European Polymer Journal. Vol. 15. pp. 379 to 387
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0014-3057/79/0401-0379$02.00/0

EFFECTS OF GAMMA RADIATION ON THE MECHANICAL PROPERTIES AND CRYSTALLINITY OF POLYPROPYLENE FILM

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(*Received* 8 *August* 1978)

Abstract—Three samples of isotactic polypropylene film with differing crystalline forms, all made from one batch of commercial homopolymer, have been gamma irradiated up to 150 Mrad. The effects on the tensile properties and crystalline structure have been measured, compared and discussed. Only slight decreases in the crystalline structure measured by density and X-ray diffraction were observed after the highest doses but there was a significant decrease in the tensile break stress and strain and a significant change in the melting characteristics after all doses. The behaviour of the annealed monoclinic sample contrasted markedly with that of the unannealed monoclinic sample. The behaviour of the latter was similar to that of the unannealed smectic sample.

INTRODUCTION

In view of the commercial importance of polypropylene, PP, it is not surprising that there have been many investigations of the effect of gamma irradiation on PP in various forms and with respect to various properties. Few, however, have been directed at the effect on the crystalline structure or on the influence of crystal structure on the effects of gamma radiation on other properties of PP. This is the subject matter of this paper.

There have been a number of gelation studies on isotactic PP resulting in values of $G(S)$ ranging from 0.16 to 0.91 and in values of $G(X)$ from 0.15 to 0.81 [1–5]. There is better agreement on the ratio of chain scission to cross-linking with values of $G(S)/G(X)$ from 0.9 to 1.4. One might predict from these values that gamma irradiation would have little effect on the strength of PP since they indicate that $\overline{M}_w$ should rise with irradiation to the gel dose and that $\overline{M}_n$ should rise or fall slightly depending on whether $G(S)/G(X)$ is $\langle$ or $\rangle$ unity. However it is well known that the strength of PP is severely reduced by even small doses of irradiation [6–8]. This is clearly related to the fact that chain scission is disproportionately high at low doses as illustrated by the work of Schnabel and Dole [1]. There is evidence which indicates that this may be partly due to the reactions of residual oxygen in the polymer [9] and to the reaction of residual radicals in the polymer with atmospheric oxygen when the sample is exposed to air [3]. However since these effects are not apparent in other polymers, it seems likely that this explanation is inadequate. It is also known that crystal structure can influence the reactions in a semi-crystalline polymer as a result of gamma irradiation. With PP for example, the effects of irradiation on isotactic PP (semi-crystalline) and atactic PP (amorphous) have been compared [4, 5]. Hydrogen evolution and chain scission occur to a significantly greater extent in isotactic PP whilst cross-linking occurs to a significantly greater extent in atactic PP. It is unclear whether this is due to differences in tacticity or crystallinity.

The only comparison of the effects of irradiation on different crystalline forms of the same isotactic PP is due to Chappell *et al.* [10], who compared the effects of reactor and electron irradiation on quenched and annealed samples of the same predominantly (91%) isotactic PP. They showed that after moderate doses (< 100 Mrad), gel formation was significantly greater in the quenched PP. They attributed this effect to the lower mobility of the polymer free radicals produced in the crystalline regions, which were presumably more extensive in the annealed PP, and their inability to produce crosslinks. Consequently the radicals eventually lead to chain scission which, therefore, occurs to a relatively greater extent in the polymer with highest crystallinity.

These observations clearly indicate that it is an oversimplification to consider that gamma ray initiated reactions occur homogeneously throughout a semi-crystalline polymer. It is of considerable importance to understand the influence of crystal structure on the effects of irradiation of PP since, by careful manipulation of conditions, it may become possible to improve or at least leave unchanged the mechanical properties of PP by irradiation. There has been some success in this direction; crosslinking has been enhanced in PP by swelling the polymer with allyl methacrylate prior to irradiation [11].

The influence of crystalline structure on radiation effects in isotactic PP is still quite unclear. This paper reports an investigation and comparison of the effects of gamma irradiation on the mechanical properties and crystallinity of three different crystalline non-oriented forms all made from the same sample of isotactic PP. The behaviour of the three forms are discussed in relation to current theories of polymer melting and the structure of semi-crystalline polymers.

