

Studies of the thermal properties of poly(2,3-dibromo-but-2-ene-1,4-diol adipate)

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Poly(2,3-dibromo-but-2-ene-1,4-diol adipate) (PDBD), molecular weight 1900, was prepared. Its i.r. and n.m.r. spectra are discussed. Its thermal properties were extensively studied by d.s.c. The polymer melted at 366 K and decomposed at 577 K. On first heating, it did not show any T_g or T_c ; but after a single heat treatment, it exhibited T_g at 250K and two cold crystallization exotherms at 310K and 342K. The effect of cooling rate on ΔH_f , ΔS_f , ΔH_c and crystallinity was studied. The polymer was annealed at 320K and 342K for various time intervals. It was found that ΔH_f exhibited a maximum at 320K, and reached an asymptotic value at 342K. The multiple endotherms observed at 342K are discussed in terms of the different crystal morphologies of the polymer.

INTRODUCTION

Although investigations on the thermal properties of polymers are attracting increasing attention¹⁻¹⁰, no unsaturated aliphatic polyester has so far been investigated. A detailed study of the thermal properties of a low molecular weight sample of PDBD is presented.

It is well known that thermal history can influence the physical state of polymers. Further, the nature of the sample viz. powder, film, fibre has a decisive effect on thermal properties like glass transition, cold crystallization, heat of fusion and temperature of decomposition. There have been no studies yet of the effect of cooling rate on thermal properties, which can give some detailed information about the crystallinity of the polymer during the cooling process.

The annealing of a polymer at different temperatures or for varying time intervals at a fixed temperature is reflected in the melting endotherm of the polymer¹¹⁻¹⁵. This gives valuable information about the morphology of the polymer material. Therefore, we studied the effect of annealing on the melting of PDBD.

EXPERIMENTAL

But-2-yne-1,4-diol (L. R. Fluka) was purified by distillation under reduced pressure (175°–178°C/4 mm). Adipic acid (ar, BDH) was used as received. 2,3-dibromo-but-2-ene-1,4-diol was prepared according to the procedure described earlier¹⁶. The polymer PDBD was prepared by the solution condensation technique, using benzene as the reaction medium and *p*-toluene sulphonic acid as the catalyst.

I.r. spectrum

The infrared spectra of the diol and the polymer were measured in a Beckmann IR-20.

N.m.r. spectrum

The proton resonance spectrum was recorded in a Varian HR-300 spectrometer. The ¹³C resonance spectrum was

recorded in a Varian CFT-20 spectrometer (DMSO-*d*₆ solvent; HMDS as reference).

Calorimetry

A Perkin-Elmer differential Scanning Calorimeter Model DSC-1B was used. Samples (2–10 mg) were weighed to the nearest 0.1 mg, encapsulated in aluminium sample holders and used in a stream of oxygen-free nitrogen. Empty aluminium sample holders were used as references. Temperature was calibrated from the melting points of pure benzoic acid, indium, lead and tin. To calculate the heat of fusion and heat of cold crystallization, the heat of fusion of indium was taken to be¹⁷ 29.2 J g⁻¹.

RESULTS AND DISCUSSION

The i.r. spectrum of 2,3-dibromo-but-2-ene-1,4-diol showed a bonded hydroxyl absorption at ~3600 cm⁻¹, but as a tetrasubstituted olefin, it showed no >C=C< stretching absorption. Its dipole moment, measured in dioxan¹⁸, was 1.446 D. This is comparable to those for aliphatic alcohols, and indicates a negligible amount of the *cis* isomer. There was a well defined ester absorption peak at around 1740 cm⁻¹ in the i.r. spectrum of PDBD.

In the proton magnetic resonance spectrum of PDBD, the peak at 1.52 ppm was due to the methylene protons of carbons 7 and 8. The absorption at 2.15 ppm was due to the protons attached to carbon atoms 1 and 4. This absorption position has been found to be similar to that obtained for ethyl-2-bromo-n-butyrate¹⁹. The peak obtained at 2.37 ppm was for the methylenic protons of carbon atoms 6 and 9.

