

Structural Changes in Glassy Polymers

M. S. ALI and R. P. SHELDON, *School of Polymer Science,
University of Bradford, England*

Synopsis

It has previously been shown that glassy poly(ethylene terephthalate) gives rise to endothermal peaks in DTA when annealed at temperatures near to the glass temperature. The present work describes results obtained from DTA and DSC on annealing a number of glassy polymers which have been rapidly cooled from above the glass temperature and on slowly cooled samples of the same polymers. The polymers which have been studied are: poly(ethylene terephthalate), poly(methyl methacrylate), atactic and isotactic polystyrene, bisphenol-A polycarbonate, poly(ethyl methacrylate) and poly(vinyl acetate). In every case, evidence of structural reorganization is observed, and the rate at which this takes place is reported. Separate studies on poly(ethylene terephthalate) reflect density changes which also take place upon annealing. These results are discussed in the context of the calorimetric observations.

INTRODUCTION

Contrary to earlier descriptions of glassy polymers as having a macroscopically homogeneous nature, reflecting a completely disordered arrangement of macromolecules, there is a growing body of evidence to suggest that such a picture is an oversimplification. Speculation as to the possibility of order should not, perhaps, be unexpected in view of the fact that polymers as a whole have long been recognized as being variable in degree of crystallinity, not only from class to class but within a class or even within a sample depending upon its previous, particularly thermal, history. Thus, it is not inconceivable that order may exist at a low level, i.e., beyond the limit of sensitivity of the usual detecting techniques such as x-ray diffraction, and thereby remain unrecognized. Such a situation may apply either to a crystallizable polymer or to one which is normally considered to be amorphous.

The evidence for the possibility of order has come from different directions and perhaps, as such, has led to different interpretations ranging from the view that a variable microvoid content associated with free volume exists and that this may be changed upon heating, through an influence on conformational states, to the view that local order reminiscent of crystallinity, albeit on a restricted scale, is an integral component of the glassy state. The work providing this evidence has been carried out on a number of polymers including polystyrene,¹ poly(methyl methacrylate),² polycarbonate,³ poly(vinyl chloride),⁴ and poly(ethylene terephthalate).⁵ It

TABLE I
Physical Properties of Polymers

Polymer	Mol wt	Ref.	Density, g/cc	Glass temperature, °C
Poly(ethylene terephthalate)	1.34×10^4	(9)	1.3350	75
Poly(methyl methacrylate)	9.34×10^4	(10)	1.171	93
Polystyrene	2.41×10^6	(11)	1.034	100
Isotactic polystyrene	4.8×10^6	(8)	1.053	89
Bisphenol-A polycarbonate	2.85×10^4	(12)	1.196	145
Poly(ethyl methacrylate)	1.22×10^6	(13)	—	65
Poly(vinyl acetate)	3.69×10^4	(14)	—	30

has involved direct electron-microscopic evidence of structural ball-like entities and indirect evidence from thermal analysis and from density calculations.⁶

Recent work carried out in these laboratories has been concerned with the differential thermal analysis (DTA) of "amorphous" poly(ethylene terephthalate).⁷ In this it was shown that amorphous polymer which had been heated to temperatures slightly above the glass temperature and then rapidly cooled gives rise to a change in the baseline of the DTA trace on subsequent analysis. If, however, the sample is slowly cooled and then analyzed, a distinct endothermal peak is recorded at a temperature near to the glass temperature. From these and related results, it was concluded that this behavior has its origin in some change of structure. Although the authors did not formally compare the relative merits of a free-volume change interpretation against a local structure model, at least it was pointed out that the behavior was not inconsistent with the latter concept. This led to the suggestion that if local order did exist, then this could arise from preferred conformations enjoying some association. Going further, the authors suggested that the phenomenon should not be limited to those polymers which had been studied but might very well be a feature of many so-called amorphous polymers. The purpose of the present paper is to describe investigations on other polymers and on polymers previously described where little information was available other than from transmission electron micrographs.