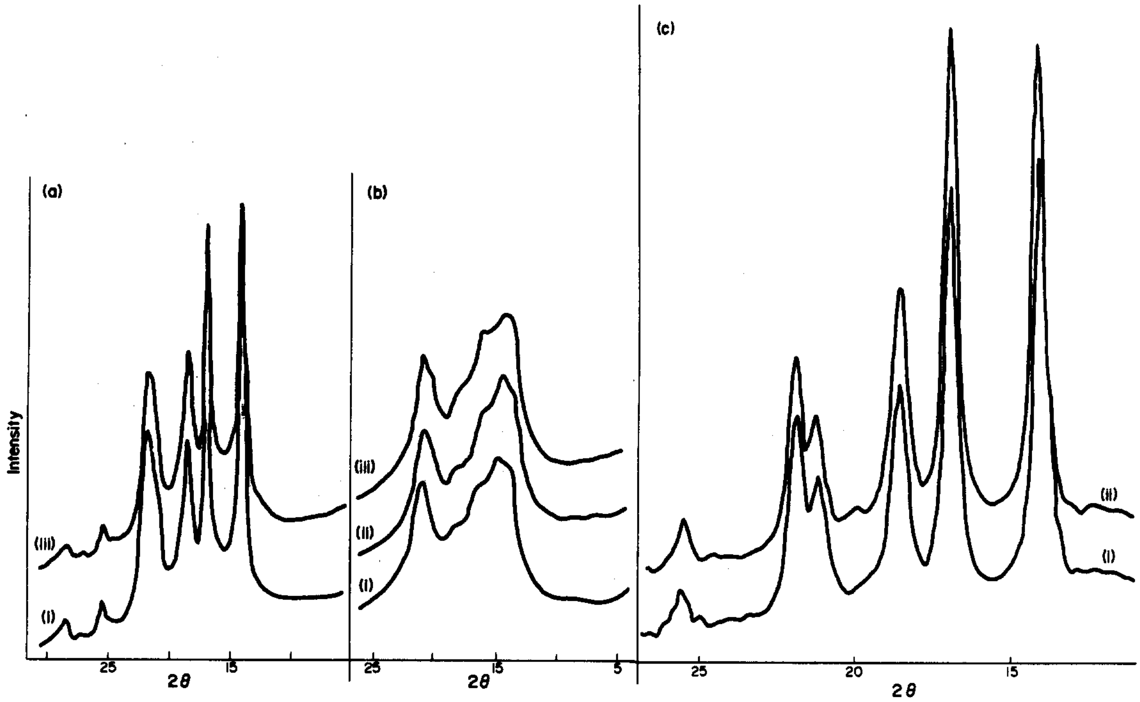

Fig. 1. X-Ray diffractometer scans of isotactic polypropylene; (a) sample A-monoclinic, (b) sample B-smectic, (c) sample C-annealed (i) unirradiated (ii) after 50 Mrad (iii) after 150 Mrad.

EXPERIMENTAL

Polypropylene samples

The polypropylene was ICI grade GWE 21F with a stated melt flow index of 4.5. GPC analysis by R.A.P.R.A. gave $\bar{M}_n = 2.64 \times 10^4$ and $\bar{M}_w = 1.39 \times 10^5$. The non-isotactic content, measured by extraction in heptane and by infrared absorption, was in the range 2 to 3% (various factors preclude a more precise determination by either method [12]). The antioxidant content as measured by acetone extraction was 0.2%.

Film samples were extruded from a laboratory extrusion unit (Plasticizers Ltd, Mark I) with a screw temperature of 250°. The molten polymer was extruded vertically downwards from a die (65 mm × 0.375 mm), through an air gap of 15 mm onto a chill roll. The chill roll temperature was controlled by circulating water from a thermostat bath through internal coils at 55° for sample A and at 9° for samples B and C. Sample C was subsequently annealed at 145° for 5 hr. The screw was operated at 50 rpm and the chill roll at a take-up rate of 51 mm s^{-1} producing film of width 55–57 mm and thickness 130–150 μm. The films used in the present study were wound directly from the chill roll at ambient temperature with the minimum of tension. Samples of width 5.0 mm were cut from the middle of each film with a multiple blade device.

The three crystalline types used in this study were made from the same sample of PP and have been labelled A-monoclinic, B-smectic and C-annealed. Their densities are, respectively, 900.6, 890.1 and 912.8 kg m^{-3}. Taking the densities of pure amorphous and pure crystalline isotactic monoclinic PP as 853 and 935 kg m^{-3} respectively [13], the percentage crystallinity of samples A, B and C are 58, 45 and 73% respectively.

X-ray scanning diffractometer tracings (Fig. 1.) show that samples A and C contain α monoclinic crystals [14] whilst sample B contains mainly smectic (paracrystalline) crystals [15] together with a small proportion of α-monoclinic crystals. The peak widths at half height indicate that the crystallites in sample C are either larger or of a higher degree of perfection (depending on one's point of view) than those in sample A. The crystal structure of the smectic modification is still uncertain. Of the various possibilities, reviewed by McAllister, Carter and Hinde [29], the X-ray diffractograms suggest that it is a microcrystalline form of the β-hexagonal modification, although we have retained the name originally suggested by Natta [30].

Irradiation

Pyrex tubes containing lengths of film were evacuated at ambient temperature for 3 h at $<10^{-2}$ Pa before sealing. Irradiations were carried out in the pond facility of the Australian Atomic Energy Commission at Lucas Heights at 35° with ^{60}Co gamma radiation at 2 Mrad hr^{-1}. Ceric dosimetry [16] was used and corrected to the dose absorbed in the polymer samples [17]. After irradiation, the tubes were stored for >3 weeks before opening to the atmosphere.

Density measurement

The densities of polymer samples were measured in isopropanol/water density gradient columns thermostatted at 23.0°.

