X-ray studies of structural ordering changes on annealing a non-crystalline polycarbonate

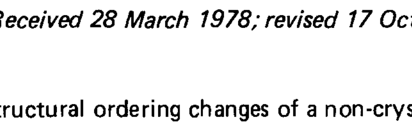
E. Turska, J. Hurek and L. Zmudziński
Institute of Polymer Chemistry, Polish Academy of Sciences, Zabrze, Poland, and Department of Polymer Chemistry, Technical University, Gliwice, Poland

(Received 28 March 1978; revised 17 October 1978)

Structural ordering changes of a non-crystalline polycarbonate (trade name 'Bistan AW') were investigated. Three interference halo signals were recorded on the X-ray diffraction patterns at reflection angles equal to $\theta_1 = 3.1°$ (d = 14.3 Å), $\theta_2 = 8.5°$ (d = 5.2 Å), and $\theta_3 = 12.7°$ (d = 3.5 Å). The areas of peaks at θ_1 were found to decrease and those at θ_2 to increase with increasing the time of annealing the previously melted polycarbonate samples at a temperature of 190°C. It was concluded that morphological changes were taking place in the polycarbonate prior to its thermal crystallization. These changes may be explained by assuming the existence of two morphological forms of structural ordering in non-crystalline polycarbonate macromolecules. On annealing, macromolecules belonging to the *cis*-form having a lower degree of structural ordering most probably tend to straighten out and assume a zigzag structure, i.e. all-*trans* conformation. After straightening out of the chains, these macromolecules link up with areas exhibiting a much higher degree of structural ordering and most probably exist in the *trans*-form.

INTRODUCTION

The crystallization of polycarbonates has been investigated since the 1950s. In 1958 Prietzschk[1] reported on the crystalline structure of a polycarbonate



On the basis of his X-ray studies Prietzschk found that polycarbonate crystallized in the rhombic system, and determined the parameters of its unit cell from a film pattern. These he found to be equal to 11.9 Å, 10.1 Å, and 21.5 Å. Later Bonart[2] published the results of his X-ray structural investigations on three different polycarbonates: 4,4′-dihydroxy-diphenyl-2,2-propane, 4,4′-dihydroxy-diphenyl-sulphate, and 4,4′-dihydroxy-diphenyl-methane.

Bonart reported the first of them to crystallize in the monoclinic system and to have the following unit cell dimensions: a = 12.3 Å, b = 10.1 Å, c = 20.8 Å, γ = 84°; these differ from those given by Prietzschk. Polycarbonates crystallize in solution, in the swollen state, and on being annealed within a suitable range of temperatures between their glassy temperature and their melting point.

The thermal crystallization process has been studied by many authors[3–7], the appearance of crystalline peaks being noticed on the X-ray patterns obtained after prolonged times of annealing[3–5]. The optimum annealing temperature has been determined[6] along with the angles and intensities of peaks characteristic of samples subjected to annealing. Schnell[3] reported that the period required to initiate thermal crystallization on annealing the polycarbonate at the optimum temperature is very long and generally equal to some 7–8 days. Research on the kinetics of thermal crystallization of Makrolon samples carried out by means of column gradient technique by Turska *et al.*[7] fully supported the above observation. It was found that Makrolon samples having molecular weights between 30 000 and 68 000 crystallized at 190°C after some 200–230 hours.

Similarly long induction times were also found by Neki and Geil[5] in the case of polycarbonate films, thin films having been found to crystallize more readily than the thick ones.

The extremely long time required for thermal crystallization to occur has provided the incentive for the present work. Owing to the fact that seven to eight days is required to initiate the thermal crystallization process, we assumed that thermal crystallization probably had to be preceded by certain morphological changes in the polymer, e.g. either a preliminary ordering of macromolecules with respect to one another, or a change of polymer chain conformation. A long period of time is generally required to bring about these changes. However, some suggestions concerning the possibility of polycarbonate macromolecules altering their arrangement during that period may be found in the literature[5,7,8], but they were not supported by any experimental experimental evidence. Recently, Turska and Tekely[9] in their wide-line n.m.r. studies on the swelling crystallization of a polycarbonate observed the existence of two morphological forms in a non-crystalline polymer state. Hentze[13] put forward a similar suggestion.

