Liquid-induced crystallization of a bisphenol-A polycarbonate

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The liquid-induced crystallization of bisphenol-A polycarbonate films in the presence of CCl_4 and acetone as swelling agents has been investigated by means of differential microcalorimetry and differential scanning calorimetry (d.s.c.). Results of microcalorimetric measurements were used to obtain thermokinetic curves and to determine heat effects in the liquid-induced crystallization process. Results of calorimetric measurements were subjected to Avrami analysis. The d.s.c. experiments revealed a maximum crystallinity of about 17% in the case of samples swollen in CCl_4 and 20% for those swollen in acetone.

INTRODUCTION

One of the methods of crystallizing a polymer which is amorphous but capable of undergoing crystallization involves the action of suitable low molecular weight organic liquids upon it. There are very few data available on this subject in the literature, although the technique of liquid-induced crystallization has already been used for studying polymers which either cannot be crystallized or crystallize very slowly under conditions of thermal crystallization from the melt. Investigations on the liquid-induced crystallization have been carried out on such polymers as cellulose triacetate[1], poly(ethylene terephthalate)[2–5], polysulphones[6], poly(methyl methacrylate)[7] and polyoxyphenylene[8,9].

The bisphenol-A derived polycarbonate [poly(4,4′-dioxydiphenyl-2,2-propane) carbonate] does crystallize, but the process proceeds very slowly from the melt[10]. However, this polymer crystallizes readily under the influence of such swelling agents as acetone, chloroform, carbon tetrachloride, xylene and others[11– 6], and also in the presence of plasticizers[17]. It was the aim of the present work to investigate the liquid-induced crystallization of the bisphenol-A derived polycarbonate in the presence of carbon tetrachloride and acetone by a thermochemical method. Experimental results obtained using a BMR-type non-isothermal non-adiabatic differential calorimeter developed by Zielenkiewicz, and a DSC-2 Perkin–Elmer differential scanning calorimeter will be presented.

The application of differential calorimetry for investigating liquid-induced crystallization of polycarbonates has not yet been described in the literature. However, its application has been found useful in some cases[9,18,19]. Consequently, the demonstration of the possibility of using microcalorimetric measurements for characterizing the whole process of the liquid-induced crystallization was one of the objects of this work.

EXPERIMENTAL

Materials

Bisphenol-A polycarbonate films 10, 20, 40, 60 and 100 μm thick were used in the present work. Polymer films were obtained at room temperature by casting the polycarbonate solutions in methylene chloride onto a glass plate. The films were then vacuum dried for several weeks. The samples were found to be amorphous, as confirmed by d.s.c. and X-ray measurements and results of observations made using a polarizing microscope.

The bisphenol-A polycarbonate (trade name, Bistan AF) was obtained from the Institute of Industrial Chemistry, Warsaw and had a viscosity-average molecular weight of 62 500. The glass transition temperature of amorphous samples of polycarbonate films was 422K. Acetone. supplied by VEB Laborchemie 'Apolda', GDR and carbon tetrachloride, made by POCh, Gliwice, Poland, were used as swelling agents.

Measurements performed using the BMR-type microcalorimeter

Thermokinetic characteristics of the liquid-induced crystallization process were determined using a BMR-type non-isothermal non-adiabatic differential calorimeter[20]. After reaching thermal equilibrium, measurements were started on breaking a sealed glass ampoule containing a known amount of the polycarbonate film, placed in the calorimetric cell filled with the swelling agent. The mass of the polycarbonate film sample was between 0.4 and 0.1 g; 16 ml of the swelling agent was used. The thermoelectric force generated by the calorimeter thermopile was recorded on an EZ-10 recorder (Laboratorni Pristroje, Prague, Czechoslovakia). Changes of the thermoelectric force are known to represent thermal effects characteristic of the process investigated. The amount of heat evolved during the liquid-induced crystallization process was calculated from the relation:

$$Q(t)\Big|_{t_0}^{t_1} = K\theta(t)\Big|_{t_0}^{t_1} + \alpha\int_{t_0}^{t_1}\theta(t)\mathrm{d}t$$

where $Q(t)\big|_{t_0}^{t_1}$ is the amount of heat evolved in the calorimetric cell in the time interval (t_0, t_1); $\theta(t)\big|_{t_2}^{t_1}$ is the change in thermoelectric force over the same time interval (t_0, t_1); $\theta(t)$ describes the thermoelectric force changes with time;

