conference papers

Structure and morphology of highly oriented radiation crosslinked polyethylene fibres

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(Received 20 August 1990; accepted 10 October 1990)

Gel fraction, crystal size, melting temperatures and dynamic mechanical properties in tension have been measured for electron-beam irradiated high modulus polyethylene fibres. The fibres were irradiated either in nitrogen or acetylene gas, and post-treated by soaking in one of these atmospheres at 293 and 353 K. Wide angle X-ray measurements indicate that the crystal size remains unaltered by the irradiation. The results from d.s.c. and dynamic mechanical α-relaxation behaviour indicate that the presence of acetylene, either during or post-irradiation, increases the ratio between crosslinking and chain scission reactions.

(Keywords: crosslinking; polyethylene fibre; d.s.c.; X-ray; dynamic mechanical properties)

INTRODUCTION

In recent years, much attention has been devoted to the subject of irradiated polyethylene. A considerable body of information exists concerning the effect on the mechanical properties[1–4] of the oriented materials, for example their creep and yield behaviour. In addition, studies have been made of the rubber elasticity of the crosslinked polyethylenes above the melt[5,6]. In several publications from this group, attention has also been paid to the use of acetylene gas to enhance the crosslinking[1,3,6]. From careful examination of mechanical properties, the indication is that irradiation in acetylene also produces a network containing fewer chain scission points compared to a network of similar crosslink density produced by irradiation in an inert atmosphere. The purpose of the present investigation is to acquire more direct structural information concerning the effect of irradiation, using the techniques of differential scanning calorimetry (d.s.c.), X-ray diffraction and dynamic mechanical analysis. An additional, new feature of the present sample preparation is the exposure of the fibres, after irradiation, to different atmospheres and temperatures, a treatment which sheds some light on the reactivity of the longer lived free radicals within the polymer. The results, especially from the d.s.c. work, are entirely consistent with previous work, indicating the beneficial effects of acetylene on the network structure.

EXPERIMENTAL

Sample preparation

The high modulus melt spun polyethylene fibre used in these experiments (supplied by SNIA Fibre, Italy) was drawn at 120°C to a draw ratio of around 30:1. The weight average molecular weight, M_w, of the polyethylene was approximately $130\ \mathrm{kg\ mol^{-1}}$. Some experiments were also performed on fibres produced from Alathon 7050 (supplied by Celanese Fibres Co.) details of which can be found in a previous publication[1].

For the irradiation experiments on the SNIA fibre, approximately 20 m of fibre was wound on a 25 mm diameter glass tube which was then placed in a 45 mm diameter vacuum tube, fitted with a glass joint for inserting the sample and a glass tap for evacuating the tube and introducing gas. Before irradiation, the tube was evacuated to less than 10 Pa and then filled with dry, oxygen-free nitrogen, or acetylene, to atmospheric pressure.

The samples at ambient temperature were passed at constant speed through an electron beam produced by a Dynamitron 4.5 MeV electron beam accelerator. The dose could be varied from 0.25 Mrad to 5 Mrad by adjusting the sample speed and the machine current, the dose rate varying from 0.5 to $2.5\ \mathrm{Mrad\ s^{-1}}$ over this range. To obtain a higher dose, multiple passes were used. The sample tube was rotated about its longitudinal axis during irradiation to ensure uniform treatment. This gave a slight reduction from the direct dose and was allowed for in the red perspex dosimeter calibration.

After irradiation, the fibres, still in the vacuum tube, were subjected to a post-treatment involving a 1 h soak in nitrogen or acetylene, at 293 and 353 K. For convenience, the following abbreviations will be used in the text:

Irradiation atmosphere	*Post-treatment atmosphere*	*Abbreviation*
Nitrogen	Nitrogen	N–N
Nitrogen	Acetylene	N–A
Acetylene	Acetylene	A–A

Gel fraction measurements

The gel content (weight fraction insoluble material) of each sample was determined by extraction in refluxing decalin containing an antioxidant at 465 K, using standard procedures[1]. A few measurements were repeated after several months and, within experimental error, gave the same result. This indicates complete reaction of all free radicals within the fibres at the time of testing.

