JOURNAL OF MATERIALS SCIENCE 12 (1977) 1443–1450

Effect of γ-irradiation on the melting behaviour of poly(trioxane)

Y. NAKASE, I. KURIYAMA
Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, 370–12, Japan
H. NISHIJIMA, A. ODAJIMA
Department of Applied Physics, Faculty of Engineering, Hokkaido University, Sapporo, 060, Japan

Poly(trioxane) obtained by radiation-induced polymerization in the solid state, was subjected to 1 Mrad γ-rays and the change in melting behaviour and the thermogravimetric curve examined. Little structural change in the X-ray scattering patterns was observed. The heating curve of as-polymerized poly(trioxane) exhibited a double endothermic peak under a high polymer yield, but the endotherm on the higher temperature side disappeared at a heating rate lower than 8° C min^{-1}. On irradiating over 25 krad, or rolling, the endotherm was again absent even at heating rates above 16° C min^{-1}. The endotherm at higher temperatures is interpreted as being due to superheating caused by entropy restriction. The irradiation or rolling causes chain scission at a selective point in the crystallites. These scissions reduce the superheatability of a poly(trioxane) with a high polymer yield. The lamellar-type poly(oxymethylene) crystal was also studied for comparison.

1. Introduction

The effects of radiation on poly(oxymethylene) has been studied extensively, but only a few of papers have dealt with structural changes and changes of related properties; that is, production of lattice defects by irradiation with electrons [1], changes in melting point, refractive index and density caused by X-irradiation [2].

A cryoscopic study [3] on γ-irradiated poly(oxymethylene) showed that depression of the melting point (the decreasing rate of which approaches a constant value over 100 Mrad) and thermal decomposition in a sample irradiated to 13.2 Mrad occurred at a temperature lower than that in the original material, although the profile of the melting endotherm was almost unchanged.

It was found [4] that layer-like voids were formed in poly(trioxane) irradiated over 10 Mrad, and that irradiation below 1 Mrad affected the melting behaviour of poly(trioxane) (PTOX) obtained by radiation-induced polymerization in the solid state.

Jaffe *et al.* [2, 5] reported that an extended-chain crystal such as poly(trioxane) exhibited superheating, i.e. a shift in its melting point to a higher temperature with increasing heating rate. The heating curves of the extended-chain crystal of PTOX which they used showed a single endothermic peak. On the other hand, Amano *et al.* [6] reported that the heating curve of poly(trioxane) was a double endotherm. They suspected that an endotherm on the lower temperature side (lower endotherm) was of a lamellar crystal transformed from the extended-chain crystal and the one on the higher side (higher endotherm) was of the melting of the extended-chain crystal itself.

The effect of irradiation of PTOX on its melting behaviour is very valuable in clarifying the origin of the double endothermic peak in the heating curves of poly(trioxane) obtained by radiation-induced polymerization. This paper describes the change in melting behaviour of PTOX irradiated with γ-rays below 1 Mrad.

2. Experimental

Trioxane, purified by sublimation, was placed in a glass ampule 5 cm diameter to prepare a large single crystal by a zone-melting method. The single crystal was pre-irradiated with γ-rays (1 Mrad) $h^{-1} \times 1\,h = 1$ Mrad $= 1 \times 10^6$ rad) at room temperature, and then polymerized for a given time at 55° C in air. The polymer yield was determined gravimetrically after washing the sample with acetone. The large poly(trioxane) crystal thus prepared was white in colour, and was cut into pieces suitable for measurements. The molecular weight (M_w) of PTOX was estimated [7] to be 3×10^5.

Delrin 500 ($M_w = 3 \times 10^4$) sheet drawn four times at 150° C, and Takafest [8] ($M_w = 5 \times 10^4$) poly(trioxane) acetylated in a solution of acetic anhydride and benzene at 180° C, and subsequently precipitated in solution by cooling, were used. The samples were placed in an open glass ampule and irradiated with γ-rays with an exposure rate of 10 krad h^{-1} (1×10^4 rad h^{-1}) for a given time at room temperature. The sample, even after the irradiation up to 1 Mrad, remained almost constant in weight, i.e. the weight loss was less than 1%.

