

# ***Separation of the Diffusion and Crystallization Fronts on Swelling a Bisphenol-A Polycarbonate***

## **INTRODUCTION**

The liquid-induced crystallization of polymers involves chiefly two main sequential processes, namely, the diffusion of a low-molecular-weight substance into the interior of the polymer sample and the crystallization of the polymer which has already reached a sufficient degree of swelling. In many cases a third process is also found to take place, namely, the diffusion of the swelling agent the excluded from the crystallization area. The overall course of the above phenomenon depends on the ratio between the rates of the said three processes. When crystallization is the faster process, its course will be controlled by the diffusion of the low-molecular-weight substance into the interior of the polymer sample. In the opposite case, the independent observation of both these processes ought to be possible.

In their investigations of the liquid-induced crystallization of poly(ethylene terephthalate), Wilkes et al. found that process to begin directly behind the distinctly formed penetration front moving toward the interior of the polymer sample.<sup>1-3</sup> On the other hand, our studies on the crystallization of a bisphenol-A-derived polycarbonate carried out in several swelling liquids showed the existence of quite separate diffusion and crystallization fronts under certain experimental conditions.<sup>4,5</sup> The magnitude of the distance between those fronts was found to depend on the swelling liquid used and on the temperature of the process.

Initially, we did not note any changes of that distance during our measurements. However, theoretical considerations suggest that the distance between the crystallization and diffusion fronts may change with time. In order to extend the scope of our earlier investigations it was decided to study that problem in greater detail.

## **EXPERIMENTAL**

Samples of 40- and 100- $\mu\text{m}$  thick films obtained from the Bistan AF polycarbonate with a viscosity-average molecular weight of  $\bar{M}_v \approx 62,500$  were used in the present study along with 100- $\mu\text{m}$  thick plates, obtained from the press-molded chips of Makrolon 3000 polycarbonate ( $\bar{M}_v \approx 24,500$ ).

Acetone was the swelling agent employed. The measurements were made at the temperature of 294 K in the following way. A film sample measuring  $5 \times 5$  mm was sandwiched between the cover glasses of the microscope and the whole placed in a thermostatted vessel installed instead of the object stage. The sample was then covered with acetone at a suitable temperature. The swelling liquid could penetrate into the polymer only starting from the edges of the sandwiched polymer film. The distance between the diffusion and crystallization fronts observed under these conditions was determined with an accuracy of up to  $\pm 1.5 \mu\text{m}$  by means of a microscope eyepiece provided with a Vernier scale.

## **RESULTS AND DISCUSSION**

Results of measurements of the distance between the diffusion front and the crystallization front moving behind it are shown in Figure 1 as a function of time. Individual experimental points plotted are the average results of 20 and six independent measurements carried out on the Bistan AF films 100 and 40  $\mu\text{m}$  thick, respectively, five measurements being performed on samples of the Makrolon 3000 polycarbonate. The time dependence of  $\Delta d$  was found to be similar for all types of samples studied. That would seem to suggest that both the thickness of the film and the difference in the molecular weight of the samples did not have any significant influence on the course of the phenomenon investigated in the above-mentioned system, i.e., at least for the experimental period employed (about 1 hr). It also follows from the plot obtained that the distance between the diffusion front and the crystallization front moving behind it increased on swelling at a variable rate, and especially so in the initial phase of that process.

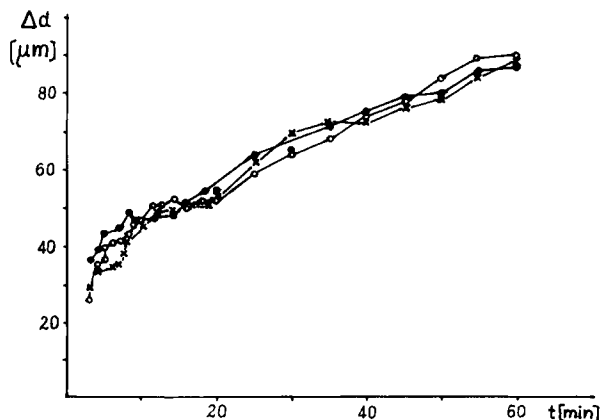


Fig. 1. Time dependence of the distance between the diffusion and crystallization fronts (swelling agent: acetone,  $T = 294$  K); (O) Bistan AF, 100  $\mu\text{m}$ ; (X) Bistan AF, 40  $\mu\text{m}$ ; (●) Makrolon 3000.

