

Studies of Liquid-Induced Crystallization of Bisphenol A Polycarbonate

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Synopsis

The course of liquid-induced crystallization of a bisphenol A-derived polycarbonate was investigated using acetone, methyl propyl ketone, methyl isobutyl ketone, and xylene as swelling agents. It was found that above a certain temperature, characteristic of a given polycarbonate-swelling agent system, the diffusion process takes place with the formation of a sharp boundary. The velocity of motion of the diffusion front was determined at various temperatures, and these data were then used to calculate the apparent diffusion coefficients and diffusion activation energies for the different swelling liquids employed. Moreover, a distinct separation of the diffusion and crystallization fronts was observed in the systems investigated, changes in the distance between these two fronts having been determined for various swelling temperatures. The above phenomenon was used to determine the experimental conditions making possible the characterization of a crystallization process not controlled by the diffusion of the swelling agent into the sample. The dependence of half-times of crystallization on temperature was determined based on crystallization kinetics studies performed by means of a light depolarization technique.

INTRODUCTION

The course of liquid-induced crystallization of polymers depends on the relation existing between the rate of diffusion of the low molecular weight species into the polymer and the rate of crystallization of the swollen polymer. The rate of polymer crystallization is generally higher than that of the diffusion. Consequently, the space within which the degree of swelling of the polymer will be sufficiently high to initiate the crystallization process is determined by the rate of diffusion of the swelling liquid into the polymer sample investigated.

Liquid-induced crystallization has hitherto been studied mainly on poly(ethylene terephthalate)¹⁻⁴ and on a bisphenol A-derived polycarbonate,⁵⁻⁹ and also on polyoxyphenylene,^{10,11} polyamide 6,¹² and isotactic polystyrene.¹³ It is to be emphasized, however, that the relationship between the diffusion and crystallization has not been experimentally studied in any of these papers.

In our former work¹⁴ concerning the methyl isobutyl ketone-induced crystallization of the bisphenol A-derived polycarbonate, it was shown that the diffusion and crystallization fronts were not superimposed on each other. It was the aim of the present work to get a better insight into the nature of both these processes taking place on swelling the polycarbonate in question by other liquids and also to find such a set of experimental conditions under which it would be possible to characterize the liquid-induced crystallization process as a separate process, independent of the course taken by process of diffusion of the swelling liquid into the sample.

EXPERIMENTAL

Materials

The amorphous samples of the Bistan AF films 20 and 100 μm thick ($\bar{M}_v = 62,500$) were obtained by casting from a methylene chloride solution. The swelling liquids (acetone, methyl propyl ketone, methyl isobutyl ketone, and xylene) were purified by standard techniques and freshly distilled before all measurements.

Procedures

Simultaneous observation of the course of the diffusion and crystallization processes was carried out using a microscope technique. Samples of film 100 μm thick were clamped between the microscope cover glasses, placed on a thermostated microscope object stage (temperature control accuracy ± 0.05 K), and then covered with a swelling liquid at the same temperature. Permeation of the liquid into the polymer was possible only at the sides of the sample lying flush with the object stage. Changes in the relative position of the diffusion and crystallization fronts visible under the microscope were measured by means of a suitably graduated eyepiece. Results of these measurements have made possible the selection of conditions ensuring the observation of the crystallization process alone.

The kinetics of the liquid-induced crystallization of the swollen polycarbonate was determined by a light depolarization technique described by Magill.¹⁵ The measurements were carried out using polycarbonate film samples 20 μm thick placed on a thermostated object stage and swollen simultaneously from both sides, i.e., from top and bottom with a liquid maintained at a suitable temperature. We were thus able to show that the use of the film of the above-mentioned thickness had made possible the experimental separation of the crystallization process.

Measurements of the amount of the swelling liquid in the 100- μm -thick foil samples were performed by gravimetric technique.

RESULTS

In the first stage of the experimental procedure, the changes taking place on permeation of the swelling liquid in a sample placed between the cover glasses were observed under the microscope. Figure 1 is the microscope image in polarized light (with polarizer and analyzer crossed) of a sample swollen by acetone at a temperature of 293 K.

The following details are to be distinguished: (1) the nonswollen sample core, shining slightly due to stresses produced during the sample preparation procedure, (2) the sharp liquid diffusion front, (3) the swollen zone without any definite morphologic species, (4) the bright crystalline layer, and (5) the edge of the sample. Needle-like fissures in the direction of the motion of the diffusion front were also observed, their lengths and number increasing with low swelling process temperature.