Differential scanning calorimetry

Differential scanning calorimetry measurements were made with a Perkin–Elmer DSC model 1B Instrument using sample weights of 3–7 mg. The features of polymer melting and polymer crystallization curves are strongly dependent on scan rates and sample thermal history. In this study a fixed scan rate of 8 K min^{-1} was used for both melting and crystallization thermograms. In order to ensure a constant post-irradiation thermal history for each sample, a standard scanning procedure was used. The sample was heated from ambient to 190° to obtain the melting thermogram, held at 190° for 1 min, and then cooled from 190° to ambient in order to obtain the crystallization thermogram. Indium was used to calibrate the temperature scale (melting point, 156.6°) and the heat energy response of the instrument ($\Delta H_{\text{fusion}} = 28.45$ J g^{-1}). The melting point of a polypropylene sample was taken as the temperature at which the last trace of crystals disap-

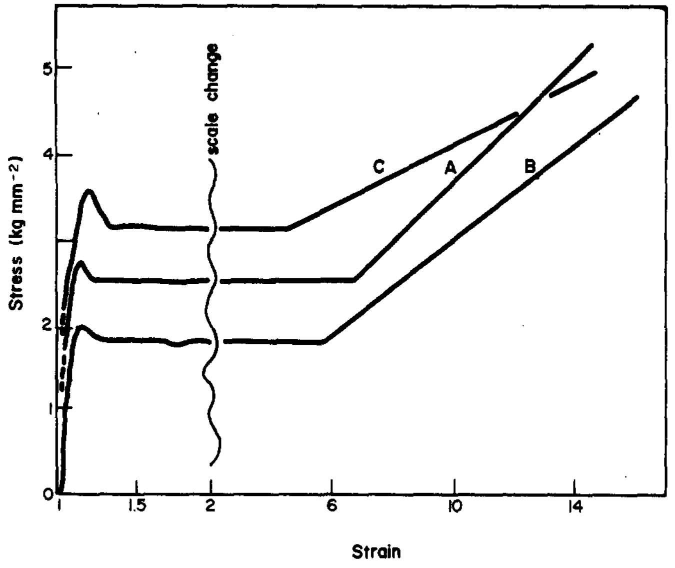

Fig. 2. Typical stress-strain diagrams for unirradiated samples A-monoclinic, B-smectic and C-annealed. Stresses are nominal. Note change of scale above strain of 2.

peared; it was found in practice by extrapolating the final descent of the melting peak to the baseline. The temperature of crystallization was taken as that where the first trace of crystals appeared on cooling the sample; in practice this was also found by extrapolation.

The area under a peak resulting from an endothermic or exothermic transition is proportional to the enthalpy change associated with that transition for the sample under test. Peak areas were determined by cutting and weighing tracings of the peaks. Values of the crystallization enthalpies were reproducible for any one sample cooled under fixed conditions (see above); the values are accurate to better than ±2%. It was not possible however to obtain reproducible values of the melting enthalpies, almost certainly because of the difficulty of determining the point at which melting commenced i.e. where the melting curve initially departed from the base line.

X-ray diffraction

Diffraction patterns were recorded with a Phillips Scanning Diffractometer using Cu Kα radiation and a scintillation detector.

Tensile strength measurements

Tensile stress-strain measurements were made on an Instron Model 1026 instrument at ambient temperature (23°) with a sample length of 10.0 mm and a crosshead beam speed of 10 mm min^{-1}. Stress data recorded in this paper are nominal, i.e. a constant cross section is assumed. At least two measurements were made on each sample. In the case of discordancy, measurements were repeated until at least three concordant results were obtained. The precision generally obtainable was within ±5% for the breaking stress and within ±15% for the breaking strain.

RESULTS

Tensile measurements

Typical tensile stress-strain curves for the unirradiated samples are shown in Fig. 2. The initial elastic modulus was similar for each of the unirradiated samples and was not significantly affected by irradiation.

The yield stress and the flow stress (stress required in the necking region) for the unirradiated samples both increased in the order B-smectic, A-monoclinic, C-annealed, indicating a progressive increase in resistance to orientation. The flow stress was not always constant during the complete necking process, but the variations were not reproducible. Small doses of irradiation produced a small increase in the yield stress for all samples as shown in Fig. 3. In sample A-monoclinic and sample B-smectic, higher doses produced a slight decrease in the yield stress. Further irradiation had a profound effect on sample C-annealed; after 10 Mrad the sample fractured before the yield point.

The ultimate tensile stress and strain at break were similar for all three unirradiated samples, see Fig. 4. After low doses of irradiation the breaking stress of all samples was markedly reduced, see Fig. 4 (a); the effect was greatest for sample C-annealed, 5 Mrad reducing the breaking stress by 32%. The effect of irradiation on the breaking strain [Fig. 4(b)] was similar to the effect on the breaking stress but there was a clear correlation with the density and hence the overall degree of order in the three samples. Thus the breaking strain of sample B-smectic was little affected up to 50 Mrad, that of sample A-monoclinic was little affected up to 20 Mrad whilst that of sample C-annealed was severely reduced after only 5 Mrad.