The melting behaviour of the sample was investigated using a differential scanning calorimeter (Perkin–Elmer DSC-1B). The sample used weighed about 1 mg and the heating rate was usually 16° C min^{-1}. The instrument was calibrated with indium (Spectroanalytical grade, Johnson Matthey Co).

Thermogravimetry was carried out using a thermobalance (Perkin–Elmer TGS-1), and the temperature of the instrument was calibrated using the magnetic standards, alumel and nickel.

3. Results

Fig. 1 shows the heating curves of poly(trioxane) as-polymerized with different polymer yields. The profiles of the endothermic peak change quite clearly with polymer yield of the sample. The double endothermic peak is obtained in the polymer with a low yield (6%). The higher endotherm of the 6% polymer increases with increasing polymer yield, and the profile becomes single but broad. The profile changes again to a double peak for a yield of 80%, but shifts towards a quite high temperature. Therefore, the higher endotherm of the 6% yield seems to correspond to the lower endotherm in the 80% yield sample. At the same time, the extrapolated starting temperature of the endotherm (T_s) shifts towards a higher temperature with increasing polymer yield, as shown in Fig. 1.

Fig. 2 shows the heating curves of the samples of (a) 6% and (b) 80% yield with various heating rates. The heating curves of the 6% yield sample always exhibited a double endothermic peak, irrespective of the heating rate, even at a rate of 1° C min^{-1}. On the other hand, the profile of the double endothermic peak of the 80% yield sample changes to a single peak, when the heating rate is lower, as mentioned by Amano *et al.* [6], although they did not give the polymer yield in their paper.

The thermogravimetric (TG) and heating curves of poly(trioxane) of 6% and 80% yields are shown in Fig. 3. The TG curves of both samples are similar, although the endothermic peaks in the heating curves are observed at different temperatures. The weight loss in the TG curve is noticed over the peak temperature of the endotherm, at about 190° C. Therefore, the enthalpy change

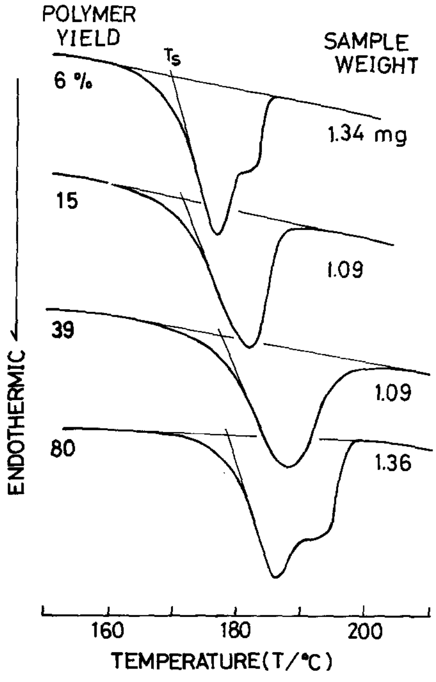

Figure 1 Heating curves of poly(trioxane) at various polymer yields. Heating rate: 16° C min^{-1}, polymer yield and sample weight used are indicated on the figure.