Our aim was to investigate whether these observations would also prove valid in the case of a polycarbonate sample first fused and then subjected to annealing. It was

0032–3861/79/030321–03$02.00

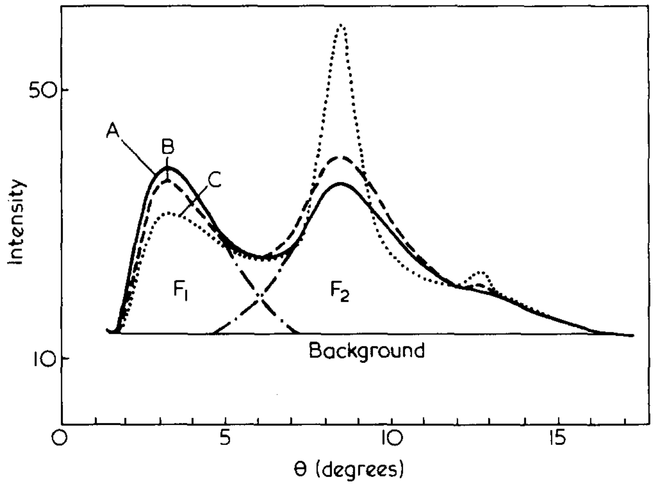


Figure 1 X-ray diffraction patterns $I = f(\theta)$ of polycarbonate (Bistan AW). A – fused and non-annealed sample; B – sample fused and annealed for 15 days; C – sample of partly crystalline polymer

the object of this work to ascertain whether in the induction period preceding the thermal crystallization of the investigated sample there really exist two different morphological forms of that polymer, and also whether any transitions of polycarbonate molecules from one form to another occur. Wide-angle X-ray technique was employed in the present work, the changes in the character of the relationship $I = f(\theta)$ being recorded as a function of time of annealing.

EXPERIMENTAL

Preparation of the samples

A polycarbonate derived from bisphenol A (trade name 'Bistan AW') was used in the present study. Its viscosity average molecular weight M_v was equal to 18 200. Before being subjected to the annealing treatment the samples were prepared in the following manner. The polymer, obtained in the form of a powder, was placed in glass phials and degassed for 5 hours under a vacuum of 10^{-3} mmHg. After sealing the phials, the polymer was fused for 1 hour in an oven maintained at a temperature of 280°C. The samples were then placed in an oven maintained at the optimum temperature of 190°C as indicated in the literature[6,7]. The samples were annealed for periods ranging from 1 to 15 days. After being removed from the phials, the samples were cut to a size of 25 x 10 x 2 mm required for fastening them in the holder of a commercial counter diffractometer, and polished to obtain a smooth surface.

For comparison purposes, X-ray diagrams of non-fused partially crystalline samples were also recorded. The latter samples were prepared in the form of pellets obtained at a pressure of 50 atm and having a diameter of about 30 mm and a thickness of 2 mm.

Measurements

The X-ray diffraction patterns of such prepared samples were obtained using the Ni-filtered CuK$_\alpha$ radiation at U = 37 kV and I = 15 mA. The diffractograms were obtained by means of an X-ray diffractometer type Dron–1.5 equipped with a scintillation counter.

Results

Three diffused signals (halos) were found to be present in all X-ray patterns recorded at reflection angles θ equal to 3.1°, 8.5°, and 12.7°. Two of these observed at smaller angles were strong, while the third one was weak (it was observed in the case of samples with the longest annealing times). The typical X-ray patterns are shown in *Figure 1*, in the form of appropriate diagrams, the depicted curves being produced by the symmetrical transmission method. The curve A shows the functional dependence $I = f(\theta)$ for the fused and non-annealed sample, the curve B – for the sample first fused and then annealed for 15 days, and the curve C – for the sample in a partially crystalline state (starting polymer before being fused). The curves shown in this figure were previously normalized to equal X-ray optical density and equal intensity of the direct beam, and corrected for air scatter[10,11]. Then the values of respective quoted angles θ were determined. As the diffraction angle θ we took that angle which suited the point situated at the midpoint of the line called the breadth at half-maximum intensity. The values of diffraction angles determined as mentioned are $\theta_1 = 3.1°$, $\theta_2 = 8.5°$, and $\theta_3 = 12.7°$, respectively. The d-spacing values assigned to them following the Bragg equation are d_1 = 14.3 Å, d_2 = 5.2 Å and d_3 = 3.5 Å, respectively.

The area bounded in *Figure 1* by the peak at 3.1° (14.3 Å) was denoted F_1 and that bounded by the peak 8.5° (5.2 Å) – F_2. The resolution of the overlapping halos is shown schematically for the curve A in *Figure 1*. We assumed after Hermans and Weidinger[11] that at $\theta = 6.1°$ in the crystalline state of PC there are no crystalline peaks. We assumed the intensities from both of the halos to be equal at that point. Then the background line was drawn as a straight line tangent to the curve $I = f(\theta)$ at the points $\theta = 1.5°$ and $\theta = 20°$.

