isothermal heat treatment at 180°C. These phenomena were all shown to be a function of the average molecular weight and polydispersity of the material. The glassy amorphous and spherulite polymer phases were investigated using a microscopic etching technique and gel permeation chromatography (GPC). Results of this investigation have established that considerable segregation by molecular weight occurs during the crystallization process. Spherulites produced have been shown to exhibit variation in morphologic texture depending on conditions of induction and polydispersity of the polymer. Examples of unusual and previously unreported spherulites have been observed.

## INTRODUCTION

Various workers[1,2] have reported spherulites in bisphenol-A-polycarbonate films obtained by evaporation of solution. Other authors[3,4] have studied the crystallization kinetics of this polymer in mixed solvent systems and have related their findings to variation in molecular weight. The investigation reported here has been concerned with morphology, in particular, the effect of molecular parameters on the structure of spherulites.

The precise theoretical basis of spherulite formation is very much an open subject. According to Keith and Padden,[5] the spherulite-forming properties of high polymers, from the melt, can be explained in terms of molecular polydispersity. Polymer melts contain molecular chains of different length possessing varying degrees of stereoregularity. According to these authors, only chains of appropriate length and flexibility can participate readily in the crystallization process. The low molecular weight and atactic molecules are accordingly preferentially rejected and segregated. These less favorable rejected molecules or components tend therefore to accumulate in the amorphous phase. The whole process can be regarded as a type of fractionation phenomenon.

Previous experimental support for this theory comes from a study of polymers which crystallize from the melt.[5] The present study has examined the applicability of the above ideas to crystallization behavior from the glassy state.

Studies made by McNulty[2] on the etching of polycarbonate films containing spherulites with various mixtures of acetone and chloroform indicated that the amorphous regions could be preferentially dissolved. Thus, by appropriate choice of solvent, spherulites could be separated from the amorphous matrix. In the present investigation, gel permeation chromatography (GPC) was used to characterize the separated amorphous and crystalline phases. GPC was therefore used as an additional analytical technique to assess the precise molecular compositional changes that take place during crystallization of polycarbonate.

## EXPERIMENTAL

Specimens were examined using a Reichert Zetopan polarization microscope using mainly polarized light and crossed polars, although unpolarized light was employed for certain studies.

### Polymer Preparation

The polycarbonic ester of 2,2'-bis(4-hydroxyphenyl)propane was fractionated into samples having various molecular weight distributions by a progressive precipitation procedure, using a methylene chloride/60–80 petroleum ether system. The high molecular weight fractions separated in a fibrous form, while the lower molecular weight fractions separated as powdery, partially crystalline precipitates. The intrinsic viscosities of all of these fractions were determined in methylene chloride solution. The viscosity-average molecular weights obtained ranged from $2 \times 10^3$ to $80 \times 10^3$. The fractions were further characterized by membrane osmometry and light scattering techniques and were used to calibrate a Waters gel permeation chromatograph.[6]

### Film Preparation

Each characterized polycarbonate fraction was dissolved in methylene chloride to give an approximately 1% w/v solution. Films were then prepared by placing a few drops of the appropriate solution onto a preheated microscope slide or cover glass (ca. 100°C). The thickness of such films could be varied by repeating the operation. The experimental procedure adopted was designed to achieve a clear amorphous film, and it was shown that variation in film thickness did not appreciably affect the subsequent growth of spherulites.

### Vapor Application and Spherulite Formation

Cover glasses on which thin amorphous films were cast were inverted and then sealed on to a cavity slide by using petroleum jelly. This con-

venient sealant was used to prevent loss of acetone which had been previously placed into the cavity. Acetone was used to bring about the formation of spherulites. The initial examination of a prepared film between crossed polars usually showed extinction due to absence of order. Crystallization was indicated by a gradual brightening of the field of vision and the appearance of spherulites.