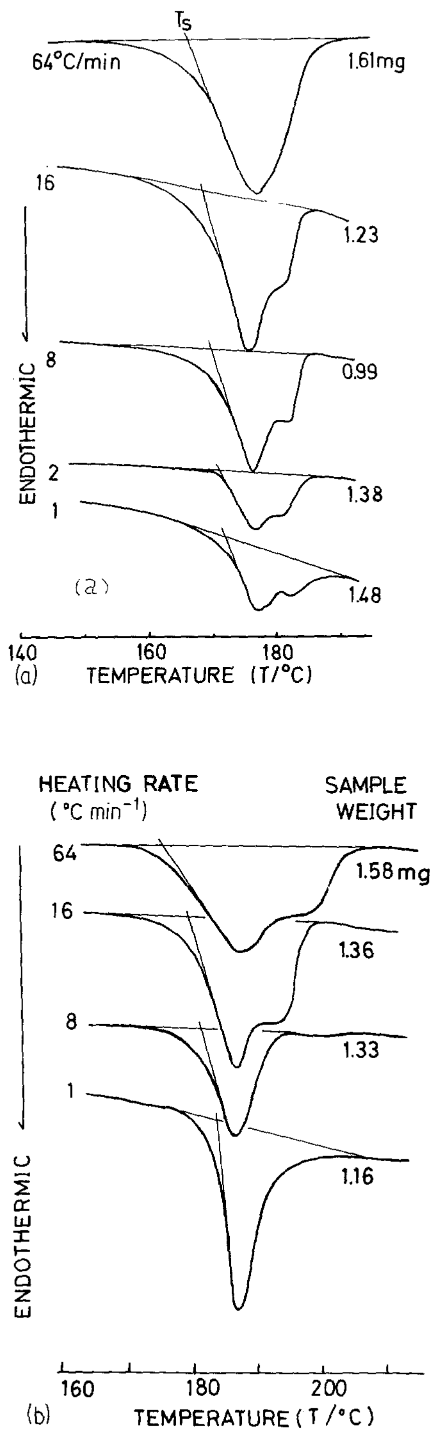

Figure 2 Heating curves of poly(trioxane) with various heating rates, (a) 6% polymer yield, (b) 80% yield. The sensitivity was changed according to heating rate; full scale 1 mcal sec^{-1} 4, 8 and 32, for 1° C min^{-1}, 8, 16 and 64, respectively, the heating rates and sample weights used are indicated in the figure.

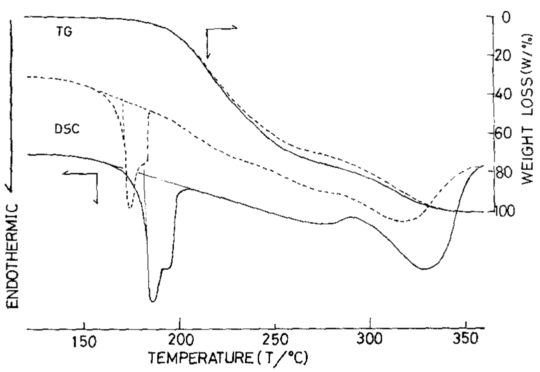

Figure 3 Thermogravimetric curves and heating curves of poly(trioxane) with the polymer yields 6% (-----) and 80% (———). Heating rate, 10° C min^{-1} in TG, and 16° C min^{-1} in DSC.

in the thermal composition which occurred during heating may not affect the profile of the melting endotherm, but it may affect its base line [9].

Fig. 4 shows the heating curves of poly(trioxane) (6 and 80%) irradiated with various doses in an open system. The heating curves of PTOX with a 6% yield were not affected by irradiation, even after 100 krad. Samples (80%) irradiated below 10 krad gave similar heating curves to the original PTOX, but those irradiated at 25 krad show that the lower endotherm increases and the higher endotherm almost disappears, the higher endotherm not being observed even at a heating rate greater than 16° C min^{-1}. The samples irradiated over 100 krad gave a very sharp melting endotherm. The profiles of the endotherm in the 80% sample irradiated over 100 krad are similar to each other. T_s of the samples remains constant, irrespective of irradiation, except for the sample irradiated at 1 Mrad. PTOX irradiated in a nitrogen gas showed similar results.

The small- and wide-angle X-ray scattering (SAXS and WAXS) patterns of the samples irradiated up to 1 Mrad were identical to those of the original (unirradiated) samples. That is, the SAXS pattern of the original showed a diffuse scattering in the direction of the equator, but little scattering in the meridian, and the WAXS patterns showed reflection caused by subcrystals, as well as patterns caused by main crystal (fibrous reflections) as reported by Chatani *et al.* [10]. The influence of oxygen is observed in SAXS and WAXS patterns as well as in the heating curves of PTOX irradiated over 1 Mrad [4].