In outline, samples of polymers have, on the one hand, been cooled rapidly from temperatures slightly above the glass temperature and then have been annealed for various times at predetermined temperatures. Other samples were cooled at controlled rates from the same temperatures before, as with the previous samples, being examined by DTA and/or differential scanning calorimetry (DSC). Some separate studies on the density changes that occur during annealing were also undertaken. The polymers investigated were poly(ethylene terephthalate), poly(methyl methacrylate), polystyrene (atactic and isotactic), bisphenol-A polycarbonate, poly(ethyl methacrylate), and poly(vinyl acetate).

EXPERIMENTAL

Materials

The properties of polymers used in this study are presented in Table I. Molecular weights were obtained by viscometric measurements carried out with the solvents (A.R. quality), temperatures, and Mark-Houwink constants indicated in the appropriate references, except in the case of isotactic polystyrene, for which molecular weight determinations had already been made.⁸

Density values were obtained as described below. Glass temperatures (T_g) quoted are those measured in the course of the present investigations using either DTA or DSC, and reflect the intersection of extrapolated lines at point *a* in the schematic diagram, Figure 1. In all cases the values were found to be in close agreement with those published elsewhere.

In order to confirm the "amorphous" nature of the potentially crystallizable polymers, poly(ethylene terephthalate) and isotactic polystyrene, x-ray diffraction photographs were made before and after annealing. In all cases no indication of crystallinity at this level was observed.

Equipment

Calorimetric studies involved the use of a Perkin-Elmer DSC 1B or a du Pont differential thermal analyzer 900. The separate use of one or the other of these pieces of equipment is defended in the text. The former, used in some of the quantitative aspects, was calibrated by means of benzoic acid and by sapphire. Incidental equipment is described, again, where appropriate in the text.

Technique

Annealing Studies

With the exception of poly(ethylene terephthalate), all samples were placed in boiling tubes which were then immersed in a thermoregulated oil

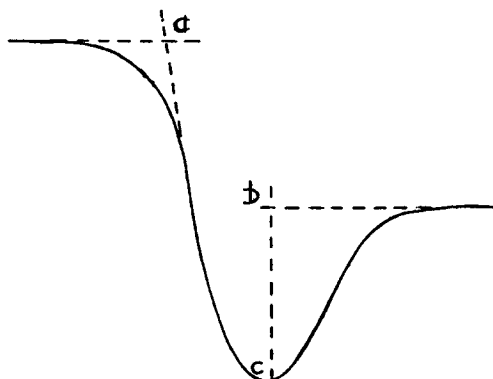


Fig. 1. Schematic endothermal peak.

bath, having a temperature control better than $\pm 0.2^\circ\text{C}$, at temperatures of $(T_g + 20)^\circ\text{C}$ for 20 min. In the case of poly(ethylene terephthalate), heating was carried out at 90°C because of the danger of initiating thermal crystallization at temperatures slightly above this. These temperatures had previously been found to be suitable for quenching to an amorphous state as judged by DTA or DSC.

Following this heating procedure, the boiling tubes were plunged into ice water baths. Samples of each polymer were then annealed at different temperatures near to the corresponding T_g for predetermined times, as indicated in the results (see below). From these, samples were taken for evaluation by DSC using a heating rate of $16^\circ\text{C}/\text{min}$ with a sensitivity of 8 m cal/sec/full scale. The actual weight used in all cases was 0.0204 g, this being identical to the weight of a disc of film of poly(ethylene terephthalate) used in the first studies. The magnitude of the peak height was arbitrarily recorded for the present work, using the technique adopted by previous workers on poly(vinyl chloride), and is represented by the length of the line *bc* in Figure 1.

For the one polymer, poly(vinyl acetate), where only a qualitative assessment of any development of an endothermic peak was required, DTA was used. The amount of polymer, for same reasons as for DSC, was 0.0346 g, and the operating conditions consisted of a heating rate of $20^\circ\text{C}/\text{min}$ at a sensitivity of $\Delta T = 0.2$. The same conditions were maintained for the investigations into the effect of cooling rate described below, except for polycarbonate, for which $\Delta T = 0.5$ in view of the greater heat changes observed with this material.

