Intercrystalline Crosslinking of Polyethylene

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Synopsis

The heat distortion temperature (British Standards Method 102C) and DTA nominal melting point of high density polyethylene have been raised to 140°C by nonrandom crosslinking in which the crosslinks are superimposed on the existing semicrystalline structure. The crosslinking agent was a mixture of dicumyl peroxide and allyl methacrylate, and the crosslinking temperature was 120°C, just below the crystal melting range. In contrast, random crosslinking by the same system above the melting range at 160°C lowered the HDT (heat distortion temperature). Conventional peroxide crosslinking also lowered the HDT. The gel swelling of randomly crosslinked polyethylene was higher than that of nonrandomly crosslinked polyethylene having the same gel content. This dependence of the gel swelling on the crosslink distribution can be correlated with the HDT. The effect of γ-radiation and carbon black loading on the HDT has also been studied.

INTRODUCTION

Polyethylene has a range of different amounts and types of crystallinity, and this crystallinity not only affects the placement of crosslinks, but, conversely, the process of crosslinking affects the crystallinity and the resultant mechanical properties of the material. Properties especially affected are those at high temperatures, since melting is a function of crystallite size and distribution. Crosslinking by radiation produces a gradual reduction of the crystallinity and crystal melting point of low density polyethylene until in the region 100–1000 Mrads the material has a very low modulus, although higher radiation doses raise the modulus again as a glassy material is produced.[1] Doses up to 75 Mrads can raise the heat distortion temperature (British Standards Method 102C) of high density polyethylene by about 10°C.[2] The efficiency of crosslinking by radiation can be increased by the use of polyfunctional comonomers. Odian and Bernstein soaked low-density polyethylene in the comonomers allyl methacrylate, allyl acrylate, and diallyl maleate at room temperature and found that they increased the amount of gel for a given amount of radiation.[3] The equilibrium swelling time was about two days, and comonomer absorptions of up to 4.5% were obtained. It was pointed out

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that the comonomer would be absorbed by the amorphous areas only, as is generally accepted for the absorption of liquids by semicrystalline polymers. It would be expected in this case that, although the crosslinking would be mainly confined to the amorphous areas, some breakdown of crystallinity would be caused by the radiation. Crosslinking could be restricted to the amorphous areas entirely by a chemical, rather than an irradiation process, if a peroxide could be located in the intercrystalline regions.

The possibility of confining high degrees of crosslinking between the crystallites offers the prospect of preparing a polyethylene with new properties. According to Flory,[4] if an ordered system is crosslinked and the crosslinked units participate in the crystallization in an unrestricted manner, then an increase in melting point can be expected because of the reduced configurational entropy of the melt. This is analogous to imposing crosslinks on an ordered, crystalline structure. Certain fibrous proteins, such as collagen, do show an increased melting temperature with increasing crosslink concentrations.[5] The retention of crystallinity means that a high modulus can be retained at high levels of crosslinking, unlike the situation with radiation crosslinking where the modulus progressively decreases. Thus, considerable creep resistance may be obtained without sacrificing stiffness. The retention of crystallinity also means the retention of other properties that depend on it, such as tensile strength, resistance to solvents, etc. The relative levels of crosslinking and crystallinity obviously depend on the density of polyethylene used.

It was decided to introduce peroxide into the intercrystalline regions by two methods: (1) swelling polyethylene in a *p*-xylene–peroxide mixture below the crystal melting point and evaporating the *p*-xylene and (2) swelling polyethylene in a comonomer–peroxide mixture, also below the crystal melting point. The peroxide was decomposed at the beginning of the melting range so that the crystallinity was preserved. High-density polyethylene was used so as to provide the maximum initial crystallinity. The comonomer chosen was allyl methacrylate, which has been shown to produce a large increase in the efficiency of radiation crosslinking.[6] The peroxide used was dicumyl peroxide, which is commonly accepted as an efficient crosslinking agent for polyethylene and has a half-life that suited the temperature range of the experimentation. The chief property of interest was the HDT, (heat distortion temperature), since this determines the maximum useful temperature.

EXPERIMENTAL

Materials

Two high-density polyethylenes were used, Rigidex 50 chips (Distillers Company) and HD03 powder (Plastics Division, I.C.I.). The usual molding procedure for preparing sheets for swelling and irradiation was to place about 27 g of polyethylene in a 12.5 cm $\times$ 12.5 cm $\times$ 0.2 cm mold, heat at 170°C for 5 min under slight force, apply a force of 14,000 kg for

5 min, raise to a force of 18,500 kg, and immediately cool to around room temperature while maintaining the force constant at 18,500 kg.