X-Ray diffraction

X-Ray diffraction scans of samples A-monoclinic and B-smectic before and after 150 Mrad and of sample C-annealed before and after 50 Mrad are shown in Fig. 1. There is no significant change for sample A or C indicating that there is no significant decrease in the highly ordered state of the polymer. For sample B there is a slight indication that the monoclinic content increases with dose at the expense of the smectic content, but after 150 Mrad the increase is only about 5%. In comparison polyethylene requires over 1000 Mrad before a significant change in the X-ray diffraction pattern is observed [6].

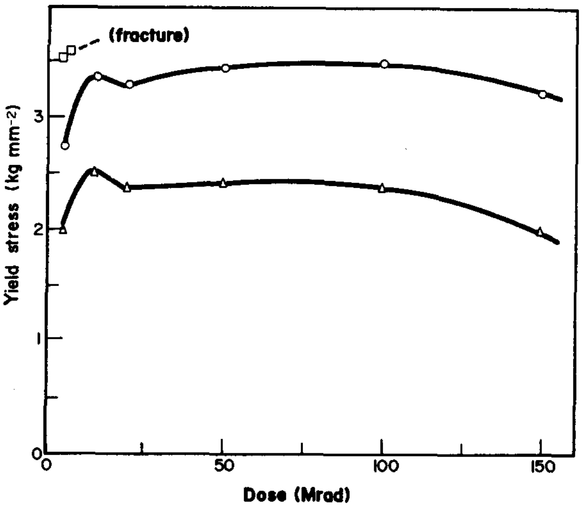

Fig. 3. Yield stress for samples A-monoclinic (circles), B-smectic (triangles), C-annealed (squares) as a function of dose. Sample C broke before yield after greater than 5 Mrad.

Density measurements

The density of a polymer sample measures the overall packing of the polymer molecules. When used quantitatively, a simple two-phase structure is assumed in which the densities of the crystalline and amorphous phases are uniform. Irradiation up to 150 Mrad produced only a very small change in the density of any of the three samples, see Fig. 5, confirming that there was no appreciable disruption of the crystalline structure. There may be a slight rise in the density of sample B-smectic after low doses (10 Mrad). The densities of samples A and B decreased by about 1 kg m^{-3} after 150 Mrad (sample C was not irradiated to >50 Mrad), representing a decrease in crystalline content of 1.2%.

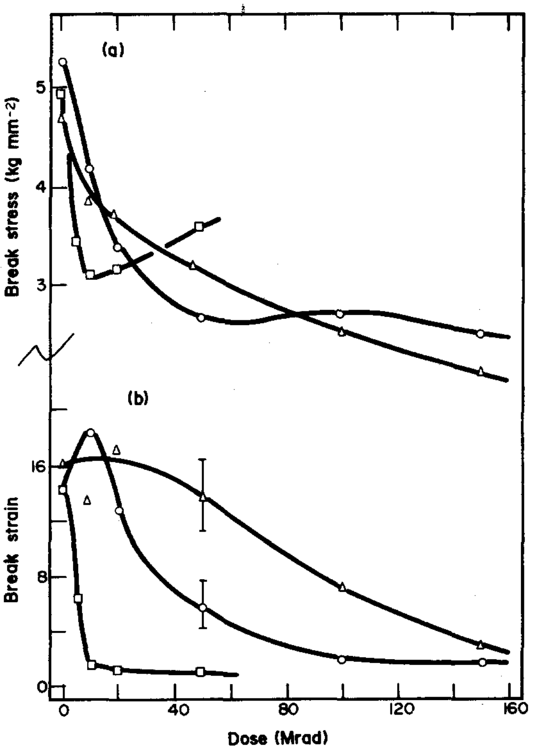

Fig. 4. (a) Breaking stress (nominal) as a function of dose, (b) Breaking strain as a function of dose for sample A-monoclinic (circles), B-smectic (triangles) and C-annealed (squares).

The observed behaviour of sample C-annealed is similar to that observed by Gee and Melia [18] for an annealed sample of isotactic (presumably monoclinic) PP (see next section for comment), except for 25 Mrad when they observed a decrease in density equivalent to a decrease of 12% in crystallinity. However, they observed a negligible change after all other doses up to 1000 Mrad.

Differential scanning calorimetry

Three items of information have been extracted from the thermal analysis of each sample. These are (i) the melting point and melting range (qualitative information only, see experimental), which should be functions of the size, shape and degree of perfectness of the crystallites in the sample; (ii) the crystallization temperature, which is a relative function of the size, shape and perfectness of the crystallites which can be formed on cooling the sample from the melt; (iii) the area under the crystallization peak which is directly proportional to the enthalpy of crystallization and hence to the amount of crystalline polymer that can be formed on cooling the sample from the melt. The last item is particularly valuable when studying irradiation effects since the amount of crystallization will be strongly affected by defects such as crosslinks in the structure.

The study of melting characteristics as a method of investigating crystallline content of a polymer sample differs from the X-ray and density methods in one important respect: the sample has to be heated to the initial melting point before the information is obtained. Obviously significant changes in structure can occur in the heating process and the observations may not be directly comparable with the results obtained by the other two methods.