Paper presented at Speciality Polymers '90, 8–10 August 1990, The Johns Hopkins University, Baltimore, MD, USA

0032–3861/91/101732–05

Crystal size measurements

Crystallite thicknesses and widths were determined by measurement of the broadening observed in the wide angle X-ray scattering[7]. The equatorial 200 and meridional 002 reflections were scanned on a Siemens X-ray diffractometer under high resolution conditions, using a scintillation counter to detect the scattered radiation. Crystal dimensions were determined from the full peak width at half height. The observed profiles were corrected for instrumental and Kα doublet broadening by using standard samples having effectively infinite crystals.

Differential scanning calorimetry

The melting endotherms of approximately 2 mg samples of the fibres were recorded on a Perkin-Elmer DSC 2, from 360 to 430 K, at 5 K min^{-1}. The melting temperatures and enthalpies of fusion were calibrated using high purity indium before and after each scan, leading to an uncertainty of ± 0.2 K in the temperature.

Dynamic mechanical measurements

Dynamic mechanical measurements were made in tension, using a home-built ensemble as described by Troughton *et al.*[8]. Sample lengths were approximately 50 mm and measurements were made isothermally at a frequency of 10 Hz. The temperature was maintained to an accuracy of ± 0.25 K by passing dry nitrogen gas through the sample enclosure. Each sample was scanned from 120 K to the highest possible temperature, which varied from 400 to 420 K, depending on the gel fraction.

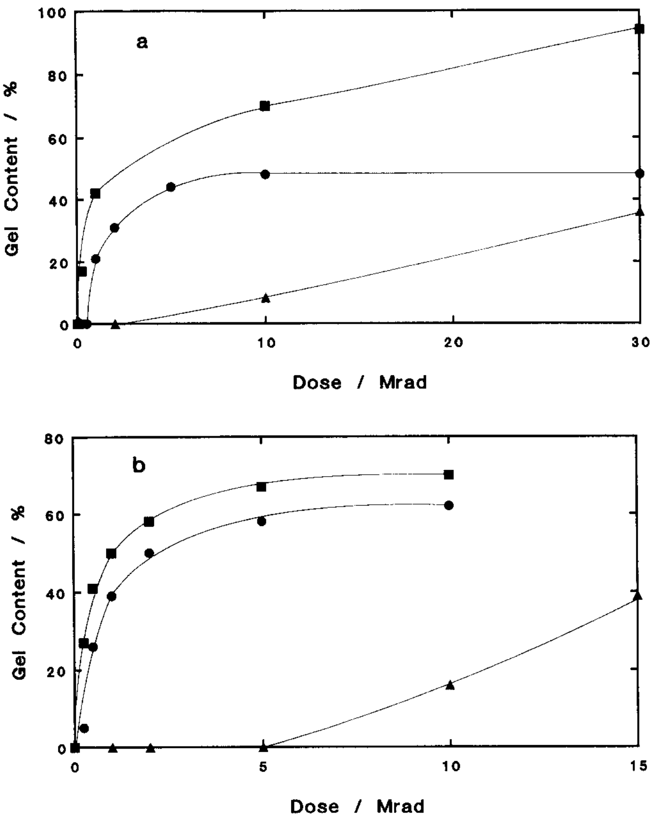

Figure 1 Gel content *versus* dose for irradiated SNIA fibres post-treated at (a) 293 K and (b) 353 K. ▲, N–N; ●, N–A; ■, A–A

RESULTS AND DISCUSSION

Gel fraction measurements

Figure 1 shows how the gel fraction varies with irradiation dose under the different conditions and at the two post-treatment temperatures. The primary effect of acetylene in enhancing the crosslinking is readily apparent. Introducing acetylene at the post-irradiation stage leads to further crosslinking reactions of the radicals formed during irradiation and therefore an increase in gel content. The maximum gel fraction is obtained by a combination of irradiating and post-treating in the acetylene atmosphere. The effect of temperature in the post-treatment is marginal for the A–A samples, but the increase from 293 to 353 K does enhance the gel fraction significantly in both the experiments involving irradiation in the inert atmosphere. For example, for the N–A treatment at 293 K, the gel fraction appears to level off around 48%, compared to about 60% at 353 K. Similarly, for the N–N treatment, a gel fraction of 40% is obtained at 15 Mrad, after post-treating at 353 K, compared to less than 20% for the same dose at 293 K.