The changes of the distance of the diffusion front to the edge of the sample on swelling were also measured. Results of these measurements, obtained for

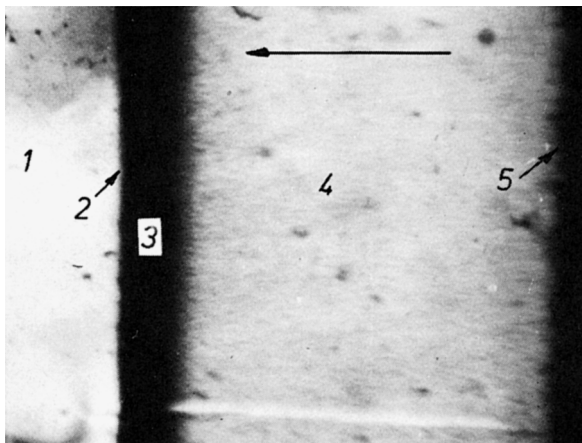


Fig. 1. Microscope image of changes taking place on penetration of liquid into sample (polarizer and analyzer crossed): 1, sample core; 2, diffusion front; 3, swollen zone; 4, crystalline zone; 5, sample edge. Arrow marks the direction of the diffusion process.

individual swelling liquids at different temperatures, are shown in Figures 2 through 4 as a function of the square root of the time of swelling.

The character of this relationship was thus found to be the same as that obtained for methyl isobutyl ketone.¹⁴ It was found initially to be a linear function of the square root of time, certain deviations from the straight-line relationship being observed later, which indicates a lower rate of the diffusion process and is to be more distinctly noticed at the upper range of the experimental swelling temperatures. Changes in the rate of motion of the diffusion front were depicted

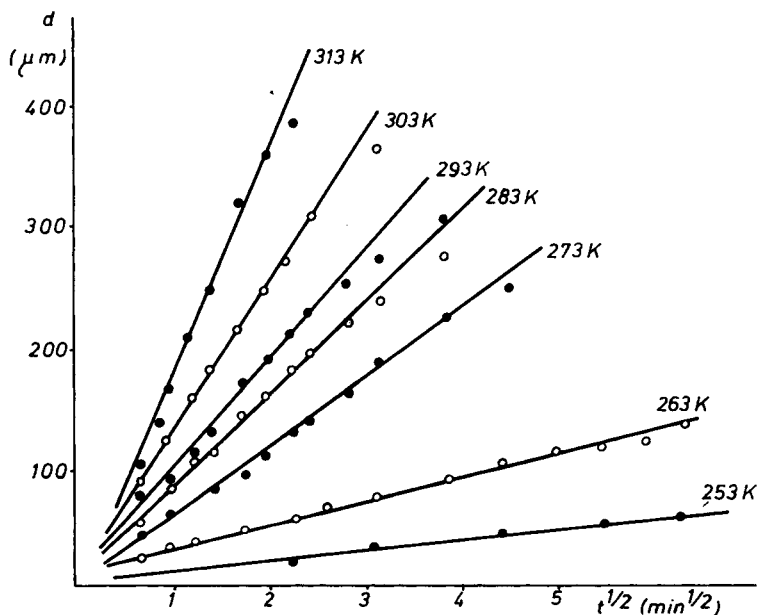


Fig. 2. Changes in position of the diffusion front of acetone with respect to the edge of the sample, expressed as function of square root of time. Numbers on the graphs indicate the swelling temperature.