The following information was inferred from the ¹³C spectrum of the polymer. The peaks obtained at 22.0, 64.8 and 31.0 ppm were due, respectively, to methylenic carbon absorptions of carbon atoms 7, 8; 1,4 and 6, 9. The double bonded carbon atoms (2,3) have a specific absorption at 117.5 ppm, whereas the carbonyl carbons (5, 10) absorb at 170.0 ppm. These data revealed that PDBD had a

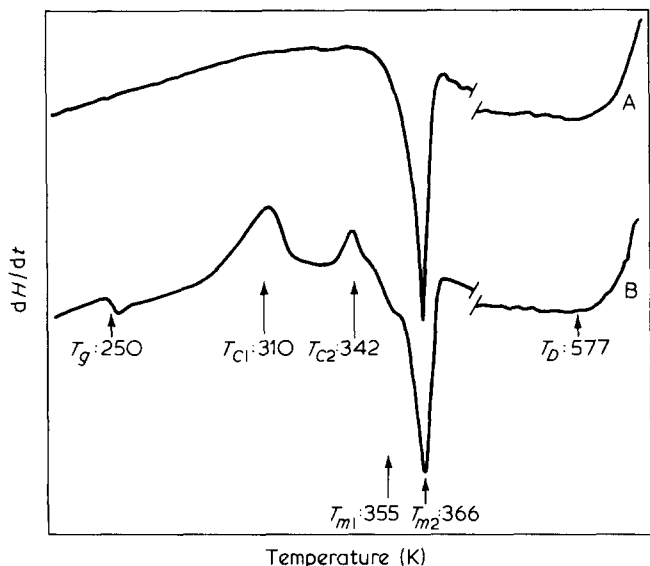
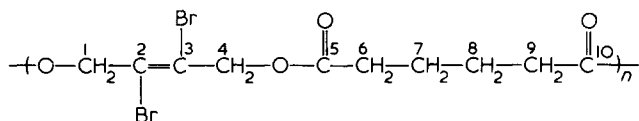


Figure 1 Complete thermogram of the polymer PDBD; scan speed 16 K min^{-1} . A, original sample; B, after a single heat treatment

linear structure:



From the cryoscopic measurements of the polymer in *o*-chlorophenol, the \bar{M}_n was found to be 1900 (approximately six repeat units).

The complete thermogram of PDBD (Figure 1A; ranging from 200–400K, 400–600K; heating rate of 16 K min^{-1}) showed melting of the polymer at 366K and its decomposition at 577K. During the first heating of the polymer, both at the low and high temperature regions, the thermogram did not indicate any T_g or T_c . However, when the polymer melt obtained by heating up to 400K was cooled at a rate of 16 K min^{-1} to a temperature of about 200K and then reheated at 16 K min^{-1} , there was a glass transition (T_g) at 250K; two cold crystallization exotherms, one at 310K (T_{C1}) and another at 342K (T_{C2}); and two melting endotherms, at 355K (T_{m1}) and 366K (T_{m2}) (Figure 1B). According to Campbell and Heaven²⁰ T_g of a polymer should be approximately equal to two thirds of its melting temperature, which ratio was observed with the present polymer.

Effects of cooling rates on thermodynamic parameters and crystallinity

Following the first heating at 16 K min^{-1} , the polymer material was subjected to cooling at the following cooling rates: 0.5, 1, 2, 4, 8, 16, 32, and 64 K min^{-1} in the d.s.c. When the polymer was reheated at 16 K min^{-1} up to 401K, the shape of the thermogram obtained in each case was found to be different depending upon the cooling rate. The sample obtained in each case was subjected to cooling to room temperature and subsequent heating (both at 16 K min^{-1}). The above cycle of cooling and heating at 16 K min^{-1} was repeated. Different sets of four thermograms were obtained, corresponding to different cooling rates in the second stage. As an illustration, a set of four thermograms obtained for a 4 K min^{-1} cooling in the second stage is given in Figure 2.

The values of ΔH_c and ΔH_f for all the thermograms of PDBD were computed from the respective exothermic and endothermic peak areas by comparison with the endothermic peak area of indium. From the relation:

$$\Delta S_f = \Delta H_f / T_m$$

ΔS_f values were also computed. From the difference between ΔH_f and ΔH_c values, an estimate of sample crystallinity for each thermal treatment could be obtained⁷.