Crystal size measurements and fibre morphology

Analysis of the meridional 002 and equatorial 200 reflections indicates a crystal length of 39.0 ± 0.5 nm and a lateral dimension of 18.0 ± 0.2 nm, independent of radiation dose and conditions. The significance of the constant crystal size will be addressed in more detail later, in light of the melting and dynamic mechanical behaviour, but the absolute magnitude of the crystal length provides a useful preliminary indication of the fibre morphology. The value of 39.0 nm is significantly less than the crystal lengths of polyethylenes of similar draw ratio and draw temperature, studied by Clements and Ward[9], which indicate a value of about 50 nm for a 30:1 sample. These authors also measured the long period, and found it to be a function of draw temperature only, drawing at 115°C giving a long period of about 26 nm. Thus the indication is that the present samples have a considerably different morphology to conventional melt spun and drawn polyethylenes. Consideration of the morphological model proposed by Gibson *et al.*[10] leads to the conclusion that the fibres have very few intercrystalline bridges. We will assume therefore that the morphology of these fibres is predominantly lamellar rather than fibrillar, and hence the discussion of the possible structural modifications of the irradiated polymer will proceed on this basis.

Melting behaviour

Figure 2 shows typical melting endotherms for two sets of irradiated fibres (N–N and A–A). In general, the melting temperature decreases with irradiation dose and the endotherm tends to broaden, suggesting an increase in the crystal size distribution, or changes in the entropy of fusion, or a combination of both effects. Although the two sets of results cover the same range of dose, the acetylene treated samples, in accordance with the previous discussion, encompass a much greater range of gel fractions. It is apparent that the high gel fractions of 70 and 94%, corresponding to doses of 10 and 30 Mrad in acetylene (*Figure 2b*), have a pronounced effect on the melting behaviour. The enthalpy, however, is little affected by the irradiation, except at highest doses where it decreases by approximately 10%.

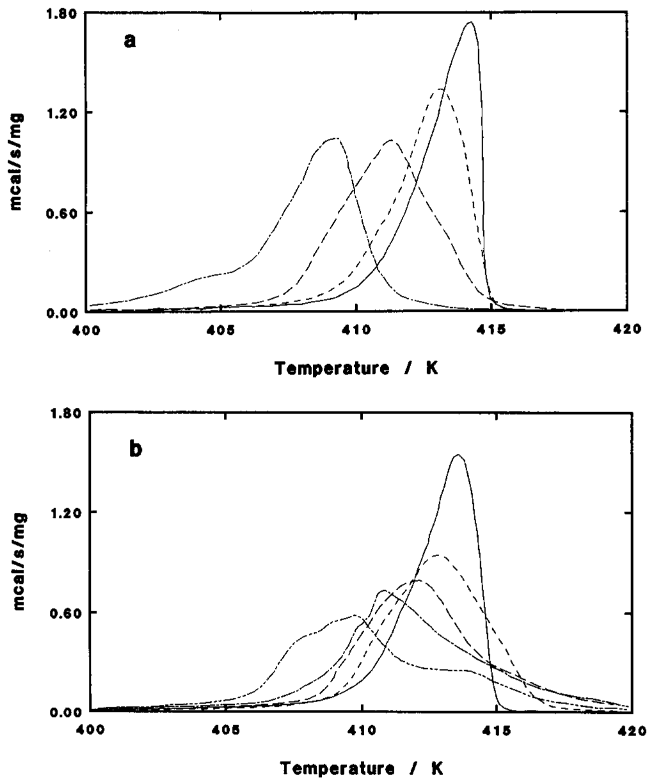

Figure 2 Melting endotherms for irradiated SNIA fibres. (a) N–N, (b) A–A. In (a) irradiation doses are 0, 2, 10 and 30 Mrad and in (b) 0, 0.25, 1, 10 and 30 Mrad: dose increases from right to left in each case

A more detailed analysis of the melting behaviour of these samples can provide significant information on the location of the crosslinks and chain scission sites, and on the role of acetylene in the structural modification of the polymer. In terms of the current state of knowledge concerning the structure of irradiated polyethylene, we would expect crosslinks to be confined to the amorphous phase and the fold surfaces of the lamellae. Chain scission reactions, however, can occur at all sites within the morphology. The manner in which these two radiation-induced modifications affect the melting temperature can then be qualitatively predicted as described by Zoepfl *et al.*[11]. First, there is the consideration of crosslinks or chain scission reactions in the amorphous phase, which is addressed in the following expression:

$$T_m = \frac{\Delta H^0}{\Delta S} \qquad (1)$$

where T_m is the melting temperature of the irradiated polymer, ΔH^0 is the enthalpy of fusion of the perfect crystal and ΔS is the entropy change on melting. Crosslinks in the amorphous phase will provide a configurational constraint, thereby decreasing the melt entropy. Since the entropy of the crystal will be less than that of the melt, the effect of crosslinking will be to decrease ΔS, and therefore T_m will increase with irradiation dose. Conversely, chain scission reactions in the amorphous phase will have precisely the opposite effect on the melt entropy leading to a decrease in T_m. However, the formation of a gel on irradiation is evidence that crosslinking dominates, and the net effect of this entropic factor alone will be to raise the melting temperature; to what extent will depend on the relative balance between crosslinking and scission.

Superimposed on this, however, is the effect of crosslinks on the crystal fold surfaces, and chain scission within the crystal lattice. The way in which the melting temperature might be changed due to these events is given by the following equation[12]:

$$T_m = T_m^0 \left[1 - \frac{2}{\Delta H^0}\left(\frac{\sigma_f}{L} + \frac{2\sigma_s}{D}\right)\right] \qquad (2)$$

where T_m^0 is the equilibrium melting temperature, σ_f is the crystal fold surface free energy, σ_s is the crystal side surface free energy per unit area, L is the lamellar thickness and D is the width. Crosslinking at the crystal edges will increase their free energy, thereby decreasing T_m. Chain scission within the crystal might be expected to have two possible effects. Firstly a decrease in crystal size, L, which would decrease T_m. Secondly there is the creation of chain ends within the lattice, which represents a defect formation, which will also decrease T_m. *Figure 3* shows a plot of the melting temperature as a function of the experimentally determined gel fraction, for all the different treatments. The rationale behind plotting gel fraction rather than dose as the abscissa is that it allows comparison between samples having the same crosslink density. The general trend is a decrease in T_m. However, it is quite clear that at any particular gel fraction, T_m is higher for samples post-treated in acetylene (N–A), and highest for samples irradiated and post-treated in acetylene (A–A). Comparing samples of the same gel fraction suggests, to a good approximation, equivalent numbers of crosslinks on fold surfaces, and equivalent crosslink density in the amorphous phase. Furthermore, the results from the X-ray diffraction studies indicate that both the lamellar thickness and width are unchanged by the irradiation treatment and hence the parameters L

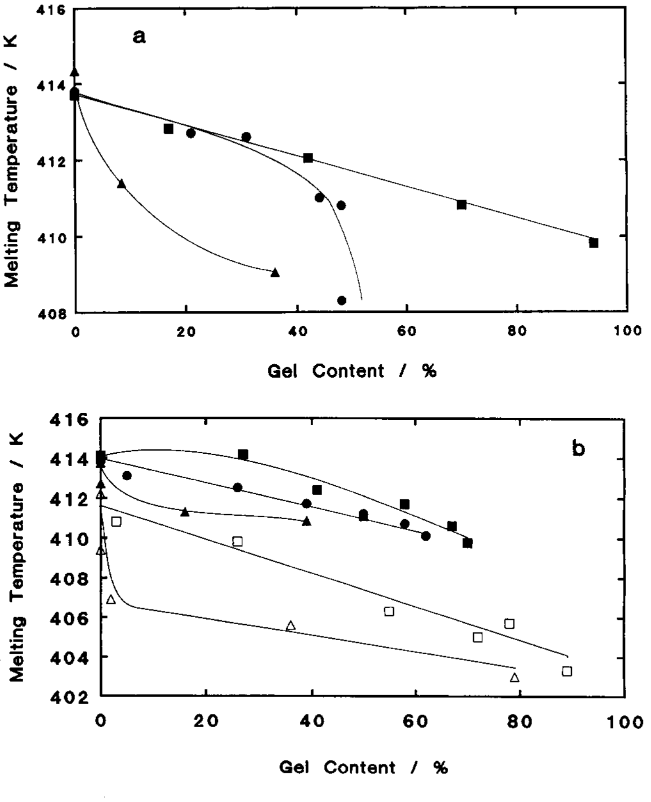

Figure 3 Melting temperature *versus* gel content for irradiated fibres post-treated at (a) 293 K and (b) 353 K. ▲, SNIA N–N; ●, SNIA N–A; ■, SNIA A–A; △, Alathon N–N; □, Alathon A–A

and D are constant in equation (2). The remaining explanation for the discrepancy between melting temperatures is the relative balance between crosslinking and chain scission. Since theory predicts that the effect of scission, either in the amorphous or in the crystal phase, is to decrease T_m, it would appear that the presence of acetylene during the irradiation, and to a lesser extent during the post-treatment, significantly shifts the balance in favour of crosslinking.