### Spherulite Formation on Prolonged Annealing

The selected polycarbonate fraction was fused on a preheated glass slide (ca. 300°C) and the melt was pressed down under a glass cover slip producing a thin amorphous film. On occasions, the cover glass was removed from the melt pressed sample prior to annealing treatment. Experiments were also carried out with the cover glass intact. The cover glass did not affect the final result appreciably.

These specimens were then isothermally annealed in an oven for periods of 1 hour up to 48 hours at 180°C. This treatment brought about the steady growth of spherulites. The temperature selected was above the glass transition point for each polymer fraction, as determined by differential scanning calorimetry. The highest glass transition temperature recorded was 165°C for the highest molecular weight fraction ($\bar{M}_w$ 41,200, $\bar{M}_n$ 32,200).

### Examination of Crystalline and Amorphous Forms by Gel Permeation Chromatography

**Acetone Vapor-Induced Spherulites.** Films of the unfractionated polycarbonate were cast from methylene chloride solution onto a microscope cover glass in the way previously described. The films were then treated with acetone vapor so as to bring about spherulite growth. These films, which now contained large numbers of spherulites, were then placed into contact with a droplet mixture of 80/20 v/v chloroform/acetone[2] supported on a microscope slide. After a few minutes, spherulites were observed to be mobile in the solvent system. The spherulites and solvent extract were separated by means of a micropipette, and the extract was then evaporated to dryness. Both solids were then dissolved in methylene chloride and separately analyzed by GPC. The results are given in Table I.

**Annealed Specimens.** A solvent-cast film from a low molecular weight fraction was annealed for 8 hr at 180°C to induce crystallization. It was

TABLE I
GPC Analysis of Acetone-Induced Spherulites and Glassy Matrix
Carried Out on Commercial Polymers

| | $\bar{M}_w$ | $\bar{M}_n$ | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|
| Unfractionated polycarbonate film | 30,400 | 14,500 | 2.10 |
| Solvent-etched crystalline polymer (residue) | 32,854 | 15,285 | 2.15 |
| Solvent-etched amorphous polymer (extract) | 5,518 | 1,552 | 3.56 |

Table II
GPC Analysis of Heat-Induced Spherulites and Glassy Matrix
Carried Out on Low Molecular Weight Fraction

|  | $\bar{M}_w$ | $\bar{M}_n$ | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|
| Polycarbonate before heat treatment (total analysis) | 8,800 | 7,200 | 1.22 |
| Polycarbonate after 8 hr at 180°C (total analysis) | 8,750 | 7,200 | 1.21 |
| Solvent-etched crystalline polymer (residue) | 15,144 | 8,338 | 1.82 |
| Solvent-etched amorphous polymer (extract) | 5,000 | 2,100 | 2.4 |

then etched as above, and a similar GPC analysis was carried out on the residue extract. It was important at this stage to determine whether thermal degradation occurred during prolonged annealing. To this end, a total GPC analysis was also carried out before and after thermal treatment. The results given in Table II illustrate that thermal breakdown has not occurred during the 8 hr at 180°C.

## DISCUSSION

This study has shown that whatever the method employed to bring about spherulite formation, whether by acetone action or by heat treatment, the morphology is very much dependent on the concentration of low molecular weight material.

The combination of the etching technique of McNulty[2] and GPC of the present work have shown that the ideas of Keith and Padden[5] can be applied to crystallization from the glassy state.

The results of such analyses show that $\bar{M}_w$ of initially unfractionated polycarbonate becomes raised in the spherulite during crystallization to a value higher than that of the bulk polymer.

Also, smaller molecules are rejected into the amorphous phase. This trend was observed in all the crystallization processes investigated. This phenomenon is probably due, in part, to the inability of small polymer molecules to chain fold easily and become ultimately incorporated within the crystal unit cell.

### Spherulite Texture

Spherulites of polycarbonate grown in films in the presence of acetone all showed the usual extinction cross when examined between crossed polars. The texture of these spherulites was compact and fine (see Figs. 1 and 2 for typical examples). The sign of birefringence was shown, by use of a sensitive tint retardation plate, to be always negative. This condition applied to spherulites produced by heat treatment.

