# Effect of draw ratio on the structure and properties of electron beam crosslinked polyethylene

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*(Received 18 January 1993; revised 26 July 1993)*

Polyethylene fibres of various draw ratio up to 30:1 have been crosslinked by electron beam irradiation in acetylene. The gel fraction increased with dose and showed a significant increase with draw ratio above 10:1. The fibres were examined by differential scanning calorimetry, dynamic mechanical analysis and X-ray crystallography. Fibres of higher draw ratio showed a sharper decrease in melting temperature with dose, ascribed to crosslinking at fold surfaces and greater chain scission, due to higher crystallinity. The main finding was that crosslinking increases the $-50°C$ dynamic storage modulus at intermediate draw ratio (10:1), but not at low or high draw ratio. The results were interpreted via the random intercrystalline bridge model, which suggests that at 10:1, there is good interlamellar contact but very few intercrystalline bridges. The crosslinking can therefore link together adjacent lamellae at fold surfaces and hence provide crystalline continuity, increasing the modulus.

**(Keywords: polyethylene; crosslinking; draw ratio)**

## INTRODUCTION

We have recently reported on the effect of electron beam irradiation on the structure of highly oriented (30:1) polyethylene fibres[1,2]. Attention was focused mainly on the melting behaviour (d.s.c.), dynamic mechanical properties[1] and creep[2]. A main conclusion was that optimum crosslinking efficiency, with minimum chain scission, was achieved by performing the irradiation, and a post-irradiation annealing treatment, in an acetylene atmosphere. The structural modification of the polymer by irradiation, and hence the effect on the mechanical properties, is strongly dependent upon the morphology[3]. Recently, Sangster and Barry[4] reported on the irradiation, in acetylene, of die drawn polyethylene rods of draw ratio 14:1. An interesting result of their work was the increase (by up to 100%) of the tensile modulus with irradiation, and it is the aim of the present investigation to examine the possible origins of this effect by studying irradiated fibres of different draw ratio, as a means of controlling morphology, from the isotropic fibre up to 30:1. It is shown that the gel fraction, and the sensitivity of the melting temperature to irradiation are both influenced by the degree of orientation. The effect of crosslinking on the tensile modulus of the fibres is discussed in terms of the extent (or otherwise) of crystalline continuity and the efficiency of interlamellar contact, concerning which a quantitative estimation is made from small- and wide-angle X-ray (SAXS and WAXS, respectively) studies.

## EXPERIMENTAL

### *Sample preparation*

The 30:1 and isotropic polyethylene fibre were supplied by Celanese Fibres Co., New Jersey. The polymer grade, Alathon 7050, has a weight-average molecular weight of $61\,kg\,mol^{-1}$. The intermediate draw ratio fibres were produced at Leeds University using the same continuous drawing process[5] and drawing temperature (120°C) as for the supplied drawn Celanese yarn.

The fibres were irradiated with electron beam in an acetylene atmosphere at 80°C using procedures described previously[2], at several doses up to 4.8 Mrad. After irradiation, the samples were annealed in acetylene at 110°C for 2 h to ensure complete reaction of all free radicals. The gel fraction (weight fraction of insoluble material) was determined by extraction in refluxing decalin containing antioxidant, at 192°C, using standard procedures[2].

### *Differential scanning calorimetry*

The melting temperatures and crystallinities of the samples were measured on a Perkin–Elmer DSC-7 instrument, at a scan rate of $10°C\,min^{-1}$. The temperature and heat flow were calibrated using high purity indium and zinc samples, and the crystallinities of the fibres were calculated using a value of $293\,J\,g^{-1}$ for the theoretical 100% crystalline polyethylene[6]. The melting temperatures are considered to have an accuracy of $\pm 0.5°C$.

### *Dynamic mechanical analysis*

Measurements were made in tension, at a frequency of 1 Hz, using home-built apparatus described previously[7].

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0032-3861/94/10/2044–05

Sample lengths were ~50 mm and of sufficiently high aspect ratio to minimize end effects. The temperature has an accuracy of ±0.25°C and the dynamic storage modulus ±1%.