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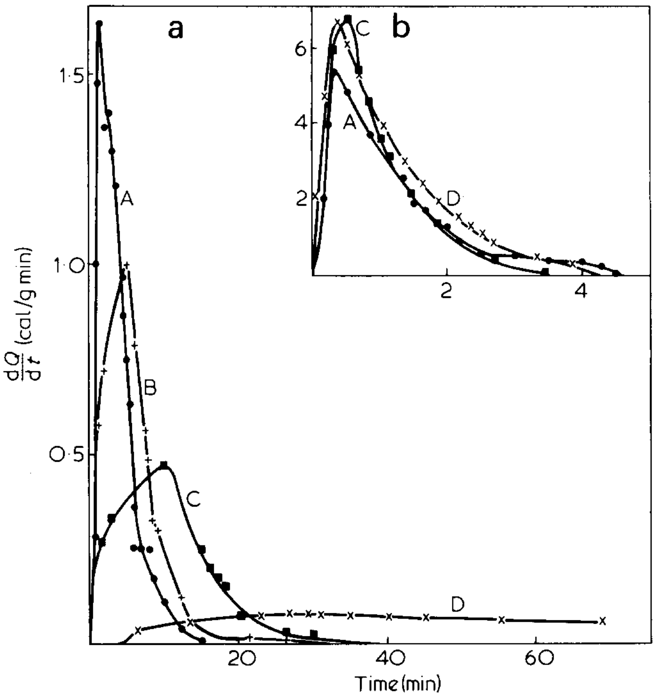

Figure 1 Thermokinetic curves obtained for the swelling and crystallization of a bisphenol-A polycarbonate in (a) carbon tetrachloride; (b) acetone 40° (A); 35°C (B); 30°C (C); 20°C (D). Film thickness = 20 μm

and t is time; K is the thermal capacity of the calorimeter.

The heat loss coefficient $\alpha = 0.4072$ cal (mV min)$^{-1}$ was determined experimentally when calibrating the calorimeter. The thermal capacity of the calorimeter was determined after each measurement (7.27–7.00 cal mV^{-1}) using equations given earlier and based on the assumption that the calorimeter may be treated as a single-body system[8].

Measurements performed using the DSC-2 differential scanning calorimeter

Amorphous polycarbonate film samples were subjected to liquid-induced crystallization by immersing them in carbon tetrachloride and acetone at several constant temperatures (318, 308, 298 and 295K). After a fixed time the samples were taken out of the swelling liquid and dried for several days or investigated immediately in the swollen state by d.s.c.

A Perkin-Elmer DSC-2 differential scanning calorimeter was used to obtain thermograms of amorphous polycarbonate samples and for film samples crystallized from carbon tetrachloride and acetone. The heats of melting were determined using the surface area bounded by the endothermic peak corresponding to the melting process. The temperature was increased at a rate of 10 K/min^{-1}.

The calorimeter was calibrated using indium as a standard. The heat of melting of indium ΔH_i was 6.80 cal g^{-1}.

RESULTS

The BMR-type calorimeter was used to determine the successive heat effects due to the swelling of polycarbonate film samples 10, 20 and 100 μm thick in carbon tetrachloride at temperatures of 293, 313, 308 and 303K, and in film samples 20, 40 and 100 μm thick in acetone at temperatures of 293, 303 and 313K. Thermograms depicting the influence of swelling agents on the polycarbonate films studied are shown in *Figures 1* and *2*.

The thermokinetic curves may be seen to have a ballistic shape. In the case of acetone used as swelling agent, the liquid-induced crystallization process was found to proceed very rapidly and to terminate after 3–4 min. On the other hand for carbon tetrachloride the processes of swelling and crystallization were found to proceed at a much slower rate, the total heat effect also being reduced.

The use of carbon tetrachloride whose molecules are much bigger in size than those of acetone results in a reduction of the total heat effect to about 7–8 cal g^{-1} whereas that measured in the case of the polycarbonate–acetone system was found to be equal to some 10–11 cal g^{-1} (films 20 μm thick swollen at 293K).

On the other hand, however, the rate of swelling determined by the rate of evolution of heat, was found to reach a maximum after some 2–5 min for films 10 μm thick swollen in the polycarbonate–carbon tetrachloride system, whereupon a slow process, lasting several hours and accompanied by a very small thermal effect [<0.1 cal (g min)$^{-1}$] was observed to take place.

In the initial stage of the process of swelling of the polycarbonate by carbon tetrachloride (the first min of the measuring period), the actual process proceeds at such a fast rate that the slopes of the curves are similar and their respective thermokinetic curves are superimposed upon each other. It is hence virtually impossible to find any difference in the respective rates of swelling during the first minutes of the process. A similar phenomenon occurs for acetone.