Since a large excess of peroxide was added to the allyl methacrylate, the inhibitor was not removed.

Luperco 130 XL [2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexyne-3] is a peroxide with a higher decomposition temperature than that of dicumyl peroxide, and is more suitable for milling to high density polyethylene. The half-lives of the two peroxides are compared in Table I. Luperco

TABLE I
Peroxide Half-Lives[a]

Peroxide	Temp., °C							
	105	110	120	130	140	150	160	170
Dicumyl peroxide	50	26	7.5	2	0.6	0.2	0.06	0.02
Luperco 130 XL	350	150	46	10	2.9	1.0	0.3	0.1

[a] Half-lives given in hours.

130 XL was supplied by Wallace and Tiernan (Lucidol Division, Buffalo, U.S.A.) as a free-flowing powder (the liquid peroxide absorbed on its own weight of chalk).

Crosslinking with Allyl Methacrylate

The polyethylene was usually swollen in a 90/10 (w/w) allyl methacrylate–dicumyl peroxide mixture, and an elevated temperature was used to obtain as high a swelling and subsequent crosslink density as possible. The equilibrium conditions for various temperatures were found by plotting weight gain against time, equilibrium being reached when the curve flattened out. The equilibrium absorption at 60°C was about 2.0% after 5 hr, depending on molding conditions, and gelation of the allyl methacrylate began to occur at longer times. At 70°C, gelation began earlier, before equilibrium had been reached (i.e., before uniform diffusion of the allyl methacrylate had taken place). Therefore 5 hr at 60°C were chosen as the swelling conditions.

The polyethylenes used had a melting range extending from about 110°C to 140°C, as shown by Figures 2, 3, and 4, where the rate of heating for the DTA thermograms was 20°C/min. Dicumyl peroxide is 80% decomposed at 120°C in 18 hr,[7] and since this is a convenient time for an overnight reaction, 120°C was chosen as the crosslinking temperature. Figures 2, 3, and 4 show that only a small amount of crystal melting takes place at this temperature. Accordingly, the polyethylene swollen with allyl methacrylate–dicumyl peroxide was blotted dry, weighed, transferred to a stoppered tube, and kept in an oven at 120°C for 18 hr. The weight loss of allyl methacrylate due to evaporation was usually 10%–20% of that absorbed. The percentages of allyl methacrylate given in the results are based on the final weights and not the swollen weights.

After being crosslinked once, the polyethylene was reswollen under the same conditions and crosslinked again at 120°C for 18 hr. This process was repeated a number of times to build up the amount of allyl methacrylate in the polyethylene, and hence the crosslink density. The weight gain in the second and third steps was usually still about 2%, but an increase to about 3% or 4% was found at the fourth and fifth steps, presumably due to gradual reduction of crystallinity. In another series of experiments, performed for comparison purposes, the crosslinking was carried out for 30 min at 160°C, at which temperature almost all the peroxide is decomposed. Sufficient crosslinking must have occurred below the melting point, before the sample was up to temperature, to prevent sample distortion. In this series, the allyl methacrylate concentration was again built up in the stepwise fashion.

A determination of the amount of allyl methacrylate in a number of samples was made by infrared analysis as a check on the weighing procedure, and the results were usually 10%–20% lower. The reason for this is not clear, but may be due to inadequate calibration.

Crosslinking with Dicumyl Peroxide Alone

Rigidex 50 was swollen in p-xylene containing various concentrations of dicumyl peroxide, the p-xylene was evaporated, and crosslinking was effected as before. A temperature of 90°C was chosen for the swelling since as high a temperature as possible was required to give a high final uptake of peroxide. At temperatures higher than 90°C, not only does the rate of decomposition of the peroxide become more appreciable (5% in 5 hr at 100°C) but solution of the polyethylene begins. Dicumyl peroxide–xylene solutions of concentrations 10/90 to 50/50 (w/w) were used. The swelling time was 3 hr, after which the xylene was removed by drying in a vacuum oven, also at a temperature of 90°C, to constant weight. One series of samples was then crosslinked at 120°C for 18 hr, and another series was heated at 160°C for 0.5 hr (practically 100% decomposition of the peroxide).