*X-ray studies*

The WAXS measurements were performed on a Siemens K-4 diffractometer employing a scintillation counter with a pulse height discriminator of 5 V. The data were recorded using a stepper motor counting for 200 s every 0.02°, over a range of seven degrees centred on the (002) reflection (74.5°). As a reference for machine broadening calculations the copper (004) reflection (74°) was studied under the same experimental conditions. The crystalline coherence size $D_{(002)}$ is calculated from:

$$D_{(002)} = K\lambda/(\delta\beta \cos\theta) \quad (1)$$

where $\delta\beta$ is the integral breadth of the (002) reflection, $\lambda$ the wavelength and $K$ a parameter assumed to be equal to 1. The contribution from instrumental broadening was removed by a deconvolution routine using the Danielson–Lanezos fast Fourier transformation[8].

The SAXS measurements were performed using a Frank camera with a sample to film distance ($D$) of 18 cm. The required exposure times varied considerably with the sample, and were 6, 24 and 72 h for the 10, 20 and 30:1 fibres, respectively. The long period $L$, was calculated from the meridional separation of the two-point pattern ($d$) via the following expression, with the condition that $D \gg d$:

$$L = \lambda(2D/d) \quad (2)$$

## RESULTS AND DISCUSSION

*Gel fraction*

*Figure 1* shows the plot of gel fraction *versus* irradiation dose for the different draw ratio samples. There are a number of features relating to the morphology of polyethylene that affect its susceptibility to irradiation, and with regard to the present samples, two important effects can be identified. Since the crosslinks are recognized to be confined to the amorphous phase[2], or the crystal fold surfaces, it follows that samples of lower crystallinity (low draw ratio) have higher gel fractions. However, the most effective crosslinks for high gel formation are those that link together adjacent lamellae[3], so samples where there is good interlamellar contact will have high gel, and this would tend to be the case for the fibres of high draw ratio, and higher crystallinity (*Table 1*). *Figure 1* shows that the gel fraction increases with dose for all samples up to a value of 60–80% for the highest dose of 4.8 Mrad. The effect of draw ratio is more pronounced at intermediate doses, and this is shown to better effect in *Figure 2*. There is a distinct jump in the gel fraction above a draw ratio of 10:1, for doses up to 3.3 Mrad. This suggests that, above this draw ratio there is very good interlamellar contact which counteracts the effect of the higher crystallinity. However, at high draw ratio, where the crystallinity is high and the crystal size is large, there are fewer sites available for crosslinking, and so the effect of chain scission is more apparent. This is seen in *Figure 1* where, for the 30:1 sample, the gel fraction is starting to level off at high dose, and in *Figure 2* the effect of draw ratio at 4.8 Mrad is not as pronounced as at the lower doses.

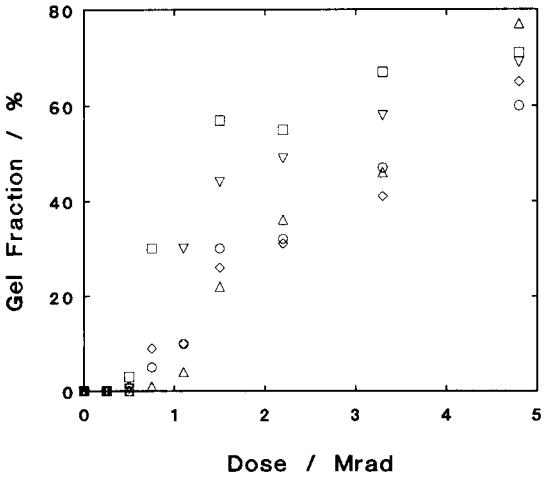


**Figure 1** Gel fraction *versus* dose for fibres at the following draw ratios: (Δ) 1:1; (○) 5:1; (◇) 10:1; (▽) 20:1; (□) 30:1

**Table 1** Crystallinity and moduli of unirradiated and irradiated fibres

| Draw ratio, $\lambda$ | $\chi$(%)[a] | $E'$ at −50°C (GPa) at 0 Mrad | 2.2 Mrad | 4.8 Mrad |
|---|---|---|---|---|
| 1 | 72.7 | 2.60 | – | 2.82 |
| 5 | 73.4 | 6.41 | 6.42 | 6.78 |
| 10 | 75.1 | 11.4 | 11.5 | 15.5 |
| 20 | 80.2 | 38.7 | 37.9 | 37.7 |
| 30 | 85.3 | 69.4 | – | 71.5 |

[a] Crystallinity of unirradiated fibre, from d.s.c.