In the series of X-ray diffraction patterns of samples fused and subsequently annealed for different periods of time the changes of the areas F_1 and F_2 were observed. X-ray diffraction patterns obtained for the samples subjected to longer annealing periods had a larger area of the peak at 8.5° (F_2) in comparison with the corresponding X-ray diffraction patterns recorded for samples subjected to shorter annealing times, and with that for the fused and non-annealed sample. The area F_2 increases simultaneously with a corresponding decrease of the area F_1. The ratio F_2/F_1 increases with increasing time of annealing, the quantitative changes being listed in *Table 1*. *Figure 2* depicts the changes observed on examining the data listed in *Table 1*. It shows the changes of the ratio of areas F_2 to F_1 as a function of annealing time i.e. $F_2/F_1 = f(\tau)$.

DISCUSSION AND CONCLUSIONS

The analysis of the diffraction patterns of a fused PC (curves A and B, *Figure 1*) leads us to the conclusion that the 'Bistan AW' polycarbonate in question does not exist in a

Table 1 Changes in the areas of the halos recorded at reflection angles $\theta = 3.1°$ (F_1) and $\theta_2 = 8.5$ (F_2)

Sample	Annealing time [days]	Area		
		F_1	F_2	F_1/F_2
1	0	39.2	52.1	1.33
2	8	39.2	52.1	1.33
3	9	38.9	52.4	1.35
4	10	38.4	52.9	1.38
5	11	38.1	53.2	1.40
6	13	34.9	56.4	1.61
7	15	34.6	56.7	1.64

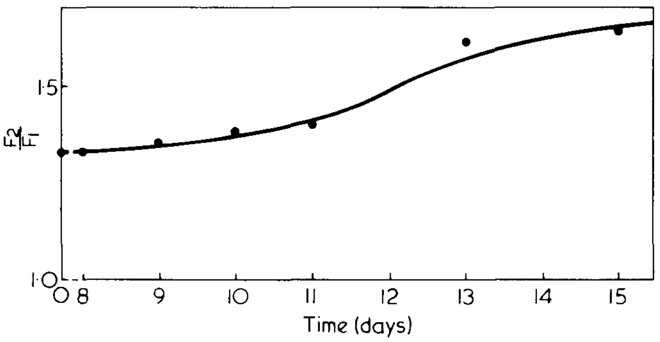


Figure 2 Changes of the ratio of areas F_2/F_1 as a function of annealing time

homogenously amorphous state, neither does it exist in a completely crystalline state, nor in a partly amorphous and partly crystalline state. This type of a diffraction pattern can be explained as a result of amorphous scattering from two morphological forms: the amorphous, and the mesomorphous ones.

All the signals are too diffused and too broad to be interpreted as being due to interference effects typical of crystallographic planes i.e. of the crystalline phase. It is known from the literature[1,2] that a polycarbonate ought to crystallize in one of the two crystal systems: monoclinic[2] or orthorhombic[1], but the distances d_1 and d_2 do not follow the quadratic equations of these systems. It is the quantity d_1 that does not fit directly these equations. If we assume that the observed signals were the result of overlapping of the lattice peaks we are led to the possibility that the nearest d-spacings to 14.3 Å ($\theta = 3.1°$) would be $d_{(001)} = 20.8$ Å ($\theta = 2.1°$), and $d_{(100)} = 12.2$ Å ($\theta = 3.6°$). It can be demonstrated, however, that this is not possible. It is known from the literature[1–3,5], that none of the authors observed these two peaks although they carried out their studies on highly crystalline PC. Besides, it can be seen from *Figure 1* that the angle 2.1° lies on the left side outside the recorded halo. Moreover, it seems to us that a formation of the crystal planes (001) immediately after melting of the sample without annealing would suggest the existence of a very perfect crystalline structure at that moment, which differs from many literature reports[3,5,7]; they are in agreement that the thermal crystallization of PC begins after a length of time of annealing. The peak at $\theta = 3.6°$ was not observed by anyone either. If we assumed the possibility of its existence then the angular discrepancy would be obvious because the peak could not move from 3.6° to 3.1° without contribution of other interference signals at lower diffraction angles. The integral breadth as well as the large intensity of the observed 'halo' are inconsistent with the fact that it could be a peak typical of a crystal lattice. The lattice planes (100), in accordance with the model of Bonart[2], have the density of a line of about two times less than for example the planes (020), so the total intensity of the possible peak at 3.6° ought to be much more reduced than is actually observed in the X-ray diffraction pattern.