Crosslinking with Luperco 130 XL

Different amounts were milled into the HDO3 polyethylene on a roll mill at temperatures of 140–160°C for times of about 15 min. The molding conditions differed from normal in that a temperature of 190°C rather than 170°C was used, so that a rapid cure could be effected during molding (the half-life at 190°C is about 30 sec).

Irradiation

Strips of Rigidex 50 sheet were placed in sealed glass tubes which had been flushed with nitrogen and exposed to radiation from a ^{60}Co source. The tubes were not opened for some weeks after irradiation to allow for decay of the free radicals.

Heat Distortion Temperature

British Standards method 102C, B.S. 2782 (1965) was used. This involves hanging a 20-g weight on a 1 in. $\times$ 0.25 in. $\times$ 0.06 in. cantilever strip and noting the temperature when the angle through which the strip is bent is 30°. Instead of an oil bath, where there is the possibility of sample contamination, a circulating hot air oven was used, with the thermometer bulb next to the sample.

Gel Swelling

Samples weighing about 0.5 g in sealed filter-paper packets were extracted in boiling p-xylene containing N,N'-diphenyl-p-phenylenediamine (antioxidant). The swollen gels were quickly blotted dry, transferred to vials, and weighed, so that liquid excluded by syneresis was not lost. The gel swelling was based on dried, extracted material, which had been dried for 16 hr at 100°C in a vacuum oven. Two determinations of each type were made for extraction, one extracted for a time of three days and one for four days, respectively, the p-xylene being changed after the first day each time. The gel contents and gel swellings of these two samples usually agreed to ±5%. If not, they were rejected. (To determine the rate of extraction, the gel contents of selected samples were measured with time. They reached a minimum value after about two days and then remained constant).

No attempt was made to correct for the density of the hot p-xylene in calculating the gel swelling, and the following expression was used:

$$\text{gel swelling} = \frac{(\text{wt. swollen polymer}) - (\text{wt. dried, extracted polymer})}{(\text{wt. dried, extracted polymer})}$$

Shear Modulus

The shear modulus was measured with a torsion pendulum on 2.5 $\times$ 7.5 $\times$ 25 mm specimens.

RESULTS AND DISCUSSION

Crosslinking with Allyl Methacrylate

If crosslinking takes place below the crystal melting point and occurs preferentially in the intercrystalline or amorphous areas, the crosslinks would be expected to "bunch" together, producing a nonrandom distribution. On the other hand, if crosslinking occurs above the crystal melting point, the crosslinks would be expected to be distributed in a random manner. Since the allyl methacrylate is localized when it is absorbed by the polyethylene in the preswelling technique used, crosslinking above the crystal melting point does not produce a true random distribution in this case but one which is much more random than when crosslinking takes place below the crystal melting point. The effect of increasing concentra-

tions of allyl methacrylate and dicumyl peroxide on the HDT of high-density polyethylene for such "random" and "nonrandom" crosslinking is shown in Table II and Figure 1. The results are not precisely comparable since only 80% of the dicumyl peroxide was decomposed in the nonrandom

TABLE II
HDTs as Function of Amount of Crosslinking Agent

Polyethylene type	Dicumyl peroxide in AM, %	Type of treatment[a]	Number of treatments	AM, %	HDT, °C
HDO3	—	—	None	—	100
	10	NR	1	2.7	114
			2	5.2	118
			3	8.3	131
			4	12.2	135
			5	15.9	140
			1	1.8	106
			5	7.5	121
			6	10.9	131
			7	12.9	135
	10	R	1	2.0	96
			2	6.2	92
			3	9.0	88
			4	13.7	95
			5	17.9	93
Rigidex 50	—	—	None	—	115
	10	NR	1	2.2	119
			2	3.7	129
			3	5.6	133
			4	7.5	138
			5	9.8	142
			1	1.6	120
			3	4.5	125
			5	5.6	135
	30	NR	2	2.9	133
			3	4.8	138
			4	6.4	140
			5	8.6	142
	10	R	1	3.7	105
			2	5.4	105
			3	6.4	107
			4	8.4	101

[a] NR = Nonrandom; R = random.