Effect of molecular weight

Figure 3b shows the plot of T_m *versus* gel fraction for a fibre prepared from a lower molecular weight (61 kg mol^{-1}) polyethylene, Alathon 7050, which is the fibre used in the previous study of mechanical properties[1]. Here it is seen that the same trend occurs with regard to acetylene and inert atmosphere treatments, but the melting temperatures of the Alathon fibres are always lower than for the SNIA fibres. This is consistent with the preceding discussion with regard to the effect of chain scission reactions on the melting temperature. Since chain scission and crosslinking reactions both proceed at a rate inversely proportional to molecular weight, it follows that a low molecular weight sample will have more chain scissions than a high molecular weight sample, for the same crosslink density (or gel fraction). The melting temperature of the irradiated low molecular weight polymer would therefore be expected to be lower.

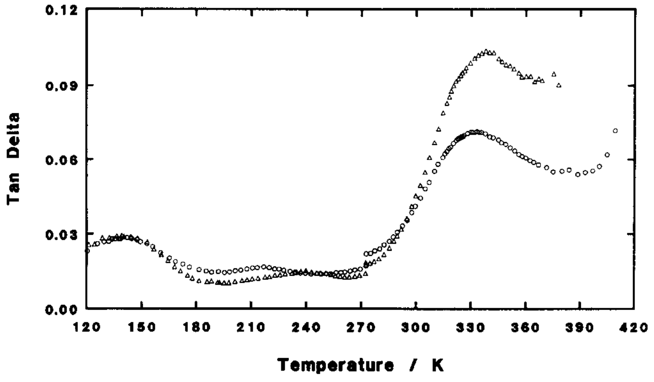

Figure 4 Tan δ *versus* temperature for SNIA fibres. △, Untreated; ○, 30 Mrad A–A. The frequency was 10 Hz

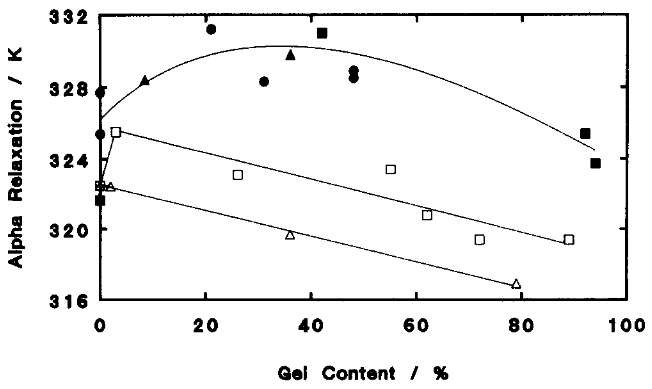

Figure 5 Temperature of the α-relaxation *versus* gel content for irradiated fibres. ▲, SNIA N–N; ●, SNIA N–A; ■, SNIA A–A; △, Alathon N–N; □, Alathon A–A

Dynamic mechanical analysis

Figure 4 shows the tan δ *versus* temperature curves obtained for two extreme samples: the untreated fibre and a fibre after 30 Mrad in acetylene. The α, β and γ relaxations are clearly seen. It is clear that the crosslinking leads to several significant changes in the dynamic mechanical behaviour. There is a shift in the temperature of the β-relaxation, although this is not systematic and in some samples this relaxation is absent. Of more interest with regard to the present work is the change in temperature and intensity of the α-relaxation. *Figure 5* shows the temperature of the α-relaxation (T_α) *versus* the gel fraction, for both molecular weight fibres. For SNIA fibre, T_α increases to a maximum around 40% gel, and then decreases. There appears to be no distinction between different treatments. The Alathon fibres irradiated in acetylene show an initial sharp increase in T_α for low gel fractions followed by a decrease, and the fibres irradiated in nitrogen show T_α decreasing monotonically over the whole range. Furthermore, for Alathon fibres there is a distinction between acetylene and nitrogen treatments in that T_α is consistently higher for the fibres irradiated in acetylene. For an explanation of these results, we must consider the structural origins of the α-relaxation process. Although there is still much discussion[13,14] concerning this, we can recognize two possible origins with regard to the suggested morphology of the fibre. One process is considered to relate to a reorientation of the chain folds at the lamellar surface, and another process is due to a rotation and translational motion of a chain along its axis through the lattice[15]. It is probable that the observed relaxation is a superposition of both these processes. It is the second process that can be used to interpret the variation in the temperature of the tan δ maximum with crosslinking based upon the site model for mechanical relaxations[15]. In this model, the location of the relaxation is given by the following expression:

$$T = T_0 \frac{(a+n)}{(b+n)} \tag{3}$$

where T_0 is equal to the ratio of the enthalpy to the entropy of a chain segment, a contains terms relating to the enthalpies and b, the entropies of chain segments and end groups and the relaxation time (for a fuller description see reference 15) and n is the number of chain segments involved in the relaxation. The essential point is that the temperature of the relaxation increases to a limiting value T_0 as n approaches infinity. With regard to the present discussion, assuming good interlamellar contact, crosslinking between adjacent crystal surfaces might be expected to increase n and thereby provide the mechanical continuity between lamellae that is not provided by inter-crystalline bridges. Against this, chain scission within the lattice will shorten the chain length, thereby reducing n, and hence T_α will decrease. It is suggested that a combination of these effects produces the maximum in the plot. The fact that the Alathon fibres show a maximum only at very low dose, or not at all, can be atrributed to the lower molecular weight. Following the same argument as for the melting behaviour, it will require a relatively high dose to achieve a moderate gel fraction for the Alathon fibre, by which time the detrimental effects of chain scission will begin to dominate. The influence of molecular weight is also apparent in that T_α for the Alathon fibres is always less than for the SNIA fibres. The distinction between nitrogen and acetylene treatments for the Alathon fibre

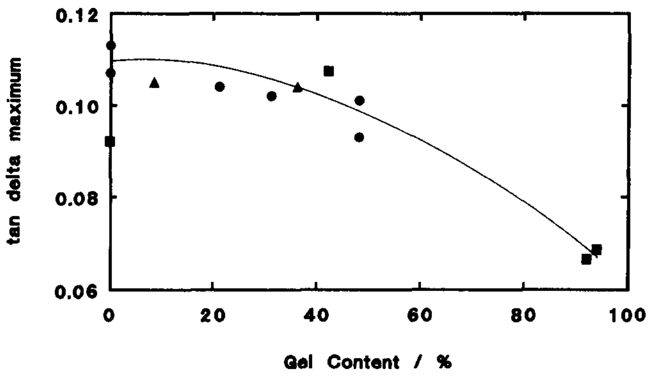

Figure 6 α-Relaxation strength (tan δ maximum) *versus* gel content for irradiated SNIA fibres. ▲, N–N; ●, N–A; ■, A–A

has exactly the same explanation as for the melting temperatures, with regard to the balance between crosslinking and chain scission. The results from the SNIA fibres do not show any distinction between treatments, which is probably due to the paucity of data points, especially in the more revealing region on the high gel side of the maximum.

In *Figure 6*, the relaxation strength (maximum value of tan δ) is plotted against gel fraction, showing a monotonic decrease. This result is perhaps not too surprising, since as crosslinking increases, the motion of chain folds and the translational motion of a chain through a crystal will be prevented, and progressively fewer sites will be able to participate in the relaxation process.

CONCLUSIONS

The results of the present structure-based investigation of irradiated high modulus polyethylene indicate that the presence of acetylene during irradiation increases the ratio of crosslinking to chain scission reactions. In this respect, the present work is complementary to the companion studies of mechanical properties[1,6]. A new observation, however, is the persistence of this feature, albeit to a lesser extent, in fibres subjected to a post-irradiation soak in acetylene. This raises interesting questions concerning the lifetime and reaction chemistry of the free radicals, and the role of gaseous diffusion, which are to be pursued. Finally, we note that although the average crystal dimensions appear to be unaltered by irradiation, the crystal size distribution, as indicated by the melting endotherms, appears to increase with dose. This may point to some large scale lamellar reorganization of the morphology prior to melting.

ACKNOWLEDGEMENT

We wish to thank Mr D. W. Woods for the irradiation and gel fraction experiments.

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