The melting thermograms are shown as a function of dose in Figs 6 and 7. Clearly the melting character-

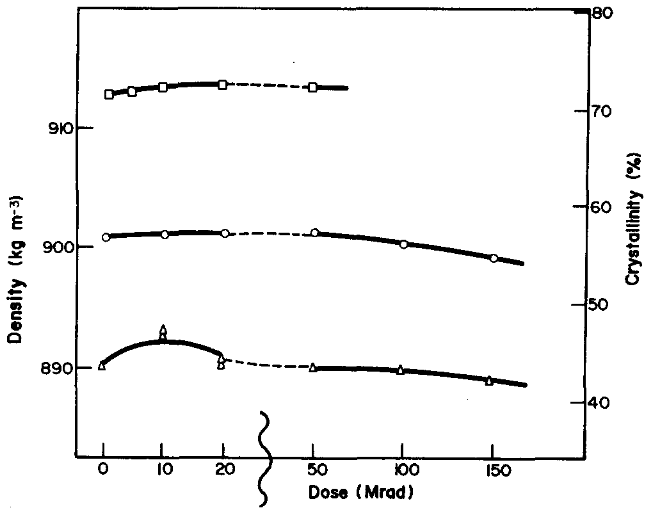

Fig. 5. Density of sample A-monoclinic (circles), B-smectic (triangles) and C-annealed (squares) as a function of dose. Note change of scale above 20 Mrad.

istics of each sample were much more affected by irradiation than the crystalline structure as indicated by X-ray diffraction or density. For samples A-monoclinic and B-smectic, the fusion curves became broader with increasing dose whilst the melting points were significantly reduced, see Fig. 8. In contrast the melting point of sample C-annealed was reduced by only about one half the corresponding reductions observed for samples A and B. In addition irradiation produced an interesting change in the shape of the melting curve of sample C. The unirradiated sample exhibited a broad, almost double peaked melting curve; after increasing doses the curve became narrower until after 10 Mrad it was a single peak. A striking feature was that the low temperature side of the peak extrapolates, after all doses, to the base line between 142 and 146°, i.e. close to the temperature at which this sample was annealed.

The crystallization thermograms for all samples were sharp single peaks, with shapes not significantly changed after sample irradiation. The crystallization temperatures and enthalpies were reduced after irradiation for all samples; they are plotted against dose in Figs 8 and 9. The decrease in the crystallization enthalpy with dose progressively increased in the order C-annealed < A-monoclinic < B-smectic. This reflects the order of increasing density of crosslinks produced by irradiation, as it has been found in other studies [4, 5, 10] that increased crystallinity leads to lower values of G (crosslink). As the density of crosslinks increases, crystallization should become more difficult and the attainable percentage crystallinity should decrease. The small increase in the enthalpy of crystallization observed for sample C-annealed after low doses, see Fig. 9, suggests that crystallization is facilitated to a small extent. This effect is probably due to the high incidence of chain scission, reported to occur at low doses [1, 3] coupled with the lower amount of crosslinking relative to the other two samples.

The effect of crosslinking on the ability of the samples to crystallize is also indicated by the decrease in the crystallization temperature as shown in Fig. 8.

There have been previous investigations of the effect of gamma irradiation on the melting characteristics of isotactic PP but none have specifically studied the effect of crystalline structure. Gee and Melia [18] studied the effects of irradiation on a sample annealed at 163° with a density of 898 kg m^{-3}. The observed melting characteristics after irradiation

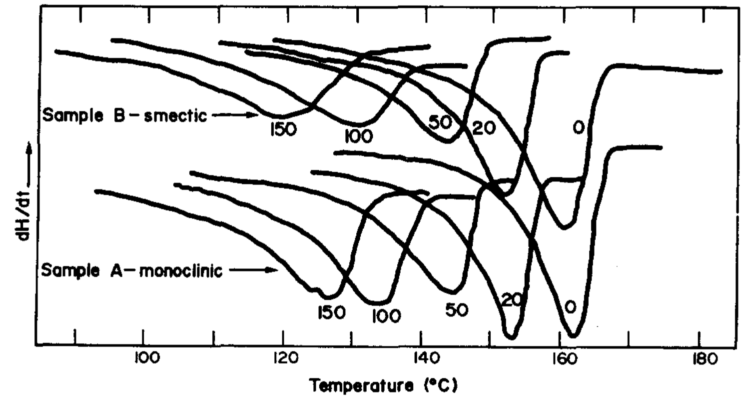

Fig. 6. DSC heating thermograms of (a) sample Z-monoclinic (b) sample B-smectic as a function of dose (indicated in Mrad) (Sample weights were not constant).