Some spherulites produced by annealing were observed exhibiting unusual bands or rings of extinction (Fig. 3). Examination of these spherulites by incident light interference showed that these rings are associated
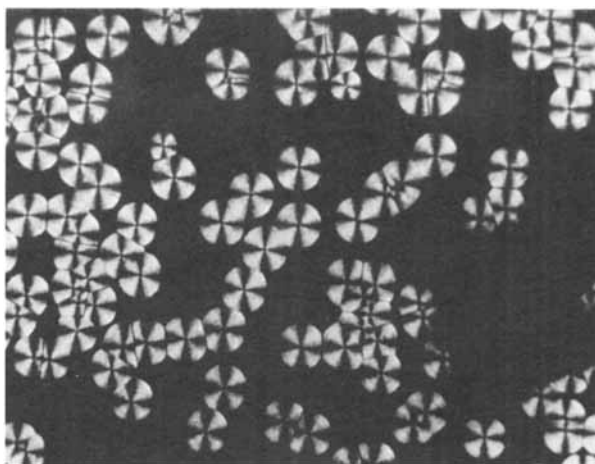
(a)
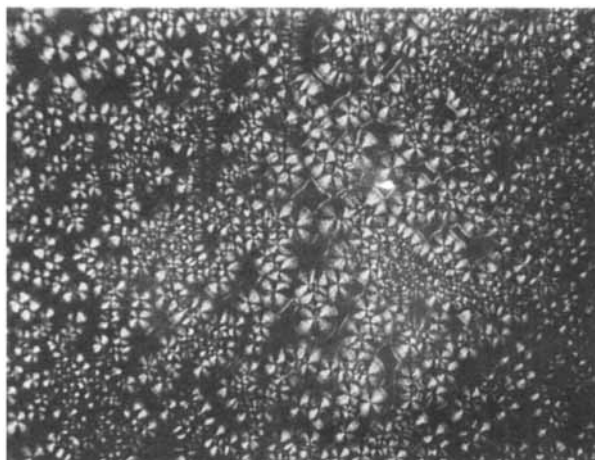


(b)

Fig. 1. (a) Spherulite discs in polycarbonate film (possessing total GPC analysis $\bar{M}_w$ 8,800, $\bar{M}_n$ 7,200, $\bar{M}_w/\bar{M}_n$ 1.22) induced from the glassy polymer by acetone vapor; mag. $\times 250$, crossed polar. (b) Spherulites produced under the same conditions as (a) but by starting with high molecular weight material ($\bar{M}_w$ 43,100, $\bar{M}_n$ 34,200, $\bar{M}_w/\bar{M}_n$ 1.26); mag. $\times 250$, crossed polars.