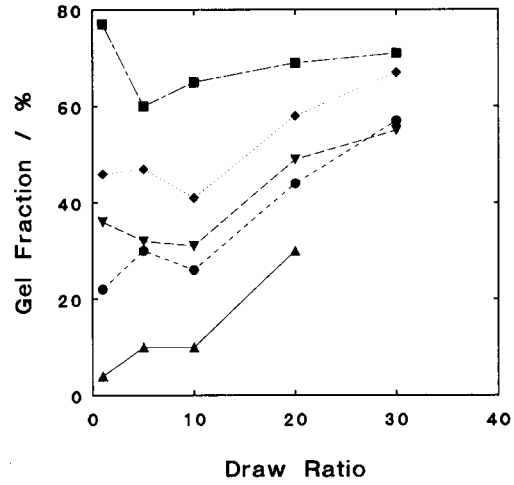


**Figure 2** Gel fraction *versus* draw ratio for fibres at the following doses: (▲) 1.1 Mrad; (●) 1.5 Mrad; (▼) 2.2 Mrad; (◆) 3.3 Mrad; (■) 4.8 Mrad

*Differential scanning calorimetry*

*Figures 3* and *4* show plots of fibre melting temperature ($T_m$) *versus* irradiation dose and gel fraction, respectively. *Table 1* also gives values for the crystallinities of the unirradiated fibres, calculated from the heat of fusion. Irradiation does not significantly affect the heat of fusion, for the doses studied. In a previous publication[1], we discussed in some detail our interpretation of the melting behaviour. We suggested that crosslinking in the amorphous phase would tend to raise $T_m$ by virtue of a decrease in the melt entropy. However, it is also the case that crosslinking in the amorphous phase and not in the

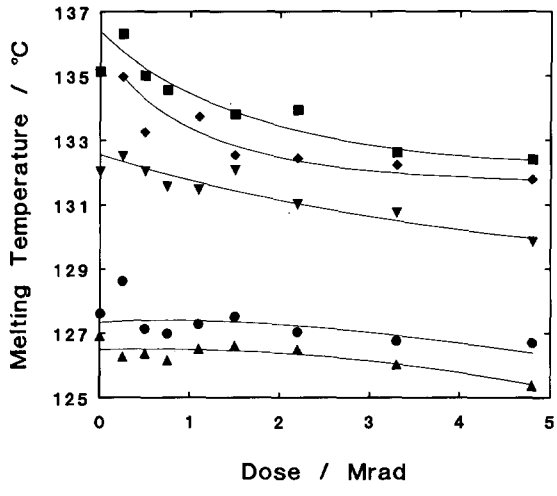


**Figure 3** Melting temperature *versus* dose for fibres at the following draw ratios: (▲) 1:1; (●) 5:1; (▼) 10:1; (◆) 20:1; (■) 30:1

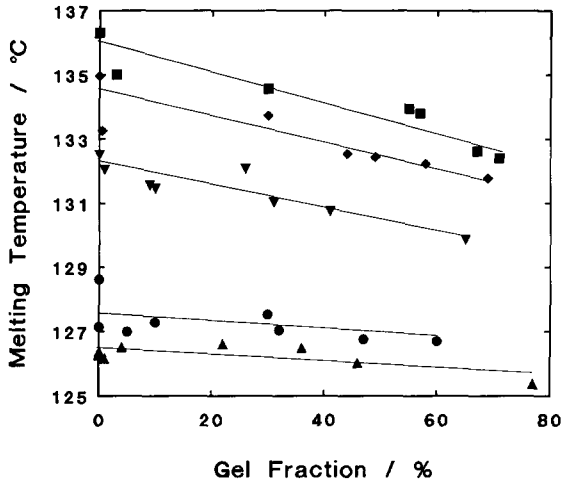


**Figure 4** Melting temperature *versus* gel fraction for fibres at the following draw ratios: (▲) 1:1; (●) 5:1; (▼) 10:1; (◆) 20:1; (■) 30:1