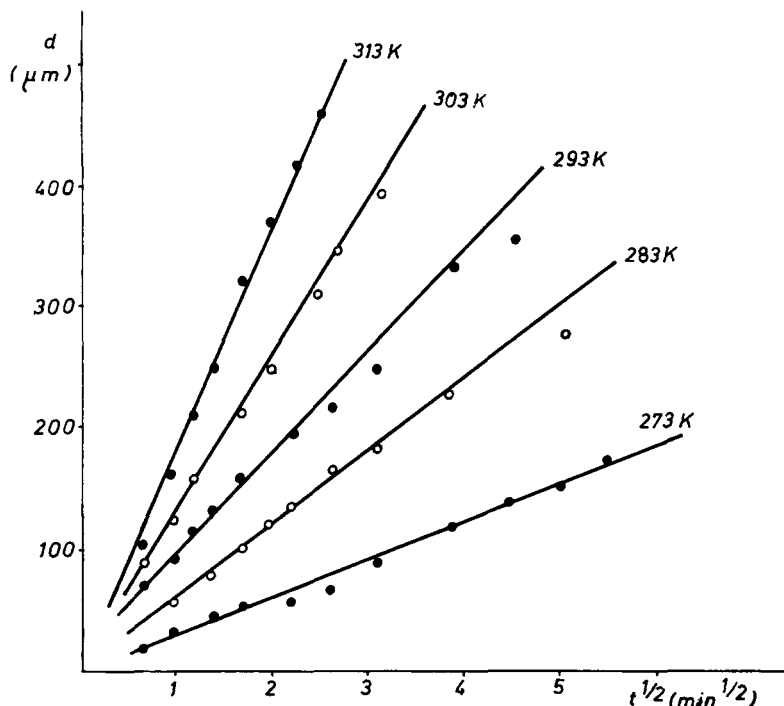


Fig. 3. Changes in position of the diffusion front of methyl propyl ketone with respect to the edge of the sample, expressed as function of square root of the time. Numbers on the graphs indicate the swelling temperature.

as a function of temperature in Figure 5 in the form of the temperature dependence of the slopes of the straight lines shown in Figures 2-4 and 1 (to be found in our earlier paper¹⁴). We were thus able to ascertain that the rate at which the diffusion front penetrates into the sample considerably decreases on lowering the temperature, ultimately reaching values difficult to measure by the experimental technique employed by us in the present work.

The above "checking" of the diffusion front occurs at the temperature of about 248 K for acetone, 260 K for methyl propyl ketone, and about 280 K for methyl isobutyl ketone and xylene. At the same time, at temperatures close to those quoted above, the formation of a large number of long branched-type fissures was observed.

Based on measurements of the changes of the position of the diffusion front on swelling the polycarbonate sample investigated, we were able to calculate the apparent values of the diffusion coefficients of individual swelling liquids used in the present study. The following equation was used¹⁶:

$$\bar{D} = x^2/2t$$

where x is the distance from the diffusion front to the edge of the sample (cm) and t is swelling time (sec). Results of these calculations are listed in Table I.

The analysis of the changes of the diffusion coefficient \bar{D} with temperature was based on the assumption of the applicability of an Arrhenius-type relationship, depicted in Figure 6 as a function of the reciprocal of the tempera-

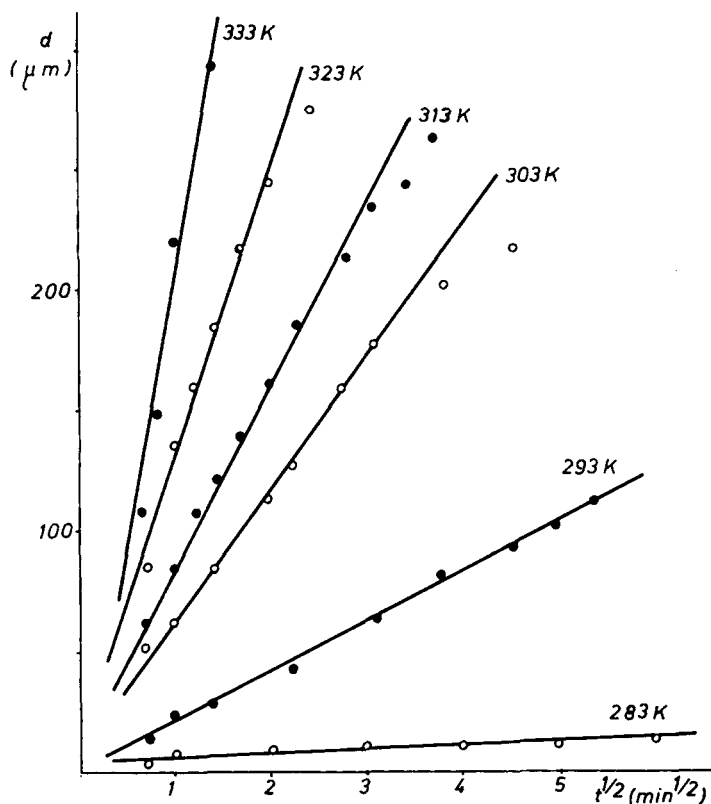


Fig. 4. Changes in position of the diffusion front of xylene with respect to the edge of the sample expressed as function of square root of the time. Numbers on the graphs indicate the swelling temperature.