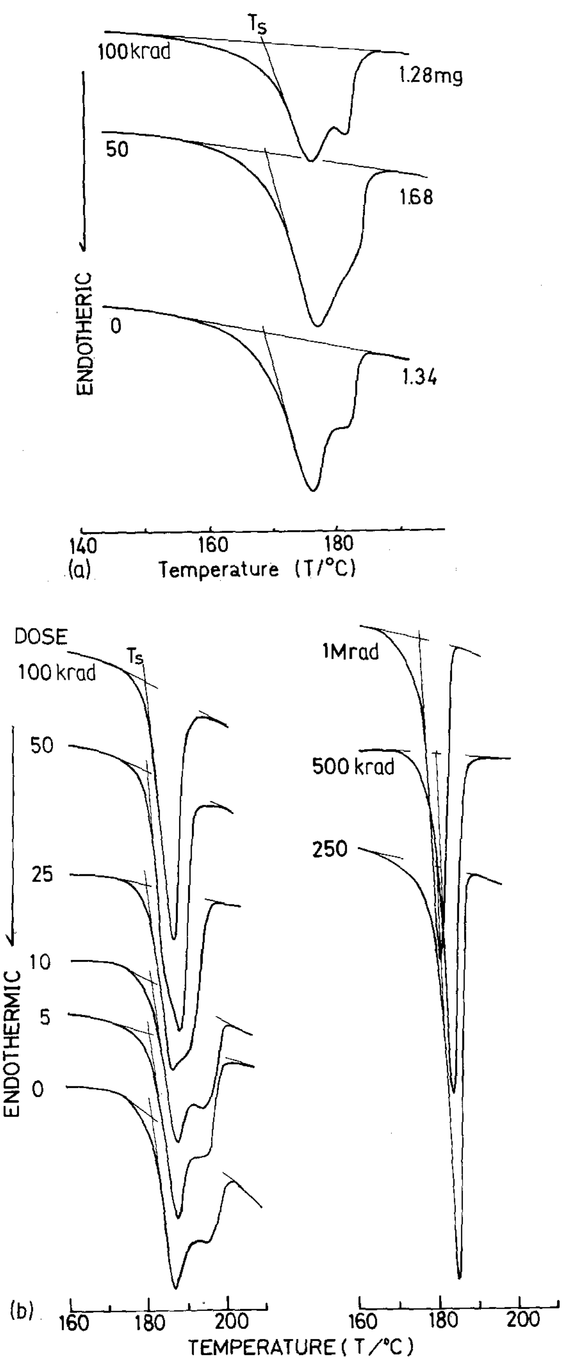

Figure 4 Heating curves of PTOX irradiated with various doses, (a) 6% polymer yield, and (b) 80% yield. Dose rate, 10 krad h^{-1}; heating rate, 16° C min^{-1}. The exposure and sample weights used are indicated on the figure.

Fig. 5 shows the TG curves of the sample irradiated to 1 Mrad (the same sample as used in Fig. 4). The weight loss due to the thermal decomposition seems to occur in two stages; the first stage in the TG curve is observed at about 200° C, and the second about 300° C. Irradiation reduces the amount of the region decomposed at the first stage and shifts the starting temperature of the decomposition to the lower temperature side.

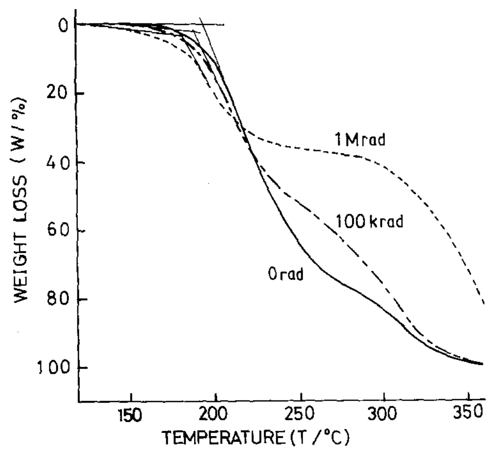

Figure 5 Thermogravimetric curve of PTOX irradiated with various doses. Dose rate: 10 krad h^{-1}, heating rate: 10° C min^{-1}. Doses are indicated in the figure.

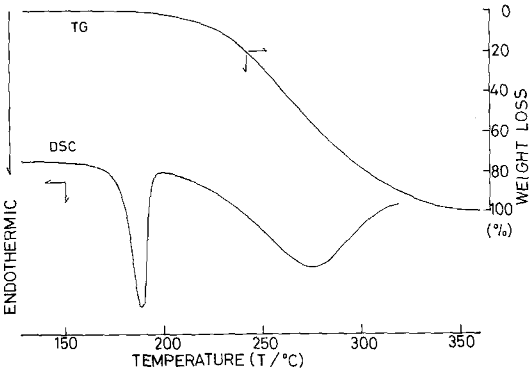

Figure 6 Thermogravimetric and heating curves of PTOX (80% yield) transformed into powder by the mixing mill. Heating rate, 10° C min^{-1} in TG, and 16° C min^{-1} in DSC.