with surface markings (see Figs. 3 and 4). They were produced only by annealing relatively to low molecular weight material. During the thermal crystallization of poly-*trans*-1,4-isoprene, Eaves[8] observed at times the presence of ringed spherulites. He found that small periodic variations in temperature during spherulite growth gave rise to concentric bands in the spherulites. In fact, rotation of the axes of the polarizer did not alter the position of the rings. When similar experiments were carried out in a carefully controlled thermostat, no ring formation was observed. It is
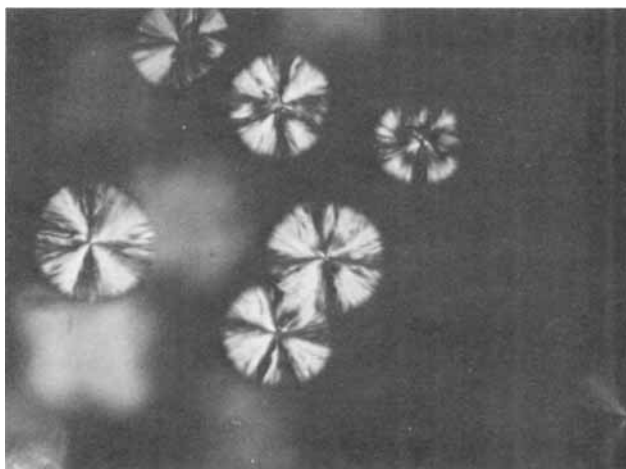
Fig. 2. Spherulites produced by heat treatment (8 hr at 180°C) of a film of polycarbonate (possessing total GPC analysis $\bar{M}_w$ 8,800, $\bar{M}_n$ 7,200, $\bar{M}_w/\bar{M}_n$ 1.22); mag. ×650.
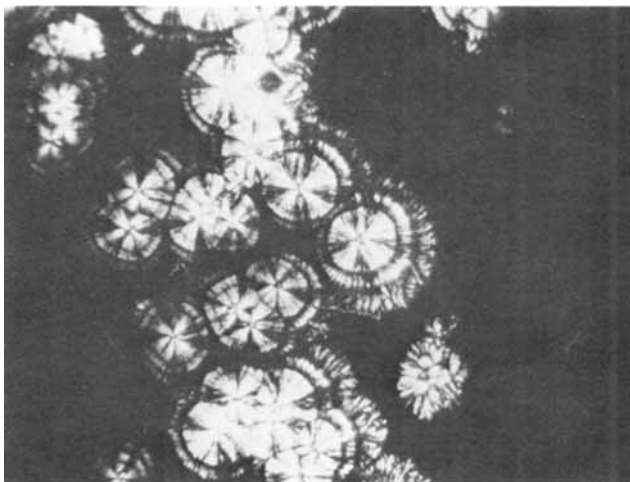


Fig. 3. Polycarbonate spherulites showing unusual ringed extinction patterns produced by annealing low molecular weight material; mag. ×650, crossed polars.

probable that the same explanation of temperature fluctuation applies to the formation of ringed spherulites in polycarbonate.

In contrast to all other examples cited, crystallization of polycarbonate of narrow molecular weight distribution ($\bar{M}_w$ 8,800, $\bar{M}_n$ 7,200, $\bar{M}_w/\bar{M}_n$ 1.22) as produced by slow evaporation of a methylene chloride solution produced large spherulites with periodic ring structure (see Fig. 5). These unusual extinction patterns are similar to those observed by Keller[7] in solvent-produced thin films of poly(ethylene terephthalate) and polyamides. The rings are not always found in large numbers; however, there is reason to

Fig. 4. Examples of polycarbonate spherulites illustrated in Fig. 3 examined by incident interference contrast showing surface markings; mag. ×900.
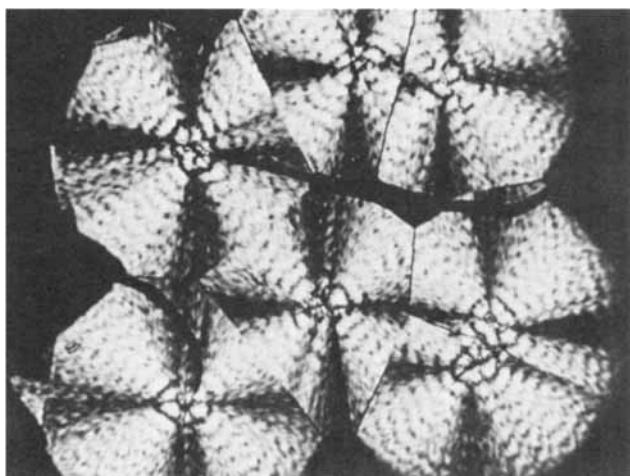


Fig. 5. Methylene chloride–deposited spherulites obtained by very slow evaporation showing periodic banded extinction patterns along the radii due to a cooperative twisting of the fibrils; mag. ×1000.

believe that their occurrence is related to the spherulite growth rate, since they are less marked in specimens which have been crystallized rather more rapidly. The alternating dark and bright rings observed with the polarization microscope have been explained on the basis of a twisting mechanism.[7] They have resulted from a cooperative twisting of the radial fibrils such that the refractive index ellipsoid twists regularly about a minor axis as one moves in or out along the spherulite radius. This type of spherulite has also been reported in polycarbonate by Kampf.[1]

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