TABLE I
Values of Apparent Diffusion Coefficients of Swelling Liquids Used in the Bistan AF Polycarbonate, Calculated Based on Changes in Position of the Penetration Front

Temperature, K	$\bar{D} \times 10^8, \text{cm}^2/\text{sec}$			
	Acetone	Methyl propyl ketone	Methyl isobutyl ketone	Xylene
253	0.8	—	—	—
263	5.0	—	—	—
273	27.0	7.2	—	—
283	54.2	30.3	0.2	0.2
288	—	—	1.4	—
293	74.2	64.2	3.0	3.6
303	130.7	124.0	13.9	27.6
313	266.1	203.9	39.9	66.2
323	—	—	79.3	138.2
333	—	—	—	268.3

ture. It becomes apparent that over a certain range of temperatures straight-line relationships are obtained for all swelling liquids, considerable deviations from linearity occurring at low temperatures. The diffusion activation energy values determined using the straight-line sections of the curves were ~ 7.3 kcal/mol for

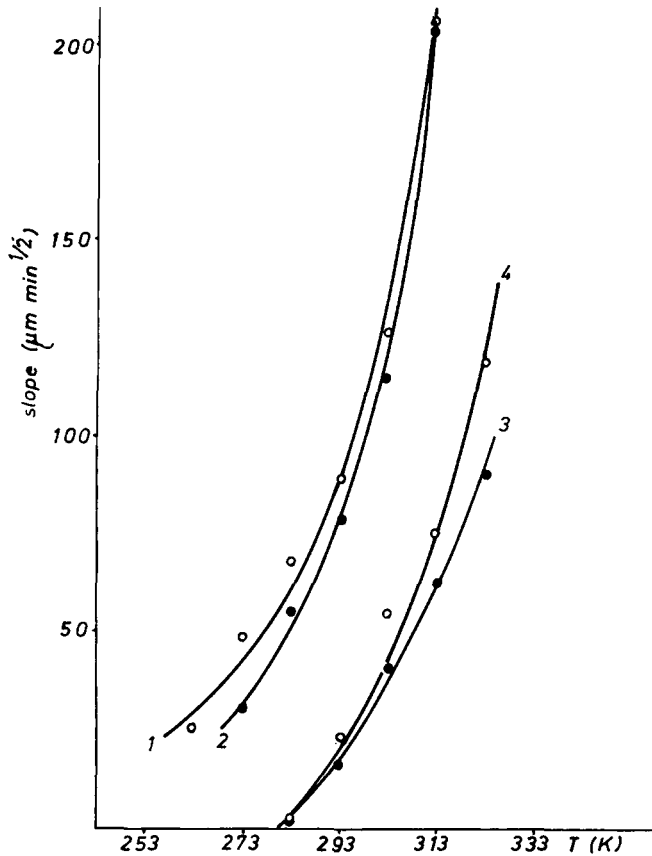


Fig. 5. Temperature dependence of slope k : 1, acetone; 2, methyl propyl ketone; 3, methyl isobutyl ketone; 4, xylene.

acetone, ~ 12.8 kcal/mol for methyl propyl ketone, ~ 13.5 kcal/mol for methyl isobutyl ketone, and ~ 14.7 kcal/mol for xylene. The increasing curvature of the dependence of \bar{D} on $1/T$ when approaching the temperature of the "checking" of the diffusion front indicates an increase in the activation energy of the process.

The distinct separation of the diffusion and crystallization fronts constitutes a most significant feature of the process studied. Changes of the position of the crystallization front with respect to the edge of the sample were also recorded when carrying out an analogous series of measurements for the diffusion front. It was moreover found in all cases that the distance between the diffusion and crystallization fronts remained constant throughout the entire observation period, no changes falling beyond the scope of accuracy of the measuring technique adopted.