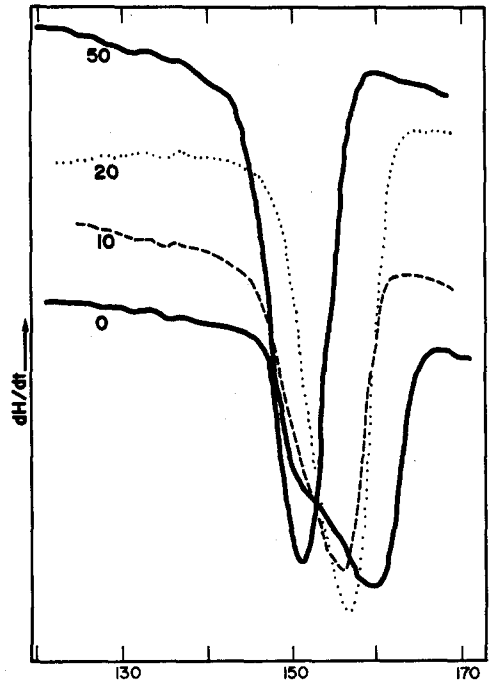

Fig. 7. DSC heating thermograms of sample C-annealed as a function of dose (indicated in Mrad) (Sample weights were not constant).

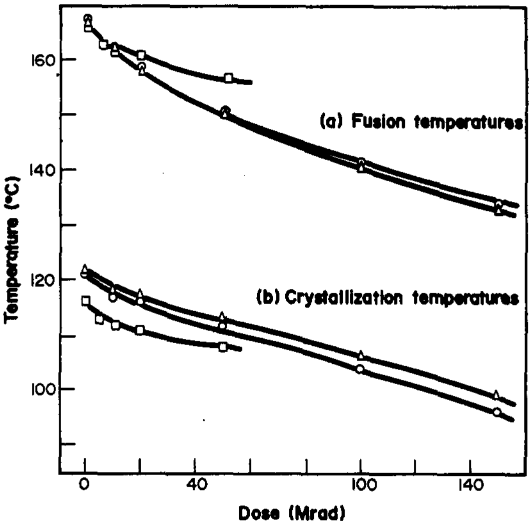

Fig. 8. (a) Melting points and (b) crystallization temperatures of sample A-monoclinic (circles), B-smectic (triangles) and C-annealed (squares) as a function of dose.

were similar to those of our sample A-monoclinic rather than sample C-annealed. This indicates that their annealing temperature was too high for successful annealing of PP; corroborative evidence is provided by the observed density (well below that of our sample C) and the results of Pae and Sauer [19] from their detailed study of the effects of thermal history on the melting characteristics of PP. Kusy and Turner [20] studied the effects of gamma irradiation on the melting characteristics of a PP fibre of unspecified crystallinity. Melting characteristics are influenced by orientation [21] and hence their results are not strictly comparable with ours. Tomlinson and Kline [22] studied the effect of much higher doses (600–1800 Mrad) of gamma irradiation on PP of 60% crystallinity with a density of 907 kg m^{-3}. They observed a large decrease in density, melting temperature and peak area after 600 Mrad showing that if their sample was annealed, us indicated by the initial density, large doses will reduce the values of these properties in contrast to the minor effects observed for sample C-annealed after 50 Mrad.

DISCUSSION

The observed decreases in the tensile breaking stress and breaking strain of all three crystalline forms of PP after small doses suggest that fairly extensive chain scission is responsible. Scission and crosslinking

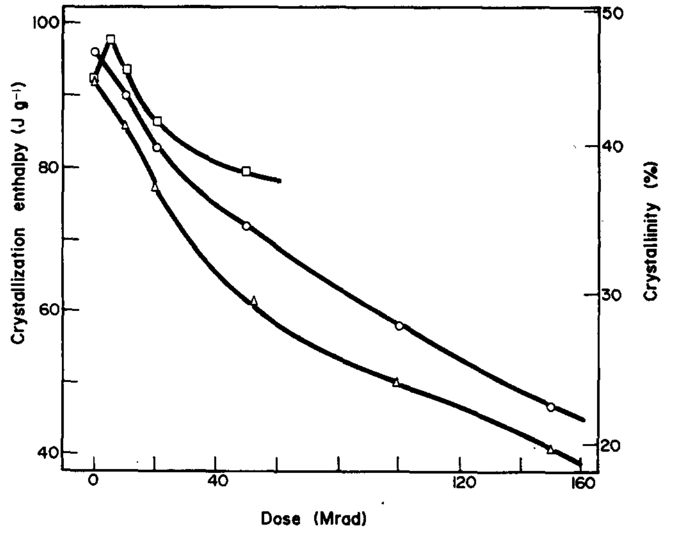

Fig. 9. Enthalpies of crystallization of sample A-monoclinic (circles), B-smectic (triangles) and C-annealed (squares) as a function of dose.

are both known to occur in isotactic PP [1–5] but there are widely differing opinions on the absolute values of $G(S)$ and $G(X)$. The literature values of the ratio $G(S)/G(X)$ vary from 0.9 to 1.4 but they have generally been measured from gel data, i.e. from measurements above the gel dose. There is evidence that scission is excessive and not linearly dependent on dose at low doses [1] especially if precautions are not taken to exclude post-irradiation reaction with atmospheric oxygen [3]. The balance of evidence therefore suggests that for moderate doses $4G(X) > G(S) > G(X)$, consequently $\overline{\mathrm{M}}_n$ will decrease, and $\overline{\mathrm{M}}_w$ will increase to $\propto$ at the gel dose, which for our sample of PP should be in the range 13–31 Mrad depending on which literature values of $G(S)$ and $G(X)$ are used in the calculation ([3, 1] respectively). It is apparent that tensile breaking stress is a function of $\overline{\mathrm{M}}_n$ on this basis. The results at high doses indicate that crosslinking (increase in $\overline{\mathrm{M}}_w$) does not compensate for the drop in $\overline{\mathrm{M}}_n$ as far as strength is concerned. Enhanced crosslinking, induced for example by irradiating PP in the presence of allyl methacrylate, does slightly increase the tensile strength of PP sheets at low doses [11].