crystalline phase results in an increase in the entropy of fusion (compared to the uncrosslinked polymer), which results in a depression of the $T_m$[9]. Crosslinks at the crystal fold surfaces raise their free energy and lead to a decrease in $T_m$. Chain scission in the crystal or amorphous phase also decreases $T_m$. In *Figures 3* and *4* there are clearly two sets of samples, one set being the isotropic and 5:1 fibre which have low $T_m$s, little affected by dose, and the other set the remaining high draw ratio fibres which have higher $T_m$s, that decrease significantly with dose. The increase in $T_m$ with draw ratio, which is preserved at all doses, can be understood simply in terms of the increase in lamellar thickness. The sensitivity of the $T_m$ to irradiation is related to the morphology of the fibre, the location of the crosslinks and the extent of chain scission. It can be seen for the low draw ratio (1:1 and 5:1) fibres that at low dose the $T_m$ increases, having a maximum around 1.5 Mrad, presumably due to predominant crosslinking in the amorphous phase of these relatively low crystalline samples. This effect then presumably compensates for the events detailed above that suppress the $T_m$, producing the rather flat plot. At higher draw ratio, the fraction of amorphous phase will be less (*Table 1*) and so there is a greater probability of crosslinking at fold surfaces and of chain scission, leading to a more substantial decrease in $T_m$. *Figure 4* is perhaps more instructive in this respect, as it shows the plot of $T_m$ *versus* gel fraction (which is proportional to the crosslink density). Therefore the greater melting point depression for the higher draw ratio samples in this plot must be attributable to effects other than those arising just from crosslinking in the amorphous phase.

*Dynamic mechanical analysis*

Measurements were made over the range −125 to +125°C and hence cover the tail end of the gamma relaxation up to the end of the alpha relaxation. A typical plot for the 10:1 samples irradiated with doses of 0, 2.2 and 4.8 Mrad is shown in *Figure 5*. Of interest with regard to the present study is the effect of irradiation on the modulus in the low temperature plateau region, and a temperature of −50°C is used as a reference point. *Table 1* gives values of the modulus for a selection of irradiated fibres. Our conclusion is that crosslinking has very little effect on the modulus of low and high draw ratio fibres, but for a draw ratio of 10:1, a dose of 4.8 Mrad (65% gel) produces a small but significant increase in modulus (*Figure 5* and *Table 1*). This increase is of the order of 35% for the 10:1 fibre, whereas the maximum increase for any other sample is 8% for the 1:1 fibre. This is an important and interesting result, and qualitatively is similar to the effect observed by Sangster and Barry on die drawn material[4]. We consider that its explanation must lie in the change in the polymer morphology with increasing extension, and this aspect is pursued in the next section.

*X-ray studies*

The crystal sizes ($D$), calculated from the width of the (002) reflection, and the long period ($L$), calculated from the meridional separation of the two-point pattern, are shown for the unirradiated fibres in *Figure 6*. $L$ remains constant with draw ratio, as expected, previous studies indicating that it is affected primarily by the drawing temperature[10]. $D$ is proportional to the draw ratio, and above 10:1 becomes greater than $L$, indicating that the assumption of a simple lamellar structure is unsatisfactory. Neither $L$ nor $D$ are significantly affected by these irradiation doses. The SAXS photographs are shown in *Figure 7*, and show a very clear two-point pattern for

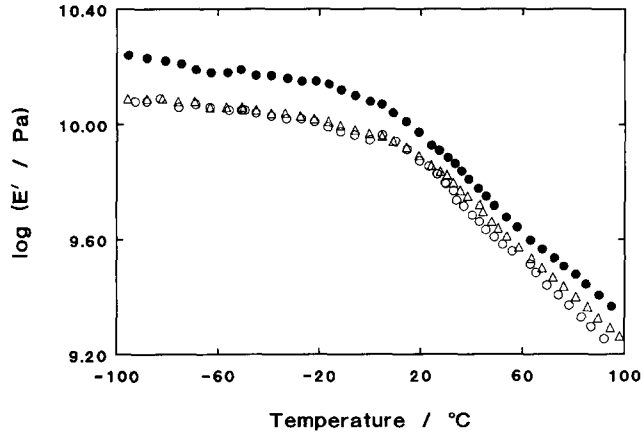


**Figure 5** Log dynamic storage modulus ($E'$) *versus* temperature for the 10:1 fibre, unirradiated (△) and irradiated with 2.2 (○) and 4.8 (●) Mrad