Cooling Rate Studies

All samples were again heated to $(T_g + 20^\circ\text{C})$ (except for poly(ethylene terephthalate) where the temperature was 90°C as before) in the differential thermal analyzer, and the temperature was again held constant for 20 min. Cooling of samples within the equipment was constrained to take place at different rates by passing air at different pressures over the samples in the cooling program mode. This experimental advantage led to the preference of DTA over DSC for this particular study. The cooling rates shown in the results were found to be approximately constant for a given experiment. After cooling to ambient temperature, the samples were reheated in the equipment under conditions as described above under "Annealing Studies." Peak heights were measured as for the DSC studies. As mentioned previously, the weight of polymer used in the DTA investigations was 0.0346 g.

Density Measurements

All density measurements were made at 25°C using an available density gradient technique for poly(ethylene terephthalate)¹⁵ and a specific gravity bottle method for the other polymers. For the first polymer, separate

determinations were made of the density of samples which had been heated for 5 hr in the annealing studies.

RESULTS

For samples annealed at temperatures near to the glass temperature but only within certain limits, an endothermal peak was recorded for all polymers. The height of each peak, expressed as a function of annealing time at the temperatures indicated, is presented in Figures 2-7. In order to get an appreciation of the rate at which changes of structure associated with the peaks take place, initial slopes of each family of curves were determined. These are presented in smoothed form in Figure 8. It should be mentioned that in order to complete these curves, zero rate values for temperatures at which no endothermal effects were observed have been included.

For the separate study of poly(vinyl acetate), a DTA thermogram showing again evidence of structure in that an endothermal peak is recorded is to be seen in Figure 9.

The results of the cooling rate studies, in which the magnitude of the DTA peak occurring just above the glass temperature is plotted against cooling time, are depicted in Figure 10.

The final graph, Figure 11, shows the change of density which takes place with poly(ethylene terephthalate) for samples which have been annealed for 5 hr—this time corresponding to the longest time of heating at each temperature.

DISCUSSION

Probably the first point to be made from the results is that, as indicated above, the endothermal behavior, whether detected by DSC or DTA, for samples annealed at temperatures near to the glass temperature is common to all polymers so far studied. This confirms the earlier suggestion that the phenomenon might be a feature of many, if not all, amorphous polymers. There appears to be, usually, a well-defined upper and a less well-defined lower temperature limit for this to take place. Isotactic polystyrene, bearing in mind the few results obtained, might be an exception to this in that the definition is in the opposite sense. The initial rate at which the endothermal process, whatever its origin, takes place is seen to increase with temperature, generally reaches a maximum at approximately 5-10°C below the recorded glass temperature, and then begins to decrease to zero somewhere between 10-15°C above the maximum rate temperature. The one exception to this is atactic polystyrene, where the maximum occurs at about the glass temperature. This anomaly is discussed later. The general behavior is consistent with compromising tendencies of structure building and breaking processes and as such does not allow for easy resolution, say, for example, for the estimation of activation energies. The greatest change, on an absolute scale, takes place with poly(ethylene tereph-

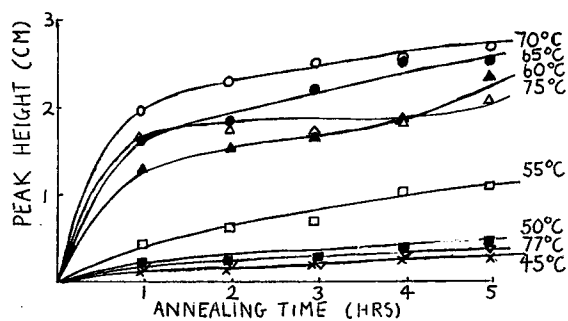


Fig. 2. DSC peak height vs. annealing time for poly(ethylene terephthalate).

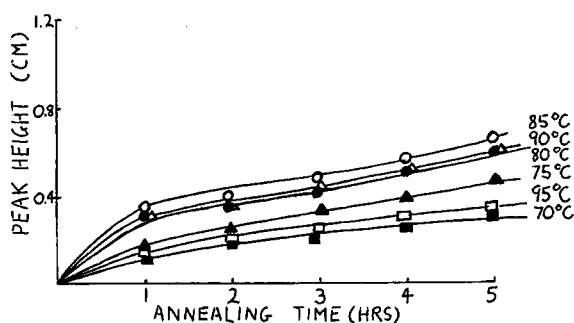


Fig. 3. DSC peak height vs. annealing time for poly(methyl methacrylate).