To sum up, we can say that the above mentioned observations show that the 'halo' at $\theta = 3.1°$ is neither due to interference effects typical of a crystal lattice nor a result of overlapping of 'crystal interferences'. Hence, it can be supposed to be a result of scattering of X-rays from that part of the polymer which belongs to the amorphous form.

According to Williams and Flory[12], macromolecules of PC may exist in two conformations (*cis* and *trans*), the *trans* conformation being more probable. The value of $d = 14.3$ Å, corresponding to the angle $\theta = 3.1°$, may be readily understood when it is assumed to be equal to the distance between identical atoms and to correspond to a double distance between monomeric units of a polymer chain in which the *cis-trans* segments are predominant. That distance is equal to 20.8 Å in the straight chain of PC.

The explanation of the presence of the second 'halo' at $\theta_2 = 8.5°$ ($d = 5.2$ Å) is possibly due to the scattering of X-rays by a form comprising a mesophase – type aggregation of macromolecules. The d-spacing characteristic of this signal is typical of the intermolecular distances of PC; it is only somewhat larger than that in a crystal lattice (5.05 Å). The parallel arrangement of the chains permits this to be a nematic-pseudohexagonal type of ordering in the crystalline form. The signal at $\theta = 8.5°$ is probably due to three paratropic planes, e.g. (020), ($\bar{2}$10), (210). If we assume that this signal is also due to the interferences on other planes with third indices different from zero (such planes in this angular range are possible), then we should observe also a distinct peak at $\theta = 12.5–12.7°$ on the planes (312), ($\bar{2}$22), (303) and (223). The lack of the planes with a non-zero third index typical for the sample after its melting can serve as a reason that the second form observed is not a crystalline phase but a meso-form with a two-dimensional ordering.

On annealing, a weak signal at $\theta = 12.7°$ can also be observed, the presence of which can be explained as a result of an increase of ordering along a macromolecular axis. The ordering seems to be due to the shift of the macromolecular segments along their axes after assuming a *trans*-conformation. These displacements can give rise to a formation of crystal planes perpendicular to the third direction. However, in the case of the samples subjected to annealing for 15 days (curve B, *Figure 1*) these planes are not shaped well yet, the peak at $\theta = 12.7°$ is not clear. We attribute the existence of a relatively clear signal at 12.7°, in the initial non-fused sample, to the presence of a crystalline phase.

We can therefore say that our studies allow us to make a hypothesis that the 'Bistan AW' polycarbonate can occur in its solid state after melting, in two morphological forms: in the amorphous in the segments of which a *cis*-conformation exists markedly and in the nematic-pseudohexagonal more ordered one, the macromolecules of which mainly comprise segments in a *trans*-conformation. On annealing the supplied energy is used for a transition of a certain number of macromolecular segments from the *cis* to the *trans*-conformation, i.e. to the more ordered form. The observed fact of the decrease of the area F_1, and the increase of F_2 seems to confirm it.

REFERENCES

1 Prietzschk, A., *Kolloid-Z.* 1958, **156** (1), 8
2 Bonart, R., *Makromol. Chem.* 1966, **92**, 149
3 Schnell, H., Chemistry and Physics of Polycarbonates, Wiley Intersci., New York, 1964
4 May, M. and Walter, Ch., *Plaste und Kautschuk,* 1974, **21** 363
5 Neki, K. and Geil, P. H. *J. Macromol. Sci. (B)* 1973, **8** (1–2), 295
6 Peilstöcker, G., *Kunststoffe,* **1961**, 59, 509
7 Turska, E., Przygocki, W., and Maslowski, K., *J. Polym. Sci. (C)*, 1968, **16**, 3373
8 Tanaka, A. and Ishida, J. *J. Polym. Sci. (Polym. Phys. Edn.)* 1975, **13**(2), 437
9 Turska, E. and Tekely, P., *J. Macromol. Sci. -Phys.*, in press
10 Alexander, L. E., X-Ray Diffraction Methods in Polymer Science, Wiley Intersci., New York, 1969
11 Hermans, P. H. and Weidinger, A., *Makromol. Chem.*, 1963, **64**, 135
12 Williams, A. D. and Flory, P. J. *J. Polym. Sci. (A-2)*, 1968, **6**, 1945
13 Hentze, G., *Thermochimica Acta* 1976, **15**, 139