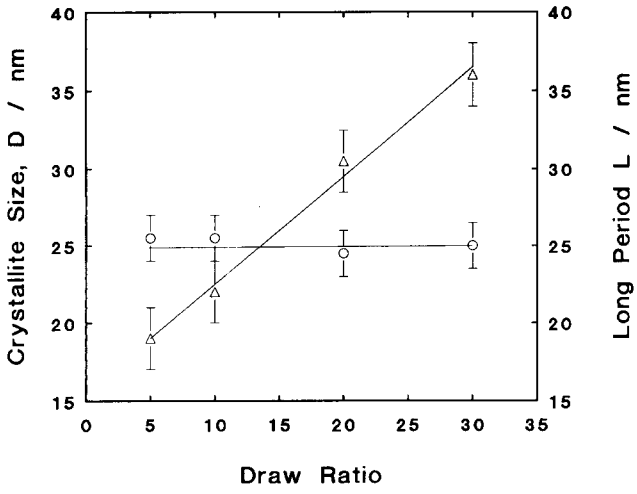


**Figure 6** Crystallite size (△) and long period (○) *versus* draw ratio for fibres

10:1, and much less intense patterns for 20 and 30:1, despite the much longer exposure times (see Experimental section). This suggests a much clearer distinction between crystalline and amorphous phases for 10:1 than for higher orientations, and can therefore be interpreted as the establishment and subsequent increase in intercrystalline connectivity at draw ratios above 10:1, in other words, a change from a predominantly lamellar to a fibrillar structure. To quantify further the development of crystal connectivity, we can apply the Random Intercrystalline Bridge (RIB) model developed by Gibson *et al.*[10]. This model considers the presence of crystalline bridges connecting the lamellae according to a binomial distribution function. The fraction of bridges ($p$) is calculated from the X-ray data as:

$$p=(D_{(002)}-L)/(D_{(002)}+L) \quad (3)$$

This can then be related to the mechanical properties and crystallinity via the Takayanagi model[11], such that:

$$E/E_C=\chi p(2-p) \quad (4)$$

where $E$ is the dynamic $-50°C$ storage modulus and $E_C$ is the theoretical maximum Young's modulus for chain extended polyethylene, which is 240 GPa. $\chi$ is the crystal fraction. *Table 2* gives the bridge fraction $p$ calculated from equation (3), and the quantities $E/E_C$ and $\chi p(2-p)$. At 20 and 30:1, the model predicts 11 and 18% bridge concentration, respectively, whereas below 20:1, $p$ is negative, indicating the model is not applicable, simply because $D$ is less than $L$. *Table 2* shows that equation (4) gives good agreement for the 20 and 30:1 samples, and again failure for the low draw ratios.

It is the interpretation of the structure of the fibres on the basis of the RIB model which we believe can explain the effect of irradiation on the modulus. At high draw ratio, it is the intercrystalline bridges that are responsible for the high value of the modulus. Crosslinking between adjacent lamellae, although promoting high gel, would not provide significant additional stiffness. At low draw ratio, $D$ is significantly less than $L$ (for example, 19.0 and 25.5 nm for 5:1). Here, we would not expect any appreciable interlamellar contact and crosslinking would not provide crystal continuity, and so again no increase in the modulus would be expected. At a draw ratio of 10:1, $D$ (22.0 nm) and $L$ (25.5 nm) are comparable. Since both these parameters must be averages of a distribution, it is reasonable to assume significant interlamellar contact. Therefore, it is suggested that crosslinking at the fold surfaces can link together adjacent lamellae, providing mechanical continuity and increase in modulus that is not provided by any intercrystalline bridging. In *Figure 6*, it can be seen that the crossover point occurs at a draw ratio of about 14:1. Interestingly, this is precisely the draw ratio of samples examined by Sangster and