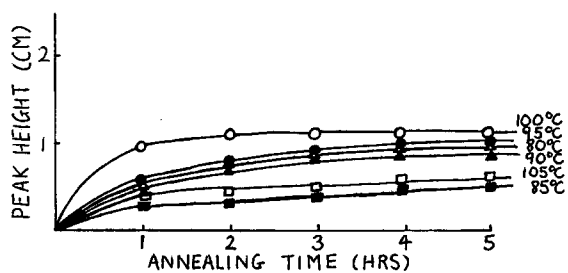


Fig. 4. DSC peak height vs. annealing time for atactic polystyrene.

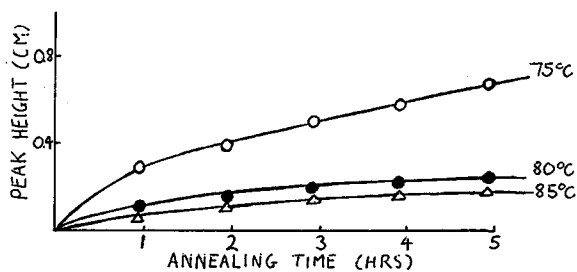


Fig. 5. DSC peak height vs. annealing time for isotactic polystyrene.

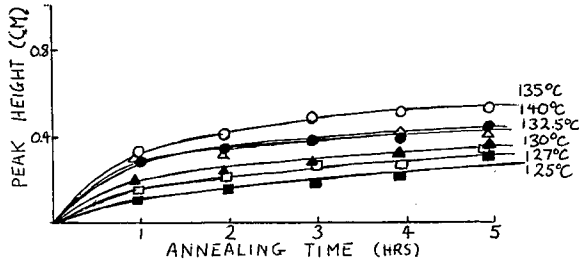


Fig. 6. DSC peak height vs. annealing time for polycarbonate.

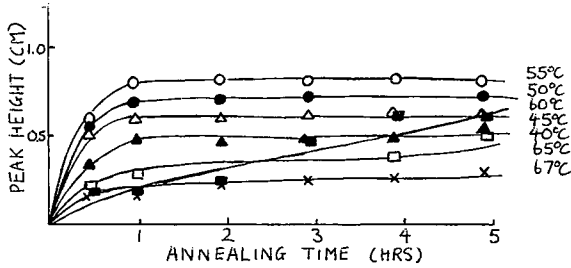


Fig. 7. DSC peak height vs. annealing time for poly(ethyl methacrylate).

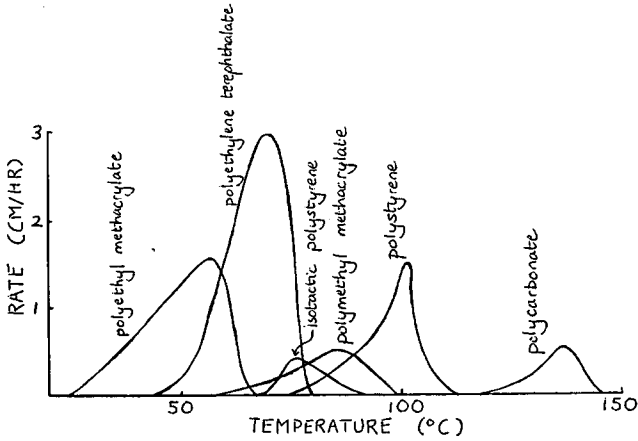


Fig. 8. Initial rates vs. annealing temperatures.

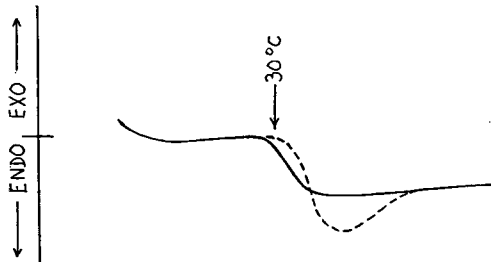


Fig. 9. DTA curve for poly(vinyl acetate).