On first heating, the sample did not show any T_g or T_c and ΔH_f was found to be 33.83 J g^{-1} . The original sample was assumed to have maximum crystallinity, as the ΔH_f values were found to decrease after thermal treatments.

Curve A of Figure 3 indicates the thermal behaviour of the sample in the second stage of the treatment. As the cooling rate was decreased from 64 K min^{-1} , the crystalline content of the sample increased and there was a corresponding increase in the ΔH_f value. At or near 4 K min^{-1} cooling rate, the sample had a maximum ΔH_f value, very nearly equal to that of the original sample. This indicates maximum order of crystallinity. However, the sample still exhibited a cold crystallization (T_{C2}) exotherm. As the cooling rate was decreased below 4 K min^{-1} , ΔH_f started decreasing. The reason for this decrease may be that thermal motions prevail over the ordering process, thereby resulting in increased amorphous content. At or near 4 K min^{-1} cooling rate, the

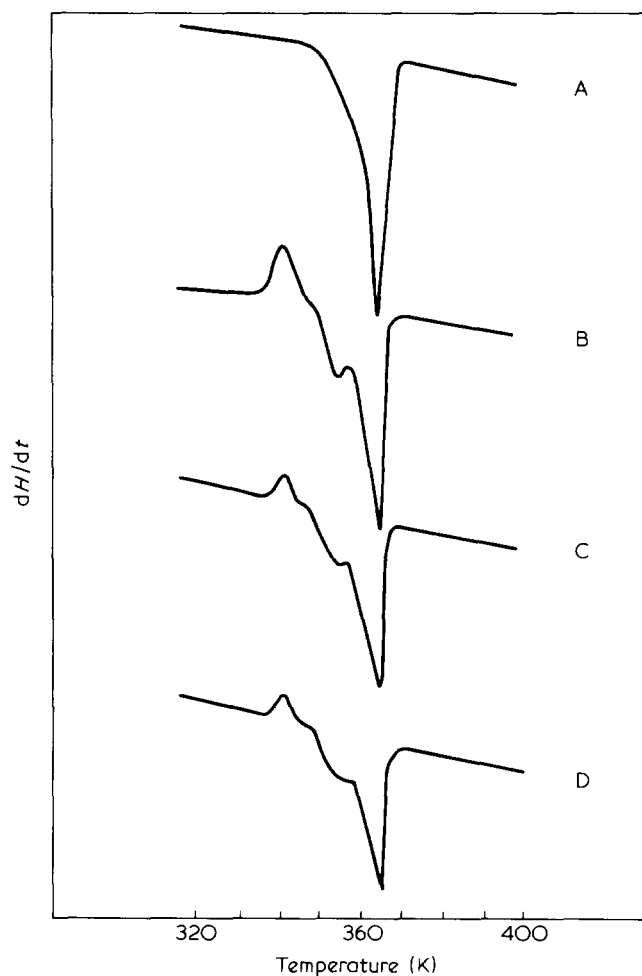


Figure 2 Thermogram of PDBD; scan speed 16 K min^{-1} . A, during first heating; B, after cooling by 4 K min^{-1} ; C, after two heat treatments; D, after three heat treatments

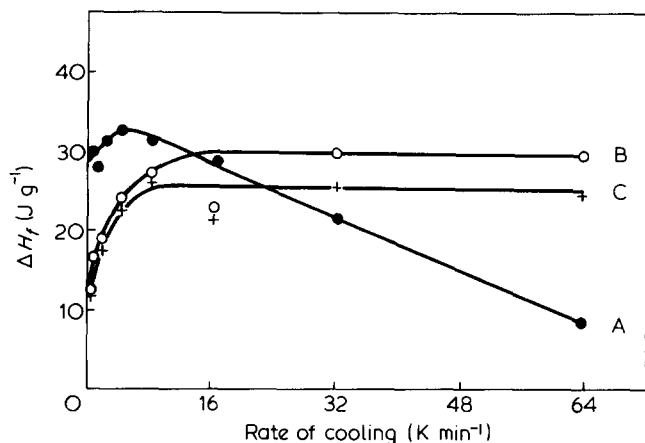


Figure 3 ΔH_f ($J g^{-1}$) versus rate of cooling ($K min^{-1}$). A, second stage; B, third stage; C, fourth stage of operation

sample attains maximum ordering. This phenomenon is reported for the first time.