Fig. 6 shows the heating and TG curves of the powdery PTOX rolled with shear stress. The endothermic peak in the heating curve is single, so that the higher temperature endotherm is lost. Decomposition occurs monotonically instead of in two stages as in the original sample.

Fig. 7 shows the heating curves of the melt-crystallized poly(trioxane) cooled at a rate of 64° C min^{-1} from the melt, namely the 2nd run of the 80% sample used in Fig. 4. The profile of the heating curve changes more sharply with increasing dose, although T_s remains constant in all samples, except that irradiated with 1 Mrad.

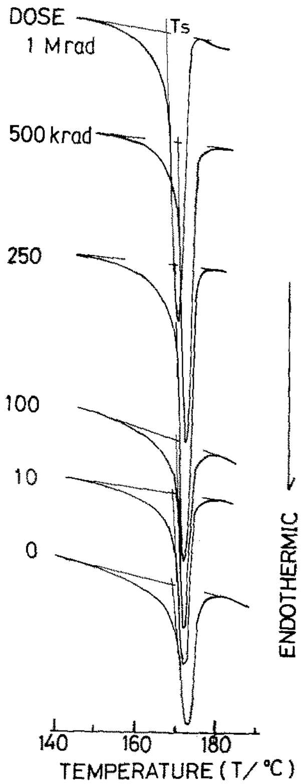

Figure 7 Heating curves of the melt-crystallized poly(trioxane) (2nd run of the sample used in Fig. 4, the cooling rate from the melt was 64° C min^{-1}). Heating rate, 16° C min^{-1}, sample weight: 1.1 ± 0.1 mg. The values in the figure indicate the exposure dose.

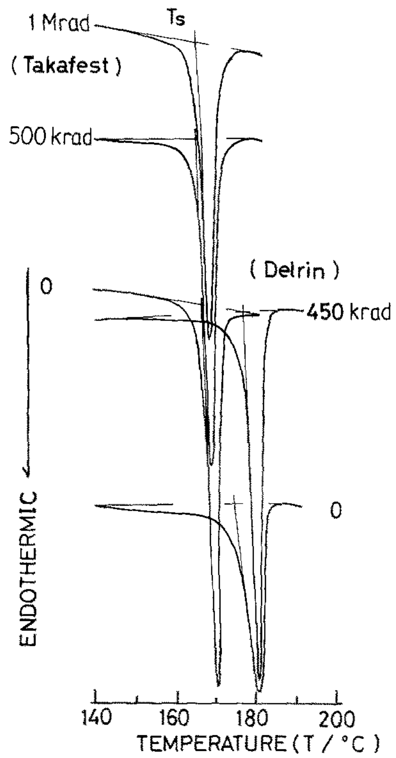

Figure 8 Heating curves of poly(oxymethylene) diacetate (drawn Delrin and Takafest). Heating rate 16° C min^{-1}, sample weight, 1.0 ± 0.1 mg. The values in the figure indicate the exposure dose.

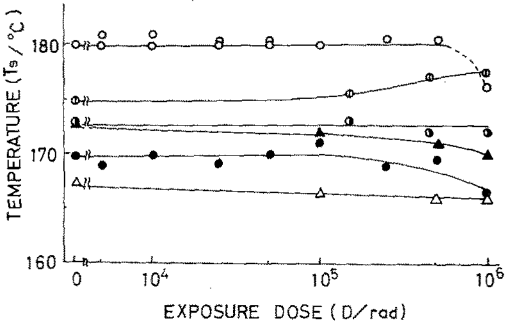

Figure 9 Relationship between the starting temperature of melting (T_s) and dose (D) in the various samples. Open symbols: as-irradiated (1st run); filled symbols: melt-crystallized (2nd run). ○, ●: poly(trioxane), ◐, ◑: drawn Delrin, and △, ▲: Takafest.

Fig. 8 shows the heating curves of two types of lamellar crystal of poly(oxymethylene) diacetate: the drawn Delrin film as an oriented lamellae sample, and the powdery Takafest as a spherulite crystal sample. The irradiated Takafest shows no particular change in the heating curve, but irradiated Delrin exhibits a shift of T_s towards higher temperatures as well as a sharpening of the endotherm.