The distance between both these fronts was found to depend on the temperature of swelling, as shown in Figure 7. The nature of changes of that distance was found to be the same for all swelling liquids employed in the present study. For every polycarbonate-swelling liquid system the separation of the diffusion and crystallization fronts was found to occur above a certain temperature; the following characteristic temperatures having been determined for the swelling

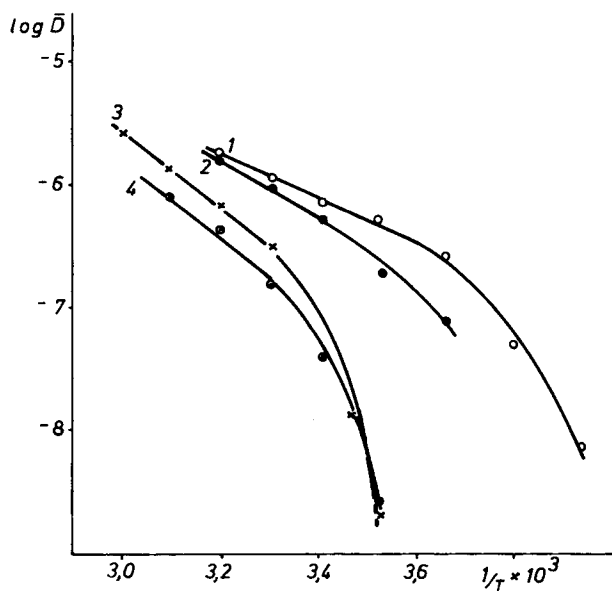


Fig. 6. Relation between $\log \bar{D}$ and reciprocal of temperature: 1, acetone; 2, methyl propyl ketone; 3, xylene; 4, methyl isobutyl ketone.

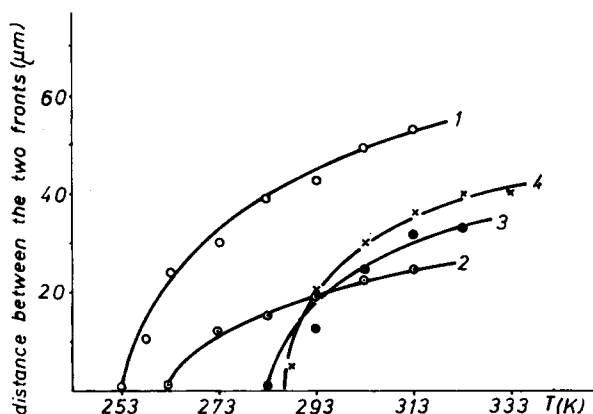


Fig. 7. Dependence of distance between the crystallization and diffusion fronts on temperature: 1, acetone; 2, methyl propyl ketone; 3, methyl isobutyl ketone; 4, xylene.

liquids used: ~ 253 K for acetone, ~ 263 K for methylpropyl ketone, ~ 283 K for methyl isobutyl ketone, and ~ 285 K for xylene. These temperatures are thus only slightly higher than those found for the "checking" of the diffusion front. At temperatures higher than those quoted above, the distance between the diffusion and crystallization fronts at first rapidly increases with increasing temperatures, the temperature effect subsequently becoming much less pronounced.

The distance between the diffusion and crystallization fronts was found to be the greatest for acetone, while the order in which all swelling liquids may be arranged was found to be temperature dependent. This effect is particularly strong in the case of methylpropyl ketone, for which the distance between the diffusion and crystallization fronts is not large and, at temperatures above room

temperature, becomes the smallest among the corresponding distances found for the other swelling liquids used in the present work.

Based on the observed distinct separation of the diffusion and crystallization fronts, it was possible to propose the following method for determining the kinetics of the crystallization process not controlled by the diffusion of the swelling liquid into the polymer sample investigated. The proposed method involves the simultaneous swelling from both sides of a polymer film sufficiently thin to become completely swollen before the crystallization process is started. The above condition was met by a polycarbonate film 20 μm thick for the temperature range over which the distance between the diffusion and crystallization fronts was greater than half of its thickness.

Owing to the high rate of the process investigated, the crystallization kinetics measurements were performed by continuously monitoring the changes in the intensity of depolarized light. By comparing the values of the polycarbonate film swelling time, determined from the earlier found rates of motion of the diffusion front (it was additionally assumed that thickness of the film increases 1.5 times), with the time required for the light depolarization effect to occur, it was ascertained that the sample had been completely swollen much earlier than the crystallization process was initiated (Table II).

The recorded, typically S-shaped curves of the change in the intensity of depolarized light were used to directly determine the half-times of crystallization. The change in crystallization half-time with temperature is shown in Figure 8. The rate of crystallization may be seen to increase considerably in the temperature range slightly above that characteristic of the "checking" of the diffusion front. This effect becomes less pronounced at the upper range of swelling temperatures employed.