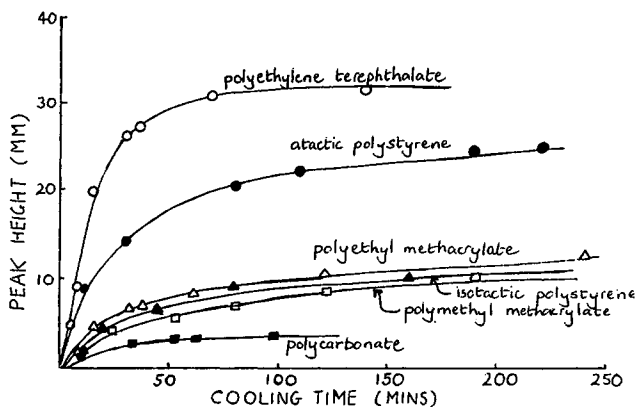


Fig. 10. DTA peak height vs. cooling time.

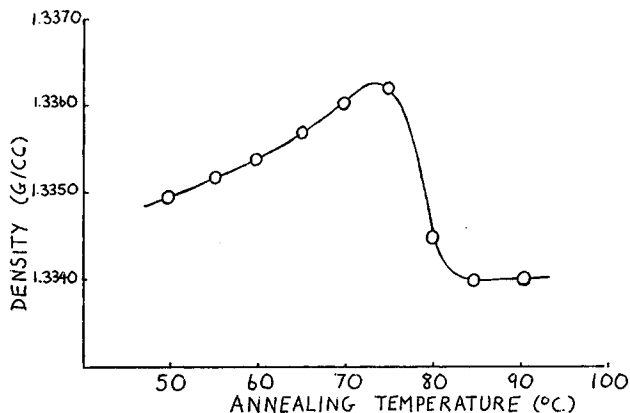


Fig. 11. Density vs. annealing temperature for poly(ethylene terephthalate).

thalate) and the smallest effect is with the polycarbonate, remembering that true equilibrium conditions may not be completely operative. The significance of absolute values remains obscure, having presumably both a kinetic and thermodynamic origin as in conventional mass diffusion studies. Ultimate equilibrium magnitudes, however, will have the latter dependence, so that for the case of poly(ethyl methacrylate), which appears to have a special place in that equilibrium, is apparently achieved for every temperature but one; and where the level decreases with decreasing temperature, one is tempted to suggest that here we have evidence of true molecular organization. If the changes were due to free-volume contractions rather than, say, to local ordering, then the equilibrium peak height should increase with decreasing temperature, since annealing would produce greater changes of free volume the further the experimental temperature is from the quenching temperature. Unfortunately the results on other polymers are

not such as to add or detract from this indication. Extra-long annealing studies might be illustrative here.

Returning to the cases of poly(ethylene terephthalate), bisphenol-A polycarbonate, and isotactic polystyrene, which exhibit different degrees of change, as all polymers are normally regarded as crystallizing polymers, it is apparent that this ability is not significant in the context of the present results. On the other hand, there may be some meaning in the fact that all polymers have β relaxation peaks in mechanical or dielectric loss spectra. If such peaks were to be identified with restricted chain motion as suggested earlier,⁷ perhaps of a nature compatible with local mode theories,¹⁶ then structural reorganization through local chain alignment can be appreciated. The particularly small β peak reported for polystyrene may be important here in having a less dominant influence in reducing the rate maximum for the glass temperature than for other polymers. However, there is insufficient data available¹⁷ to prosecute this line of attack owing to the doubt attached to the origin of the β peak and also owing to the fact that the peaks are reported to be affected themselves by the experimental approach and by a dependence also upon annealing.¹⁸ It is interesting to note that for atactic and isotactic polystyrene, in so far as the latter is apparently amorphous by x-ray analysis, the structural changes which occur are greater for the former. This would be in keeping with a view that syndiotactic sequences preferentially align as compared with sterically interfering isotactic sequences.