Curve B (Figure 3) was obtained in the third stage of the thermal operation, namely $16K min^{-1}$ cooling followed by $16K min^{-1}$ heating after the second stage of operation for the various samples of PDBD obtained by different rates of cooling (Figure 3, curve A). Curve B showed a rather steep increase initially, reached a point of inflexion and remained constant thereafter. The increase could be explained in the same way as before. At and beyond the point of inflexion, corresponding to a $8K min^{-1}$ cooling rate, the sample attained maximum crystallinity — indicated by the flat portion of the curve.

When the samples obtained in step three were further cooled and heated, both at $16K min^{-1}$, the same trend was obtained (Figure 3, curve C). In this case, however, all ΔH_f values were found to be slightly below that of curve B. Thus, the PDBD sample suffers crystallinity loss at every operation of cooling and heating. The same trend was observed for ΔS_f and crystallinity index values at different cooling rates in the second stage.

Figure 4 gives the decrease in ΔH_f with the number of operations of cooling with heating, all at $16K min^{-1}$. In the second operation, some decrease in crystallinity was observed which may be due to the breakdown of the order in the packing of the polymer molecules. There was a further large decrease in crystallinity in the third operation, due to the continuation of the same process of increasing disorder. There was only a marginal decrease after further cycles of operation which may be due to the fact that the maximum decrease in order of the polymer molecules packing has already occurred in the third stage with little further possibility of increased disorder.

Effect of annealing

(i) *Annealing at 320K.* The polymer sample was heated from room temperature to $320K$ at $16K min^{-1}$, kept at that temperature for 1 h, cooled to room temperature at $16K min^{-1}$ and reheated at $16K min^{-1}$ from room temperature to $401K$. During this heating, the thermograms were taken. This operation was repeated for 2, 3, 4.5, 6.5 and 8 h annealing time intervals. The samples exhibited a single melting endotherm with a peak at $366K$, irrespective of the annealing time. It was found that ΔH_f first increased, reached a maximum and then decreased with respect to annealing time. The maximum was obtained at 180 min. It

is known that local alignment of the chain or chain segments in polymers is made possible during annealing. Milagin and Shishkin²¹ have shown that, even at room temperature, small but observable increases in density occur with time for poly(methyl methacrylate). The local alignment increases with increasing annealing time, ΔH_f reaching a maximum in 180 min. A similar maximum in ΔH_f with annealing time has been reported for some partially aromatic polyamides²². Further, the chain segments in amorphous regions of a partly aligned polymer are under stress; once the annealing time exceeds the critical value, the formation of the ordered units is decreased, due to the increased possibility of entanglements between chain ends. The variation of ΔH_f with respect to annealing time established segmental motions in the polymer chain above T_g .

(ii) *Annealing at 342K.* The polymer sample was heated from room temperature to $381K$ at $16K min^{-1}$. The molten polymer was cooled from 381 to $342K$ at $16K min^{-1}$ and kept at that temperature for various time intervals viz. 1, 3, 9 and 18 h. After this, it was cooled to room temperature at $16K min^{-1}$ and reheated at $16K min^{-1}$ up to $381K$. The thermograms obtained are shown in Figure 5. The computed ΔH_f increased with respect to annealing time and reached an asymptotic value (Figure 6). The same trend was followed by ΔS_f values. ΔH_c decreased sharply and there was no cold crystallization at all after 9 h annealing. The crystallinity index obtained from ΔH_f and ΔH_c values increased sharply with annealing time, as crystallinity, and hence ΔH_f , will increase when the polymer is annealed in its cold crystallization region.

Annealing at $342K$ had remarkable effects on the multiple endotherms in the melting region and the cold crystallization endotherm at $342K$. As the annealing time was increased, the higher temperature endotherm (Form I; T_m , $365.5K$) becomes smaller and the lower temperature endotherm (Form II; T_m , $357.5K$) becomes larger by approximately the same amount. Figure 7 shows the variation of the percentage of Form I and Form II with respect to the annealing time. The interconversion of Form I and Form II nearly attains saturation after an annealing time of about 3 to 5 h. Thereafter, the annealing time has no effect on this conversion.