Changes in the amount of swelling liquids penetrating into polycarbonate film samples 100 μm thick were also measured. It was found that the amount of the

TABLE II
Comparison of Total Swelling Time (t_s) of 20- μm -Thick Film with Crystallization Induction Time (t_i)^a

Temperature, K	Acetone		Methyl propyl ketone		Methyl isobutyl ketone		Xylene	
	t_s	t_i	t_s	t_i	t_s	t_i	t_s	t_i
253	273	—						
258	—	420						
263	35	330	—	170				
268	—	210	—	100				
273	5	140	13	80				
278	—	127	—	—				
283	3	87	5	69			52	—
286	—	—	—	—	1155		—	—
288	—	80	—	48	90	106	—	50
292	—	73	—	—	—	—	—	—
293	2	—	2	36	52	—	31	36
298	—	—	—	31	—	—	—	29
303	1	57	1	24	9	66	5	25
308	—	53	—	22	—	57	—	22
313	1	47	1	19	3	40	3	—

^a t_s and t_i values in seconds.

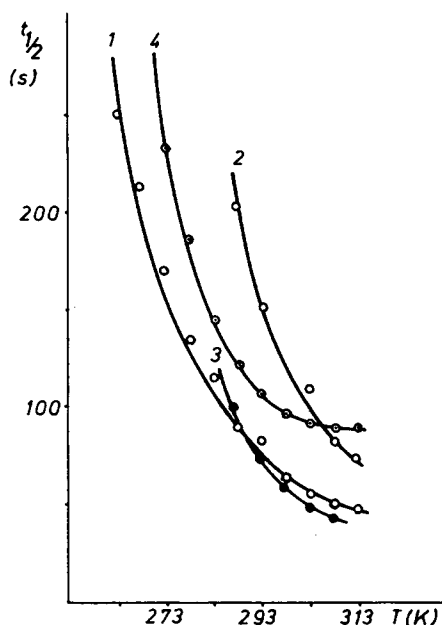


Fig. 8. Dependence of half-time of crystallization of polycarbonate film 20 μm thick on temperature: 1, methyl propyl ketone; 2, methyl isobutyl ketone; 3, xylene; 4, acetone.

swelling liquid in samples swollen by ketones used in the present study passed through a maximum and then started to decrease. It was additionally found that the time elapsed from the beginning of the swelling process to the moment at which the degree of swelling reaches its maximum value was in all cases shorter than that required for attaining the final degree of swelling. The amount of the swelling liquid contained in xylene-swollen samples was not determined. The maximum and final contents of individual swelling liquids found in polycarbonate film samples at different temperatures are listed in Table III.

The influence of the swelling process temperature on the maximum degree of swelling attained may be seen to be negligible in the temperature ranges investigated. The final content of the individual swelling liquids may also be seen to vary slightly in the experimental conditions employed. Measurements were

TABLE III
Maximum (S_m) and Final (S_f) Swelling Ratios for Individual Swelling Agents Used

Temperature, K	Swelling ratio, g/g							
	Acetone		Methyl propyl ketone		Methyl isobutyl ketone		Xylene	
	S_m	S_f	S_m	S_f	S_m	S_f	S_m	S_f
263	0.74	0.53	—	—	—	—	—	—
268	0.73	0.54	0.85	0.62	—	—	—	—
273	0.75	0.52	0.80	0.57	—	—	—	—
278	0.71	0.51	—	—	—	—	—	—
288	—	—	0.83	0.61	—	—	1.20	1.10
293	—	0.53	0.85	0.60	0.49	0.40	1.23	1.15
298	—	—	0.79	0.56	0.48	0.41	1.26	1.25
303	—	0.49	—	—	0.50	0.40	—	—
308	—	0.50	—	—	0.47	0.41	—	—

also performed below the experimentally determined temperatures of the "checking" of the diffusion front. The adsorption of the swelling liquid was not stopped completely under these conditions but proceeded at a slow rate and without formation of a sharp diffusion front.

DISCUSSION

The experimental results obtained clearly indicate the complex nature of the liquid-induced crystallization of polycarbonate swollen by the liquids employed in the present work. The course of the process is governed mainly by the temperature at which the swelling process is allowed to proceed.