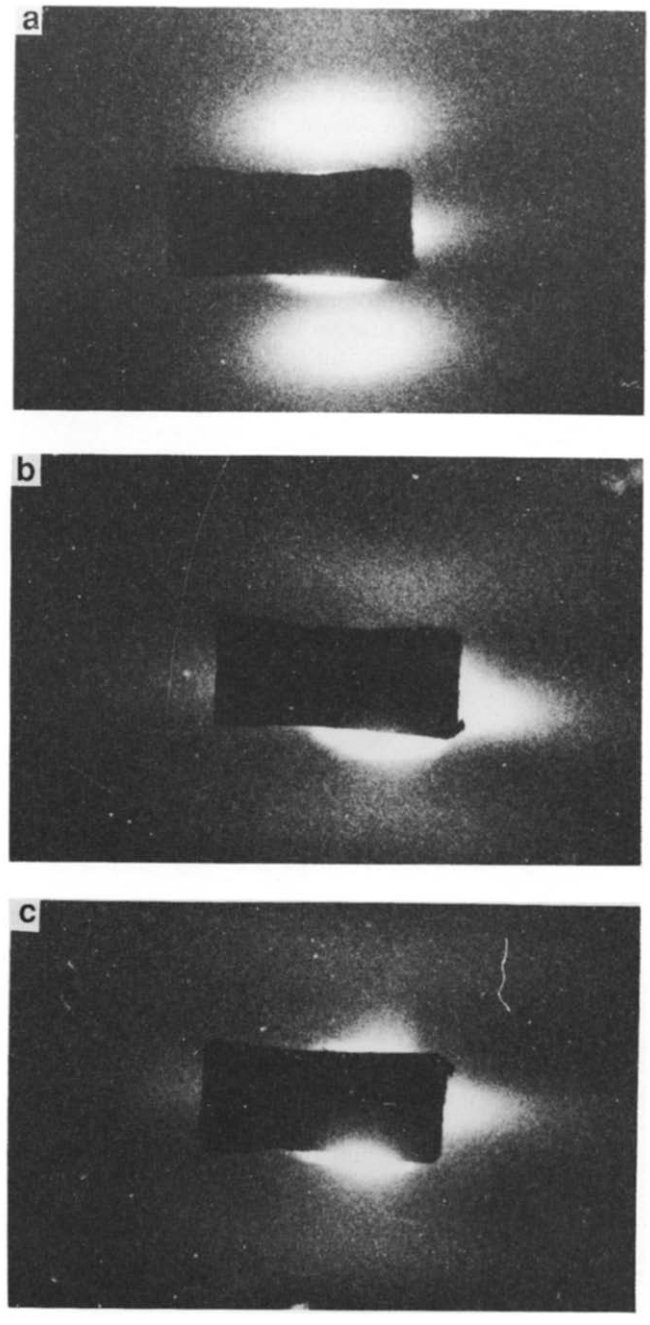


**Figure 7** SAXS photographs for fibres at draw ratios of: (a) 10:1; (b) 20:1; (c) 30:1 (1 cm ≃ 0.75 mm)

**Table 2** Analysis based on the intercrystalline bridge model

| Draw ratio, $\lambda$ | Bridge fraction, $p$ | $\chi p(2-p)$ | $E/E_C$ |
|---|---|---|---|
| 5 | (−0.15) | (−0.24) | 0.027 |
| 10 | (−0.07) | (−0.11) | 0.048 |
| 20 | 0.11 | 0.17 | 0.16 |
| 30 | 0.18 | 0.28 | 0.29 |

Barry[4] which gave such a significant increase in modulus upon irradiation.

## CONCLUSIONS

Electron beam irradiation of polyethylene fibres produces changes in gel fraction, melting temperature and modulus which are significantly influenced by the degree of orientation (draw ratio). Samples of higher draw ratio tend to have higher gel fraction, and show a larger drop in melting temperature with dose compared to lower draw samples. These effects are ascribed to enhanced crystallinity and better interlamellar contact as the draw ratio increases. The crosslinking has been found to lead to an increase in the $-50°C$ dynamic modulus for draw ratios of 10:1, but not for lower or higher draw ratios. An explanation for this effect has been provided in terms of the transition of the structure from lamellar to fibrillar morphology. Results from SAXS and WAXS studies suggest that 10:1 is approximately the draw ratio above which intercrystalline bridges start to develop. At 10:1, the crystal size is of similar magnitude to the long period, and hence for samples of this morphology, we conclude that crosslinking can provide an effective structural continuity and a mechanism for stress to be transmitted through the crystals.

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