The occurrence of multiple endotherms in the melting region has been reported in several polymers e.g. poly(ethylene

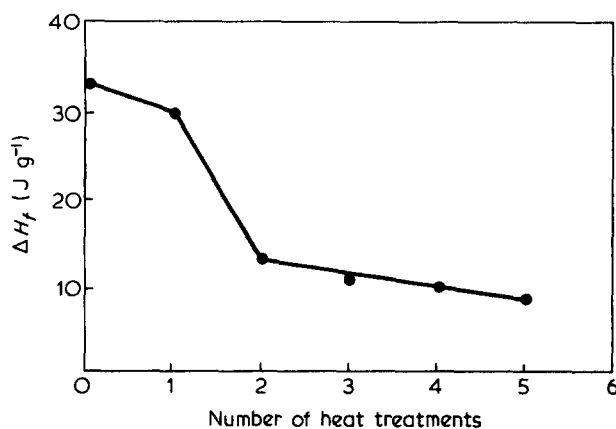


Figure 4 ΔH_f ($J g^{-1}$) versus number of heat treatments. Effect of repeated heating and cooling at $16K min^{-1}$ on ΔH_f

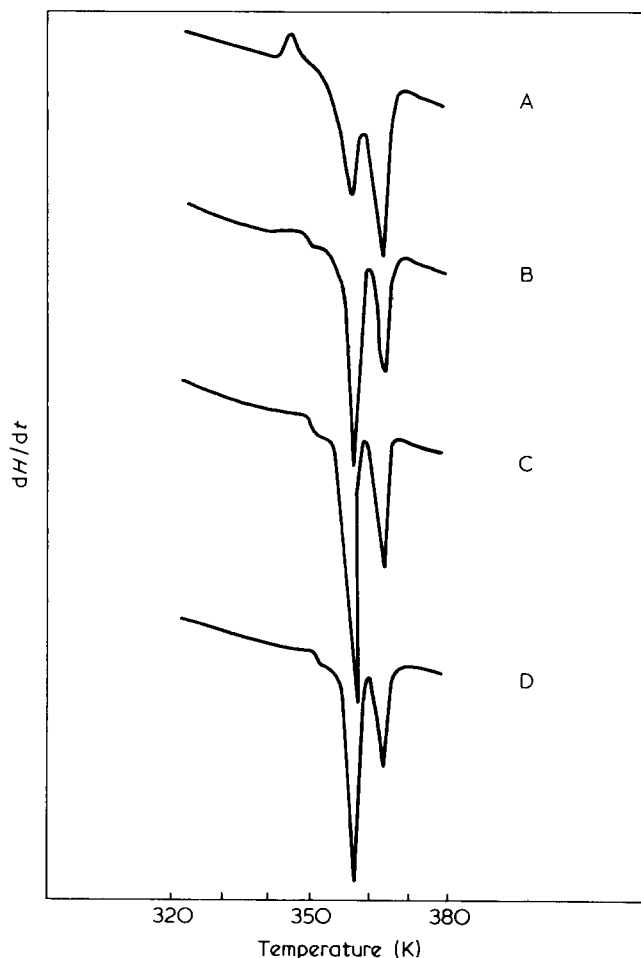


Figure 5 Effect of annealing below T_m (342K). A, Sample annealed for 1 h; B, 3 h; C, 9 h; D, 18 h