Above a certain value of the swelling temperature, which is different for each swelling liquid, the diffusion of the swelling liquid into the sample takes place with the formation of distinct penetration front. The formation of a sharp penetration boundary is explained in the literature¹⁷ as being due to the proximity of two zones, namely, of a nonswollen sample core (or of a very slightly swollen sample core) which is below the glass transition temperature T_g and of a zone of the polymer sufficiently swollen to make its glass transition temperature T_g lie below the temperature at which the experiment was performed. This is accompanied by a discrete change in the content of the swelling agent from a low level in the first zone to a value close to an equilibrium concentration in the second zone, the diffusion coefficients changing their values accordingly.

It was also to be expected in our case that the sharp diffusion front would be formed only on swelling the polycarbonate at a temperature such that the spontaneously fixed swelling agent content in the sample attains a level sufficient to bring the glass transition temperature T_g down to the temperature at which the experiment was conducted. This would seem to suggest that the temperature below which the sharp diffusion front is not to be observed may be assumed to provide an estimate of the glass transition temperature of the polycarbonate-swelling liquid system. The above suggestion was confirmed by wide-line NMR studies of the system polycarbonate derived from bisphenol A-acetone carried out in our laboratory.¹⁸ The glass transition temperature of the above-mentioned polycarbonate-acetone system determined by this technique was found to be equal to 243 K and was hence lower than that determined based on the temperature given by the "checking" of the swelling agent penetration front and equal to about 248 K. A similar agreement is to be expected for other polycarbonate-swelling liquid systems investigated by us, but clearly an experimental confirmation would be required to support this assertion.

The very distinct separation of the diffusion and crystallization fronts occurring at temperatures only a few degrees higher than the diffusion front "checking" temperature constitutes the most characteristic feature of the phenomenon investigated. It is not readily apparent why in that case the polycarbonate does not immediately crystallize just behind the diffusion front, since, owing to the very existence of the diffusion front, the polycarbonate is already sufficiently swollen for the crystallization process to be initiated. One of the possible explanations of this phenomenon is to assume in this case the existence of a crystallization induction period analogous with that known to exist in the case of the thermal crystallization of the polycarbonate.¹⁹

The actual existence of such an induction period may be demonstrated quite

simply by monitoring the properties of a polycarbonate film 20 μm thick being swollen at room temperature by acetone. Under these conditions the sample is completely swollen within several seconds and becomes highly flexible, and only after about 30 sec there appears a certain turbidity (generally ascribed to crystallization), the sample becoming more rigid. When we link the latter observation with that of the distinct separation of the diffusion and crystallization fronts, it becomes apparent that these two fronts are indeed separated from each other by a material capable of crystallizing at the given temperature. It is rather hard to explain why the crystallization front should move at a fixed distance behind the diffusion front. Since the change of the position of the diffusion front is proportional to the square root of time, this phenomenon is thought to indicate an increase in the crystallization induction time. This may be due, for instance, to a change in the concentration distribution of the swelling agent penetrating into the sample. It is to be noted, however, that our observations covered a relatively short period of time (from a dozen or so to several score minutes), and it is quite probable that longer-lasting measurements would perhaps have revealed a certain deviation from the nature of the observed separation of the diffusion and crystallization fronts.

The experimentally determined linear relationship between the changes in the position of the diffusion front and the square root of time indicates that Fick's law is valid for the diffusion process concerned.¹⁷ The values of diffusion coefficients calculated on this basis are of the same order of magnitude as the values quoted for the systems bisphenol A-derived polycarbonate- CH_2Cl_2 and $\text{CH}_2\text{ClCH}_2\text{Cl}$ and for those found for other polymer-organic solvent systems.^{20,21} However, owing to the lack of knowledge of the relation between the diffusion coefficient \bar{D} and concentration, the above values are to be treated as apparent values. The activation energy values determined for individual swelling liquids change with the size of their respective molecules.

The observed decrease in the content of the swelling liquid in the sample after previously reaching a maximum was also found by other authors in systems comprising a polycarbonate and a pair of organic solvents.^{5,6} This finding would indicate that low molecular weight substances are rejected from the crystalline areas of the sample.

As to the kinetic data, only the half-times of crystallization were determined by us. The dependence of $t_{0.5}$ on temperature was found to be in all cases similar to that given by Zachmann¹ for the poly(ethylene terephthalate)-methanol system and are typical of the crystallization of polymers from the glassy state.¹²

Owing to the fact that the degree of swelling of the polycarbonate sample was found not to vary with temperature over the range in which our crystallization kinetics measurements were performed, it could be assumed that in the polycarbonate-swelling liquid systems studied by us the rate of crystallization is mainly influenced by the temperature.

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