One of the objectives of this work was to compare the effects of irradiation on three different crystalline forms of the same sample of isotactic PP. The results of the tensile tests on the unirradiated samples clearly demonstrated a direct correlation between yield stress and density as shown in Table 1, in agreement with the results of Van Schooten *et al.* [23] who found a linear correlation of yield stress with density irrespective of the molecular weight of the samples. This work also indicates that the correlation is observed with different crystalline forms. The decrease in the breaking strain of the irradiated samples became greater in the order: B-smectic, A-monoclinic, C-annealed. This could be due to two factors: (i) $\overline{\mathrm{M}}_n$ of the irradiated samples decreased in the same order (ii) the yield stress required to draw the samples, which increased in the same order, is the significant factor and the decrease in $\overline{\mathrm{M}}_n$ in the three samples was similar, (the yield stress of samples A and B were not greatly affected by irradiation, see earlier). The corresponding decrease in breaking stress due to sample irradiation became greater in the same order, suggesting that factor (i) is at least as important as factor (ii) since yield stress is unlikely to affect the ultimate breaking stress. Thus it seems clear that the magnitude of the effect of irradiation on $\overline{\mathrm{M}}_n$ in PP is in direct correlation with the density or crystallinity. Agreement with this view is provided by the work of Chappell *et al.* [10] who showed that the gel content of irradiated PP is significantly higher if the initial polymer was quenched rather than annealed, particularly after moderate doses of 20 to 100 Mrad. They suggested this difference was due to the decreased mobility of polymer radicals in the crystalline regions and their consequent inability of crosslink; their ultimate fate was scission by reaction with oxygen. In the present study the enthalpy of crystallization of the PP samples irradiated to the same dose was found to decrease in the order: sample C-annealed, sample A-monoclinic, sample B-smectic (Fig. 9). It seems unlikely that scission would have a major effect on the crystallizability of a polymer sample, hence this observation suggests that the extent of crosslinking increases in this order and that the observed greater effect on the strength of the annealed sample is due to a lesser incidence of crosslinking rather than to an enhanced incidence of scission.

Table 1. Yield stress and densities of unirradiated samples

Sample	Yield stress kg mm^{-2}	Density kg m^{-3}
B	1.97	890.1
A	2.74	900.6
C	3.53	912.8

The generalizations made above are based on a simple two-phase model of the structure of semi-crystalline polymers. An interesting feature is that the explanation of the major effect of irradiation on the mechanical properties relates to chemical effects in the crystalline and amorphous regions and yet X-ray diffraction and density studies indicate negligible change in crystallinity and overall packing. Recent theories of the structure of semi-crystalline polymers [24] have established that much of the tensile strength of the polymer and the ability of the polymer to be drawn without failure is due to the existence of tie molecules which connect one crystalline region with another. During annealing processes, since much of the amorphous material in the neighborhood of tie molecules is converted into material of a higher degree of order, the tie molecules will be made more exposed in the sense that the excluded volume concentration around them will be increased. Also, being anchored to crystalline regions will restrict their mobility in comparison to other molecules. Consequently tie molecules are likely to be relatively more prone to scission, when exposed to gamma rays, than either molecules in crystalline regions or non-tie molecules in amorphous regions. Although excessive chain scission of tie molecules is a plausible explanation of the correlation of irradiation effect on the tensile strength of PP with the crystalline structure, there is no direct proof. However a similar proposition has been put forward to explain changes in the melting characteristics of polyoxymethylene after irradiation [25]. Also Yurkevich *et al.* have suggested that a specific degradation of tie molecules may be important in explaining the loss of strength of PP fibres following irradiation [6].

On the basis of Flory's model of polymer melting, Kusy and Turner [20] suggested that the decrease in T_M observed for various irradiated polymers was due to the production of impurities (defects: chain ends, crosslinks, branch points and non-isotactic sequences) which acted as a second component in the system and reduced the total Gibbs free energy of the liquid PP and thereby decreased T_M. However this theory would not explain the difference in depression of T_M by irradiation which we have observed between samples C and samples A and B. Furthermore Gee and Melia [18] have clearly shown that the observed melting point depressions in polyethylene are many times greater than predicted by the Flory theory (considering crosslinks only). Probably the main reason why this theory is inapplicable is that for application of the theory, the melting process must occur under truly equilibrium conditions. There is no evidence that the melting of high polymers can ever occur under such conditions except perhaps for the case of single crystals. For other semi-crystalline polymers, the scan speed would have to be infinitely slow so as to enable all the crystalline regions to attain crystalline perfection (perfect annealing) prior to the ultimate melting point.