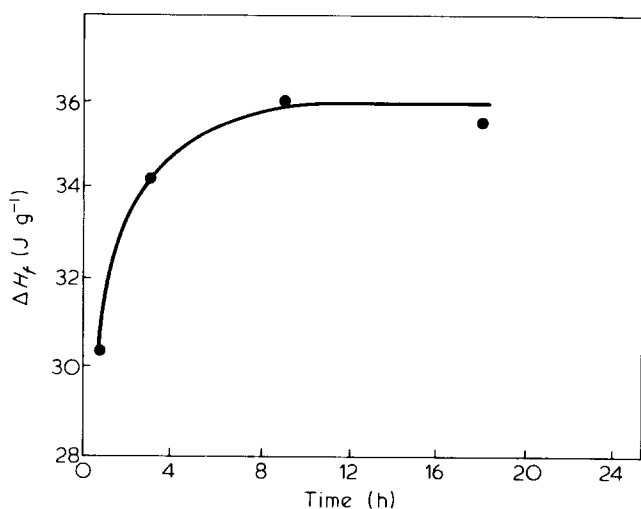


Figure 6 Variation of ΔH_f ($J g^{-1}$) with annealing time (h). Temperature of annealing, 342K

terephthalate)^{11-13,15,23-25}; Nylon-6,6^{23,26}; poly(butylene terephthalate)²⁷; polyethylene²⁸; and poly(butene-1)²⁹. For poly(ethylene terephthalate)²³, it was postulated that higher temperature endotherms corresponded to folded chain crystals and others to a crystal morphology in which some of the continuous chain folding has changed into a linear arrangement of the molecular chains, i.e., partially extended chain crystals. However, Sweet and Bell²⁴ and Roberts²⁵

conclusively proved that the higher temperature endotherm is the result of the melting of crystals which were formed by the simultaneous melting and recrystallization of the polymer at lower temperatures in the d.s.c.; but, by a variety of techniques, Bell and Dumbleton³⁰ showed that one endotherm in the melting region is caused by the melting of folded chain crystals, while the other is due to the melting of less perfect bundle crystals, for Nylon-6,6 and polystyrene. So the occurrence of the multiple melting endotherm is due to the different morphologies of the macromolecules.

Previous interpretations of multiple endotherms were with reference to high molecular weight polymers, whereas PDBD used in the present case was of low molecular weight and the phenomenon may require a different interpretation. The polymer of ~ 6 repeat units cannot have average molecular length greater than $\sim 90 \text{ \AA}$, and the phenomenon of molecular folding which is significant for high molecular weight polymers is unlikely to be shown by PDBD.

The fact that the polymer PDBD exhibited multiple cold crystallization (Figure 1, line B) clearly proved the formation of two morphologically different crystals while heating. None of the crystallizable polymers studied earlier by thermal techniques showed this: we are reporting the observation of multiple cold crystallizations in unsaturated aliphatic polyester (PDBD) for the first time.

These two different crystal morphologies are seen in the multiple melting. Once the polymer is annealed at 342K (T_{C2}) the crystallization to Form II is enhanced. This shows that more molecules align themselves in an extended chain configurational manner. Further prolonged annealing near this temperature lead to the disappearance of the T_{C2} exotherm, indicating that all the possible crystallization that has to occur at 342K is completed. As the annealing process generally leads to the perfection of the crystallites that are formed, an increase in the overall crystallinity, and hence an increase in the melting point (355–357.5K) was observed with annealing time.

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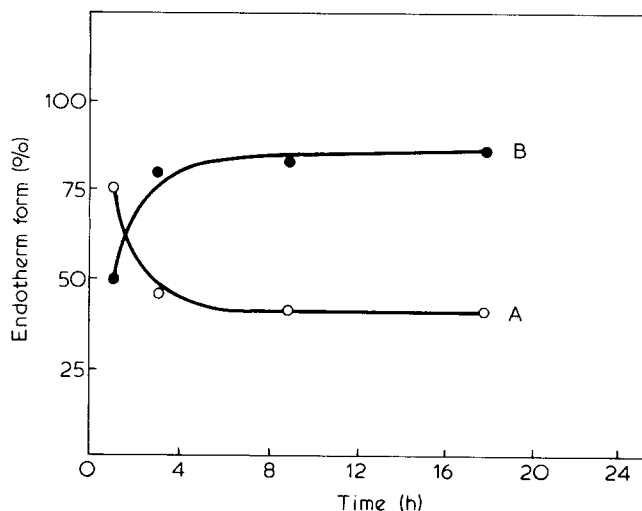


Figure 7 Variation of endotherm form (%) of Form I (A) and Form II (B) with respect to annealing time. Temperature of annealing, 342K

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