In the heating curves of the melt-crystallized Delrin and Takafest, no remarkable difference was found between the unirradiated and the irradiated samples.

Fig. 9 shows the effect of irradiation on T_s of samples as-polymerized (1st run) and melt-crystallized (2nd run) for three types of poly(oxymethylene); poly(trioxane) (PTOX), Delrin and Takafest. As mentioned above, the T_s of PTOX in the 1st and the 2nd runs remains constant irrespective of the dose below 1 Mrad, but the T_s of the sample γ-irradiated at 1 Mrad becomes lower by about 3° C than the others. The T_s of Takafest in both runs decreases gradually with irradiation, while T_s of Delrin increases gradually in the 1st run and remains constant in the 2nd.

Fig. 10 shows the effect of irradiation upon the area under the endothermic peak in the heating curves, which corresponds to the enthalpy of melting. It is remarkable that the area in the

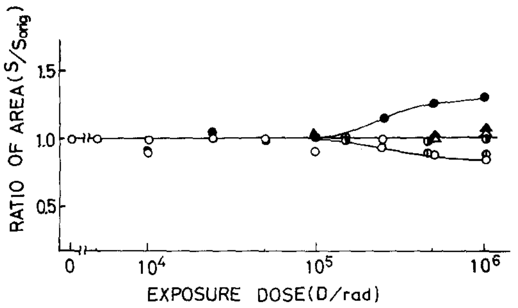

Figure 10 Relationship between the ratio (S/S_{orig}) of the area per unit weight under the endothermic peak of irradiated (S) to unirradiated (S_{orig}) samples and dose (D). The notation is the same as in Fig. 9.

2nd run of PTOX increases with irradiation over 100 krad compared with the original, indicating an increase in enthalpy of melting. The area of the other samples (Delrin and Takafest) after irradiation remains the same or a little less than that of the original (unirradiated) samples, indicating no special change in the enthalpy of melting.

4. Discussion

4.1. As-polymerized PTOX

A double endothermic peak in the heating curve in the 6% yield sample must correspond to the presence of at least two regions with different texture or aggregation of micro-fibrils in the polymer crystal produced during the course of polymerization. These two regions are not seriously affected by irradiation below 100 krad. On the other hand, the texture or aggregation corresponding to an endotherm on the higher temperature side (higher endotherm) in the 80% yield sample is affected by irradiation above 25 krad, whereas an endotherm at a lower temperature (lower endotherm) is not. Therefore, the characteristics of the higher endotherm shown in Fig. 1 are different for the 6% and 80% samples.

It is assumed that the double endotherm obtained with PTOX of 6% yield corresponds to the melting of the main and the subcrystals [11], since the subcrystal content is larger in PTOX with a lower yield than with a higher, and both crystals are observed in PTOX irradiated over 1 Mrad [4]. The subcrystal contents are reduced in PTOX with a higher polymer yield, and thus its melting may not be clearly observed. Chain scission due to irradiation takes place in PTOX, since the melt-crystallized irradiated PTOX shows a sharper melting endotherm and a higher enthalpy of melting than the unirradiated sample, as shown in Figs. 7 and 10. It is well known, as mentioned by Bair and Salovey [12], that the lower the molecular weight of the sample, the sharper the melting endotherm in the sample crystallized from the melt.

The amount of polymer decomposed during the first stage of the TG curve (Figs. 3 and 5) is reduced by irradiation, indicating that chain scission has occurred, since a thermally stable polymer is produced after irradiation [13]. These facts show that a reduction of the higher endotherm by irradiation is associated with chain scission.

As the polymer yield of PTOX is lowered, the molecular weight (M_w) becomes smaller, and the maximum molecular weight distribution M_{wd} shifts to the lower M_w side [14]. The chain scission introduced by irradiation reduces M_w and hence the M_{wd} peak shifts to the lower M_w side, judging from the data on poly(tetraoxane) [15]. The M_w and M_{wd} of the irradiated PTOX seem to correspond to those of the sample with a lower polymer yield.

It is noticed that the melt-crystallized polymer of PTOX shows a melting point (T_s) of ~170° C, as seen in Fig. 9, and annealing at a temperature lower than T_s causes reorganization of the sample to increase T_s, while annealing at a temperature higher than T_s causes partial melting in PTOX to produce two endotherms at about 170° C and about 185° C [16], similar to those given by Amano *et al.* [6].