The formation of a sharp penetration front in the system studied by us is a phenomenon commonly observed during the diffusion of low-molecular-weight substances into glassy polymers. According to the literature, the formation of a distinct diffusion front, accompanied by an abrupt increase of the concentration of the penetrating liquid, takes place in the case when the system polymer-swelling agent has reached such a state of swelling that its glass transition temperature is below that at which the experiment is performed.<sup>6</sup> Observations made in our laboratory in the course of investigations on the process of liquid-induced crystallization<sup>5,7</sup> are in full agreement with the above suggestion.

The separation of the diffusion and crystallization fronts provides direct evidence for the existence of a crystallization induction period. In this case we are dealing with a rather short induction period, whereas an extremely long induction period was observed for the crystallization of that polymer in bulk.<sup>8</sup> On the basis of results obtained in our previous studies it may be suggested that the existence of the above-mentioned crystallization induction period is connected with a gradual increase in the relative amount of trans-trans conformations<sup>9,10</sup> of the polycarbonate chains. It should be emphasized that, according to Bonart, polycarbonate chains must assume the trans-trans conformation in the crystalline areas.<sup>11</sup> In the experimental conditions employed, the relative amount of trans-trans conformations in the polycarbonate was moreover found to increase together with the increase of the degree of swelling and of the amount of the more ordered areas.<sup>9,10</sup> That would seem to explain the observed presence of the crystallization induction period and the shifting of the crystallization front with respect to the diffusion front.

The rate of such conformational changes in the swollen state is thought to be connected with the

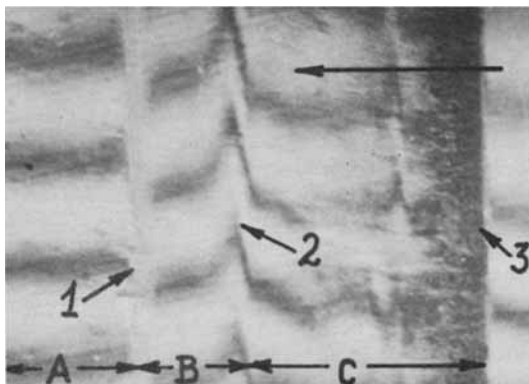


Fig. 2. Microscope picture of the acetone-swollen ( $T = 294$  K) sample, taken in the interference band field: (1) diffusion front, (2) crystallization front, (3) sample edge, (A) sample core, (B) swollen zone, (C) crystalline zone. The arrow points in the direction of the diffusion process.

mobility of macromolecular chain segments, which depends on the degree of swelling. Consequently, the increase of the distance between the diffusion and crystallization fronts taking place on swelling would seem to indicate that the rate of conformational changes gradually tends to decrease. Such a phenomenon should occur when we assume the existence of a certain concentration gradient of the penetrant in the zone situated between the said two fronts. That gradient is further assumed to change in the course of the process studied and hence to "diffuse" the concentration gradient profile in the direction of the actual diffusion process. Thomas and Windle observed the course of diffusion outlined above to occur in their studies of the system poly(methyl methacrylate)-methanol<sup>11</sup> for which, however, crystallization does not take place.

In order to check the validity of the foregoing assumptions in the case of the system studied by us, a microphotograph of the sample being swollen was taken in the interference band field by means of a polarizing microscope (MPI-5, Polish Optical Works, Warsaw). The photograph (Fig. 2) shows that the arrangement of the interference bands obtained in the zone between the diffusion and crystallization fronts does not contradict in any way the interpretation put forward by us, although a complete elucidation of that phenomenon clearly necessitates further studies.

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