Before leaving endothermal peak considerations, it is interesting to note that for poly(vinyl acetate), which was not as extensively studied as other polymers because of the proximity of its glass temperature to room temperature, there is a small, 1°C, rise in glass temperature after annealing.

Turning now to the rate of cooling studies, it is seen that the behavior is such as to support the DSC results. From Figure 10, bearing in mind that cooling rate is approximately linear and remembering that different polymers are cooled from different temperatures depending upon individual values of glass temperature, one can generalize by saying that, provided the cooling rate is lower than approximately 3°C/min, near-maximum structure develops in every case, or at least the most rapid changes have taken place for such rate conditions. This would suggest that sample geometry might very well have a bearing on the extent to which structural reorganization occurs, as cooling rate will be influenced by geometry. This conclusion supports the results of studies previously reported.⁷

Finally, having regard to the density results shown in Figure 11, it is separately evident that some structure changes take place on annealing below the glass temperature. The technique, however, does not help to suggest an origin for the changes. There appears to be some inconsistency between the temperature of maximum density and that of maximum rate although experimental error may have a bearing here, but it is clear that heating to temperatures somewhat above the glass temperature produces a polymer of lowest "amorphous density." Such refinement of data might be

of importance where more accurate values of amorphous density are required, as, for example, in calculations for the degree of crystallinity from density values of undrawn crystalline polymers.

In conclusion, there is evidence of structural changes taking place in so-called amorphous polymers when they are annealed at temperatures near to the glass temperature or when they are cooled slowly through the glass transition interval. Such structural changes, however, have an origin not yet clearly revealed but they also, no doubt, could prove to have important theoretical, physical, and presumably mechanical consequences.

The authors wish to thank I.C.I. Ltd. for samples of poly(ethylene terephthalate) and Dr. F. Zoppi (Istituto Chimica Industriale del Politecnico, Milano) for samples of isotactic polystyrene and for relevant data. Thanks are also due to Mr. P. Blakey (University of Bradford) for x-ray diffraction assistance, and to Professor M. W. Roberts (University of Bradford) and Dr. E. F. G. Herington (N. P. L.) for providing DSC facilities in the earlier part of this work.

References

1. A. Lambert, *Polymer*, **10**, 319 (1969).
2. T. G. F. Schoon and O. Teichmann, *Kolloid-Z. Z. Polym.*, **197**, 35, 45 (1964).
3. S. H. Carr, P. H. Geil, and E. Baer, *J. Macromol. Sci. (Phys.)*, **B2(1)**, 13 (1968).
4. P. V. McKinney and C. R. Foltz, *J. Appl. Polym. Sci.*, **11**, 1189 (1967).
5. G. S. Y. Yeh and P. H. Geil, *J. Macromol. Sci. (Phys.)*, **B1(2)**, 235 (1967).
6. R. E. Robertson, *J. Phys. Chem.*, **69**, 1575 (1965).
7. M. I. Kashmiri and R. P. Sheldon, *Polymer Letters*, **7**, 51 (1969).
8. F. Zoppi, private communication.
9. D. Sanderson, M.Sc. Thesis, University of Bradford, 1967.
10. R. J. Fort, M.Sc. Thesis, University of Manchester, 1962.
11. C. E. H. Bawn, R. F. J. Freeman, and A. R. Kamaliddin, *Trans. Faraday Soc.*, **46**, 1107 (1950).
12. M. A. Uddin, Ph.D. Thesis, University of Bradford, 1968.
13. S. N. Chinai and R. J. Samuels, *J. Polym. Sci.*, **19**, 463 (1956).
14. A. Nakajima and K. Kagaku, *Chem. High Polymers (Tokyo)*, **11**, 142 (1954).
15. I. M. Kashmiri and R. P. Sheldon, *Polymer Letters*, **6**, 45 (1968).
16. K. Yamafuji and Y. Ishida, *Kolloid-Z. Z. Polym.*, **183**, 15 (1962).
17. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, London, 1967.
18. K. H. Illers and H. Breuer, *Kolloid-Z. Z. Polym.*, **176**, 110 (1961).

Received July 13, 1970