PTOX in this paper gives T_s ~180° C, about 10° C higher than that of the melt-crystallized sample. The refolding of the polymer chains during the heating process [6] implies that partial melting of the sample at a temperature below T_s has occurred. This is not likely from the data on annealing effects mentioned above.

It has been reported that the melting of PTOX can probably begin only at the chain ends, and the longer the chains in the crystal lattice, the longer the time necessary for the crystal to melt [2]. The melting temperature of polytetrafluoroethylene also depends on crystallite size, particularly in the lateral direction rather than along the *c*-axis [17]. Both samples showed a double endothermic peak in their heating curves. Larger crystallites of PTOX with a higher yield, consisting of an extended-chain crystal [4], therefore seem to be the origin of the higher endotherm, indicating superheating due to the larger size crystallites. Superheating here is derived from analysis of the melting endothermic profile of PTOX with a high yield, and not from the shift in melting point to the higher temperature side with increasing heating rate [2, 5].

It was observed [22] that (1 0 0) and (0 0 5) reflection peaks were recorded in WAXS diagrams of PTOX with high yields, and that the (1 0 0) reflection peak disappeared completely and the (0 0 5) reflection peak was greatly reduced after irradiation of 50 Mrad. This implies that the PTOX crystal may contain large amounts of unoriented micro-crystals and conformational disorder. Large crystallites of PTOX cannot, therefore, be perfect, but contain several kinds of polymer aggregation, including molecular chains having an entropy restriction.

The reduction of the higher endotherm, and the change of decomposition behaviour to one stage in the TG curve of PTOX rolled by a mixing mill as shown in Fig. 6, must be also due to chain scission as mentioned above.

4.2. Characteristics of a superheatable sample

The superheatability of polyethylene (PE) with a cross-banded micro-shish-kebab structure [18], was reduced by fuming nitric acid treatment. The reduction of this ability is associated with only a limited amount of molecular scission and is lost with scission of the interplatelet tie molecules.

The superheatability of poly(ethylene terephthalate) [19] was produced or restrained in the samples annealed at about 250° C but was not present in the as-polymerized sample. This ability was not a crystal size effect, but must be caused by tie molecules between different crystals or different locations on the same lamella. Superheating effects due to reduction in entropy of melting are calculated theoretically [20] in a situation where each chain molecule can simultaneously belong to many different crystalline and noncrystalline regions. In the case of natural rubber, it is suggested [21] that the chain scission of molecules with stress, i.e. a large deformation with an extention ratio more than 2, occurs easily by irradiation, since the molecules were entropy restricted.

The reduction of the higher endotherm occurs with a small amount of molecular-chain scission by irradiation as shown in Figs. 4 and 8. A similar situation is considered in PTOX with a high yield, i.e. the reduction of superheatability is caused by chain scission, probably on polymer chains at a particular region of entropy restriction as mentioned above. This is supported [4] by the layer-like void formation in PTOX irradiated over 10 Mrad.

4.3. Folded-chain crystal

In the case of the folded-chain crystals of poly(oxymethylene) diacetate (Delrin and Takafest), the situation is a little different from the case of PTOX mentioned above, because the heating curve of the unirradiated samples is a single endotherm with rather sharp profile, and the T_s of the endotherm is increased at a heating rate lower than 8° C min^{-1}. The melting endotherm of irradiated Delrin becomes very sharp with a higher T_s by reducing part of the endotherm on the lower temperature side, as shown in Figs. 8 and 9. The enthalpy of melting of the irradiated Delrin remains almost constant, as shown in Fig. 10, which indicates that chain scission occurred probably at a non-crystalline region, to increase only the uniformity of the melting behaviour of the polymer crystal.

Takafest as-prepared in the powder form gives a very sharp endothermic peak and the profile of the endotherm does not change with irradiation up to 1 Mrad. The T_s of the melt-crystallized Takafest is higher by 4° C than the as-prepared sample, indicating a better molecular arrangement in the melt-crystallized than in the precipitated sample.

The irradiation effect ($<$ 1 Mrad) on the melting behaviour of folded-chain crystals of poly(oxymethylene) is not so clear in comparison with the as-polymerized PTOX, indicating a difference in aggregation of polymer molecules or morphology, although chain scission may occur in both cases.