The position of the maximum of the curve depicting the rate of evolution of heat, may be assumed to represent a measure of the rate of swelling and thus may only be used in the first stage of the process investigated as a very rough

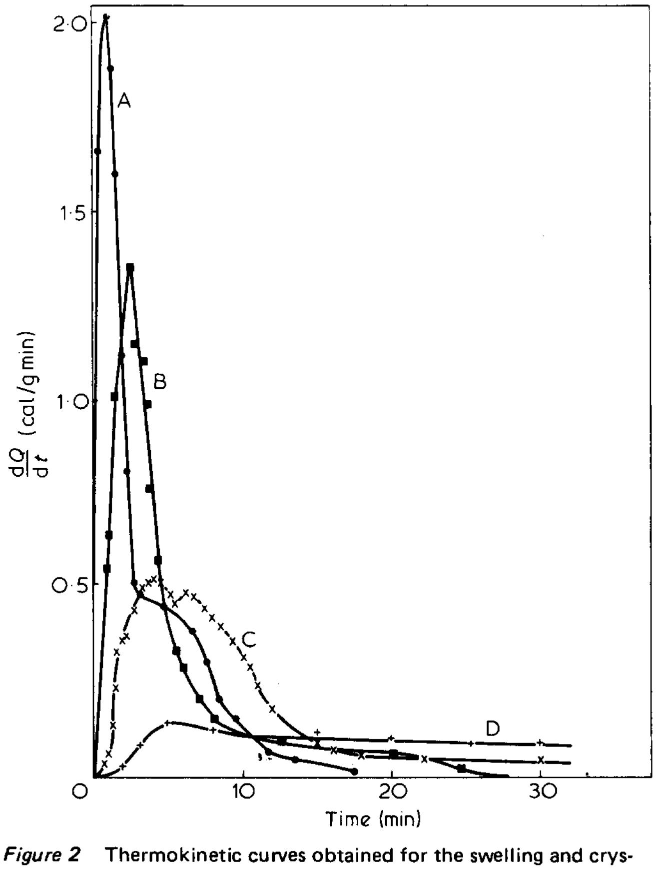

Figure 2 Thermokinetic curves obtained for the swelling and crystallization of a bisphenol-A polycarbonate in carbon tetrachloride at 40°C (A), 30°C (B), 25°C (C), 20°C (D). Film thickness = 10μm

Table 1 Heat of melting of bisphenol-A polycarbonate ΔH_m crystallized for different periods of time and different temperatures from carbon tetrachloride and acetone

Crystallization temperature (K)	Crystallization time (h)	ΔH_m (cal g^{-1})	Degree of crystallinity (%)	T_m(K) Peak I	T_m(K) Peak II
Carbon tetrachloride					
318	7	4.5	17	466	489
298	24	3.5	13	459	489
308	2	3.9	14	461	487
308	1	3.6	13	461	489
Acetone					
295	0.5	5.6	21	485	493

means of estimating the differences in the rates of swelling. Thus, for instance, for polycarbonate films 20 μm thick, crystallized at 313K, the rates of swelling in acetone and carbon tetrachloride were found to be equal to 5.5 and 1.6 cal (g min)$^{-1}$, respectively.

The curves obtained for very thin films crystallized from carbon tetrachloride were found to exhibit two maxima. Swelling of the polymer was in that case most probably taking place in the first stage of the process and was then followed by crystallization. That observation was also confirmed by results of investigations carried out using other methods. The total heat effect was found to decrease only slightly with increasing temperature of crystallization for liquid-induced crystallization processes for polycarbonate films of the same thickness, swollen in both swelling agents i.e. carbon tetrachloride and acetone.

In order to determine whether the process of crystallization takes place on swelling and to determine the degree of crystallinity of the polymer, the heat of crystallization of the polycarbonate was determined by d.s.c. at several temperatures both in carbon tetrachloride and acetone. The values of the heat of melting ΔH_m and melting points are listed in *Table 1*.

The degree of crystallinity was calculated assuming a value of $\Delta H_m^0 = 26.8$ cal g^{-1} as the heat of melting for pure crystalline polycarbonate[21]. Thermograms of the bisphenol-A polycarbonate samples subjected to the process of liquid-induced crystallizations were obtained. The samples were observed to exhibit two endothermic peaks on being heated. (*Table 1*). These correspond to the melting of the crystalline phase of the polymer, and were observed for polycarbonate film samples swollen both in carbon tetrachloride and acetone. This phenomenon is known to occur in other polymers, such as, for instance, polyoxyphenylene and poly(ethylene terephalate). In spite of the numerous data already published and different concepts put forward concerning that phenomenon, its nature has not yet been unequivocally elucidated[22–23].

An Avrami analysis was performed in order to obtain a more complete characterization of the thermokinetic curves obtained by d.s.c. Based on our own experimental findings obtained using other analytical techniques and also on pertinent data available in the literature, the processes of swelling and diffusion were assumed to be completed earlier than the process of crystallization. It was hence concluded that there exists a certain period of time when the crystallization of the already swollen polymer is the only source of heat effects observed in the system investigated.