For similar reasons it is also inappropriate to attempt to explain the decrease in melting point as a function of molecular weight by application of the equation developed by Hay [26] which correlates the melting point in a homologous series with chain length for extended chain structures and fold length of the lamella for higher polymers in the folded chain structure. His equation only applies to the melting of linear oligomer/polymers under close to equilibrium conditions (well-annealed samples); it takes no account of the presence of defect structure (such as crosslinks) other than chain ends.

Since the DSC thermograms showed much greater changes after irradiation of the PP samples than the X-ray diffraction and density measurements, it appears that considerable reorganisation of structure occurs during the heating stage of the DSC scan. The effects of previous thermal treatment on the melting thermograms of PP have been comprehensively studied by Pae and Sauer [19] and by Kamide and Yamaguchi [27]. Pae and Sauer concluded that the degree of perfection of the crystallites is a function of the time and temperature of the crystallization or annealing treatment, such that a variety of melting patterns can be obtained under different DSC conditions. Furthermore they showed that the variable melting temperature exhibited by polymers is not solely a function of the fold length or due to the presence of different crystal modifications, as had been suggested earlier. Kamide and Yamaguchi clearly showed that considerable reorganization by fusion and recrystallization occurs during the heating process in the DSC scan. In isothermal crystallization experiments, they demonstrated that at least two types of crystallite are produced during normal crystallization of PP from the melt which vary mainly in the range of perfection. Crystallites produced early in the crystallization have the highest degree of perfection and hence the highest melting point; those produced later (and also those produced by subsequent annealing procedures) are of varying but lower degree of perfection and thus contribute to the initial region of the DSC melting curve. Evidence for this conclusion included the observation that melting commenced quite close to the temperature at which annealing had taken place. The melting curves which we have observed for unirradiated and irradiated sample C-annealed (Fig. 7) are in excellent agreement with this; in each case the onset of melting is quite close to the annealing temperature of 145°. This result is in marked contrast with the behaviour of the unannealed samples A-monoclinic and B-smectic which were crystallized at much lower temperatures and thus underwent reorganization in the lower temperature range of the DSC run.

In all three samples the melting point and consequently the degree of perfection attainable by the initially formed crystallites, according to Kamide and Yamaguchi's ideas, is reduced by irradiation but significantly more for samples A and B. These changes must result from the chemical effects caused by irradiation but the crystal structure is not affected until the sample is heated towards the melting range. These observations are compatible with the model suggested by Pae and Sauer, i.e. that crystalline regions have varying degrees of perfection, and strongly support the theory of Kamide and Yamaguchi that significant reorganization of the structure occurs during heating in the DSC scan. One may therefore conclude that the actual melting point of the polymer crystallites in a sample is only slightly above the temperature at which they were produced by crystallization or annealing. When heated, the crystallites undergo continuous reorganization until they reach a maximum degree of perfection, controlled by the presence of defects (chain ends, crosslinks, branch points, atactic sequences etc.), molecular weight and to a certain extent kinetic factors such as polymer mobility and heating rate. It is this developed or reorganized structure which determines the observed melting behaviour of the sample durring the DSC scan. Irradiation introduces a range of defects into the structure such that the degree of perfection attainable in the crystalline regions during the heating process is reduced, relative to the unirradiated sample, and the ultimate melting point is decreased.

One surprising feature of the present investigation is the close similarity, with respect to the effect of irradiation on melting behaviour and tensile properties, between sample A-monoclinic and sample B-smectic. The results suggest a close similarity in crystalline structure, in agreement with the known ease of conversion of the smectic to the monoclinic form at temperatures as low as 65° [28]. After irradiation one might expect this transformation to become increasingly more difficult due to the presence of crosslinks etc. This may be the cause of the observed broadening of the melting peak of sample B relative to that of sample A, particularly after 150 Mrad, see Fig. 6.

CONCLUSIONS

Gamma irradiation up to 150 Mrad caused no major disruption of the crystalline structure of isotactic PP measured by density and X-ray diffraction but there was a significant decrease in the tensile break stress and strain and a significant change in the melting characteristics. A distinct difference was observed between the behaviour of an annealed monoclinic sample towards irradiation and the behaviour of unannealed monoclinic and unannealed smectic samples. The latter two crystalline forms were similar in behaviour. This has been attributed to the variation of chemical effects of irradiation, including scission and crosslinking, over different structural regions. It is suggested that the poor resistance of the annealed sample toward irradiation may be due to the enhanced radiation sensitivity of tie molecules.

Acknowledgements—We are grateful to Mr W. G. Wright for preparation of the polymer samples, the Australian Atomic Energy Commission and Australian Institute for Nuclear Science and Engineering for the provision of irradiation facilities, RAPRA (Shawbury U.K.) for molecular weight characterisation, Mrs C. Scrimgeour (University of Dundee) for X-ray diffraction work, Mr J. Carroll (University of Dundee) for technical assistance and the Australian Research Grants Commission for financial support.

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