5. Conclusions

PTOX with a high polymer yield shows a double endothermic peak, and an endotherm at a higher temperature is reduced by slow heating at $<8°$ C min^{-1}, by irradiation over 25 krad, and by rolling with a mixing mill.

The folded-chain crystals of poly(oxymethylene), Delrin and Takafest, give a single endotherm which is not seriously affected by irradiation up to 1 Mrad.

A limited amount of molecular chain scission by irradiation ($<$ 1 Mrad) takes place in the sample and affects the melting behaviour of PTOX, but not of Delrin and Takafest, since the weight loss by irradiation is negligibly small.

It is suggested that chain scission takes place at a selective region in PTOX where molecular chains are probably entropy restricted. Such a region where it exists is superheatable. At a heating rate slower than 8° C $\min^{-1}$, the heat conduction in the sample must be comparable to its relaxation, and irradiation over 25 krad, or shear stress, must reduce the area of the selective region mentioned above.

The effect of irradiation over 1 Mrad on the melting and X-ray scattering behaviour will elucidate more clearly the chain scission at a selective region in PTOX obtained by radiation-induced polymerization in the solid state [22].

References

1. H. ORTH and E. W. FISCHER, *Makromol. Chem.* **88** (1965) 188.
2. M. JAFFE and B. WUNDERLICH, *J. Polymer Sci. A-2* **6** (1968) 825.
3. R. P. KUSY and D. T. TURNER, *Macromol.* **8** (1975) 235.
4. A. ODAJIMA, T. ISHIBASHI, Y. NAKASE and I. KURIYAMA, to be published.
5. M. JAFFE and B. WUNDERLICH, *Kolloid-Z.* **216/217** (1967) 203.
6. T. AMANO, E. W. FISCHER and G. HINRICHSEN, *J. Macromol. Sci.-Phys.* **B3** (1969) 209.
7. M. SAKAMOTO, I. ISHIGAKI, M. KUMAKURA, H. YAMASHINA, T. IWAI, A. ITO and K. HAYASHI, *J. Macromol. Chem.* **1** (1966) 639.
8. A. ITO and K. HAYASHI, *Hydrocarbon Processing* **47** (1968) 197.
9. Y. NAKASE, I. KURIYAMA, H. NISHIJIMA and A. ODAJIMA, *Japan. J. appl. Phys.* **16**.
10. Y. CHATANI, T. UCHIDA, H. TADOKORO, K. HAYASHI, M. NISHII and S. OKAMURA, *J. Macromol. Sci.-Phys.* **B2** (1968) 567.
11. D. H. RENEKER and J. P. CALSON, *J. Appl. Phys.* **42** (1971) 4606.
12. H. E. BAIR and R. SALOVEY, *J. Macromol. Sci. -Phys.* **B3** (1969) 3.
13. S. TORIKAI, *J. Polymer Sci.* **A2** (1964) 239.
14. E. KOBAYASHI, T. HIGASHIMURA and S. OKAMURA, *Kobunshi Kagaku* **25** (1968) 313.
15. Y. NAKASE, M. YOSHIDA, A. ITO and K. HAYASHI, *J. Polymer Sci. A-1* **10** (1972) 2181.
16. Y. NAKASE, I. KURIYAMA and A. ODAJIMA, *Polymer J.* **8** (1976) 35.
17. T. SUWA, T. SEGUCHI, M. TAKEHISA and S. MACHI, *J. Polymer Sci. Polymer Phys.* **13** (1975) 2183.
18. A. KELLER and F. M. WILLMOUTH, *J. Macromol. Sci.-Phys.* **B6** (1972) 493.
19. A. MIYAGI and B. WUNDERLICH, *J. Polymer Sci. A-2* **10** (1972) 1401, 2073, 2085.
20. H. G. ZACHMANN, *Kolloid-Z.* **216/217** (1967) 180.
21. T. KUSANO, Y. SUTOH and K. MURAKAMI, *Nippon Kagaku Zasshi,* **1974** (1974) 1128.
22. A. ODAJIMA, T. ISHIBASHI, H. NISHIJIMA, Y. NAKASE and I. KURIYAMA, *Polymer Preprint, Japan* **25** (1976) 957.

Received 21 July and accepted 22 November 1976.