Using published results of studies on the kinetics of liquid-induced crystallization it may be stated that, in all cases when the process is not diffusion-controlled, the Avrami equation can be used.

It may thus be assumed that over the time interval during which other processes have been already completed and the crystallization process is still taking place, the amount of heat evolved is closely connected with the amount of the substance changing into the crystalline form.

The integral thermokinetic curve may be used to calculate the total heat effect composed of the heat of crystallization and the heats of all side processes such as swelling and diffusion. The variation of total heat effect (Q_{1t}) with time reaches a constant value at the end of the process (Q_{1k}) which may be described by the relation:

$$Q_{1k} = Q_u + Q_k$$

where Q_u is the total heat effect of all processes concerned with the sorption, swelling, diffusion, etc. and Q_k is the total heat of crystallization.

The value of Q_k was determined by d.s.c. for the time corresponding to the end of the measurement for swollen samples in the presence of the swelling liquid used. The value of the total heat effect Q_{1k} was determined experimentally by BMR when measuring the heat effects corresponding to the processes of crystallization and swelling. In this way Q_u was determined. It was further postulated that by taking the successive values of the difference $Q_{1t}-Q_u$ at fixed time intervals (beginning from the end of the measurement where Q_{1t} is the variation with time of the total heat effect of all processes) this would determine the magnitude of the heat of crystallization until the moment when all side processes had been completed. From that time, the quantity being subtracted will be too large, so that the result would be too small or even a negative quantity. However, the value of $Q_{k,t} = Q_{1t} - Q_u$ can be determined until that moment ($Q_{k,t}$ = the variation of the heat of crystallization of the sample with time).

The values of $Q_{k,t}$ thus obtained for various times made it possible to represent the results of thermokinetic measurements in the Avrami system of coordinates by plotting the natural logarithm of time against $\ln[-\ln(1-x)]$, where x represents the relative amount of the crystalline phase, as calculated from the ratio of $Q_{k,t}/Q_k$.

Such a way of calculating the relative of the crystalline phase is correct only for a time interval at which all side processes have been completed, so that the total heat effect may be attributed to the process of crystallization.

An example of the application of the interpretation of the thermokinetic curves obtained for the system polycarbonate–carbon tetrachloride is shown in *Figure 3*. The system polycarbonate–carbon tetrachloride was selected because it is also being studied by us using other experimental techniques. *Figure 2* shows thermokinetic curves obtained for the above system at different temperatures. The process may be seen to depend strongly on temperature and, as temperature is decreased, the very distinct and sharp peak maximum broadens and the whole peak becomes smaller, until it becomes extremely broad near the glass transition temperature (T_g) of the swollen polymer (303K).

The experimental points plotted in Avrami coordinates may be seen in *Figure 4* to fit a straight line rather well except for the initial section, which is thought to indicate that, most probably, side processes have not yet been completed. The deviations from the straight line relationship, also ob-

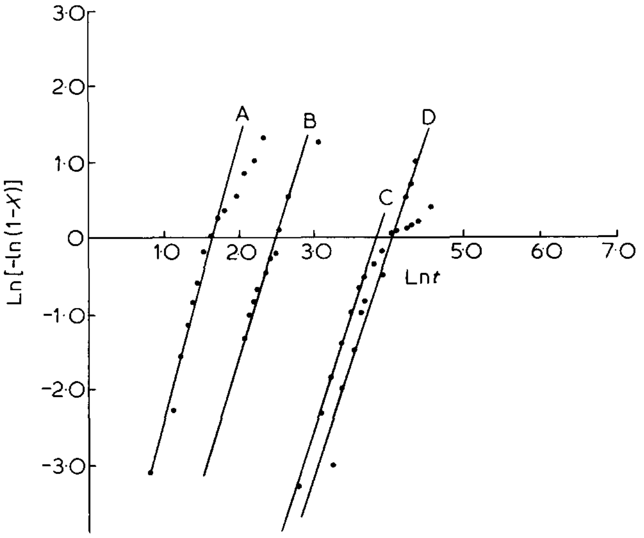

Figure 3 Avrami plot for the crystallization of a bisphenol-A polycarbonate in carbon tetrachloride at different temperatures. Film thickness A, B 20 μm and C, D 10 μm. A, 313K; B, 308K; C, 298K; D, 313K

served for the final section of the plot most probably correspond to the process of secondary crystallization.

The value of Avrami coefficient calculated from the slope of the straight-line graph was found to be nearly equal to 3 ($n \approx 3$), which is in good agreement with the value obtained using other experimental techniques.

The presented method of interpreting the experimental data is highly convenient but clearly requires further study in order to establish to what extent it is general.

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