case, whereas all of it was decomposed in the "random" samples.   However, the results definitely show that the type of nonrandom crosslinking used increased the HDT of HDO3 from 100°C to 140°C, whereas "random" crosslinking decreased the HDT to about 90°C.   Figure 1 also shows the HDTs of nonrandomly crosslinked Rigidex 50, which had a higher initial
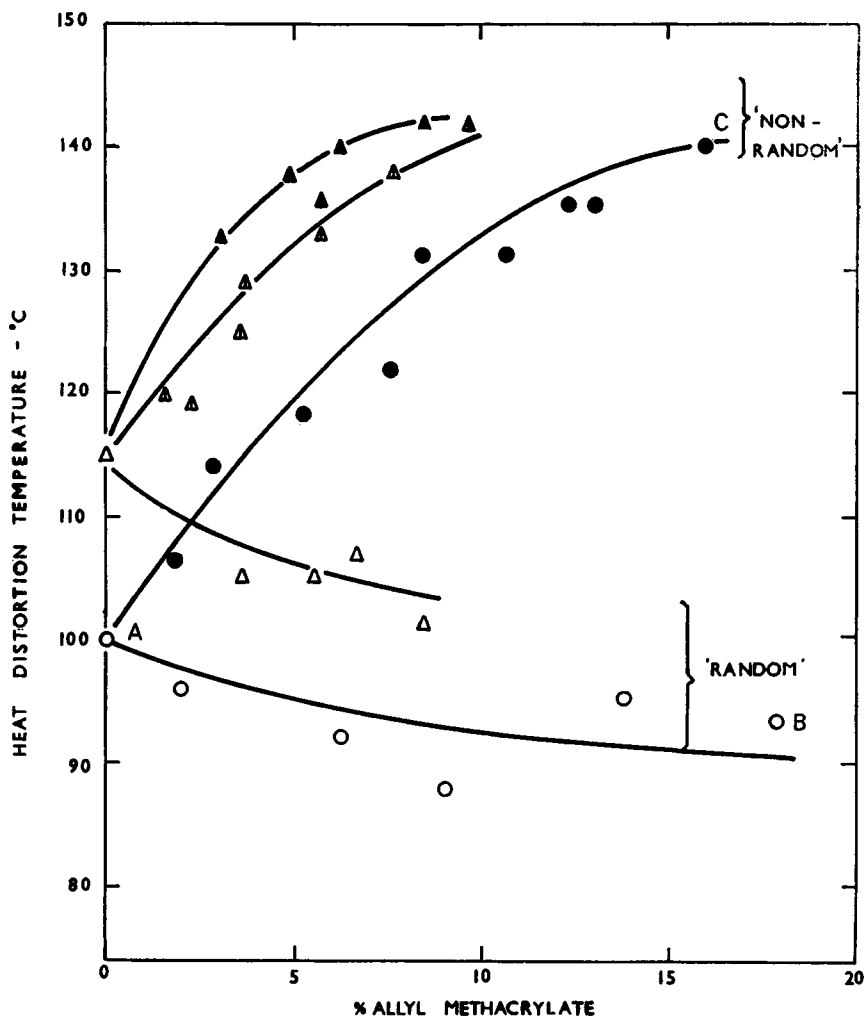
Fig. 1. Heat distortion temperatures (HDTs) of "random" and "nonrandomly" crosslinked high-density polyethylene: (▲,△,△) Rigidex 50; (●,○) HDO3; (△,△,●,○) 10% dicumyl peroxide in allyl methacrylate; (▲) 30% dicumyl peroxide in allyl methacrylate.

HDT of 115°C, for two concentrations of peroxide in the allyl methacrylate. Once again, the HDT is increased to about 140°C. The higher concentration of peroxide gives a more rapid increase in HDT. Figure 2 shows DTA thermograms for three of the samples in Figure 1, A, B, and C. A is the unmodified polyethylene, B has been randomly crosslinked, and C nonrandomly crosslinked. The nominal melting point of B has been depressed from 131°C to 122°C, but that of C has been increased to 140°C.

Hoashi and Mochizuki have investigated the effect of annealing linear polyethylene in the crystal melting range.[8] They found that annealing

close to the DTA nominal melting point caused the DTA thermogram to split into two peaks above and below the original melting point, the lower one being small. For instance, when the original melting point was 127.7°C, annealing at 118°C for 20 hr gave two peaks, one at 131.0°C and a small one at 108°C. Similarly, annealing the same material at 124°C for 60 hr gave a peak at 135.5°C and a small peak at 119°C. The small peak is due to the melting and recrystallization of crystallites which melt below the annealing temperature, while the higher peak is produced by the readjustment of the higher melting crystallites. In other words, the annealing temperature divides the crystallites into two fractions whose mean melting
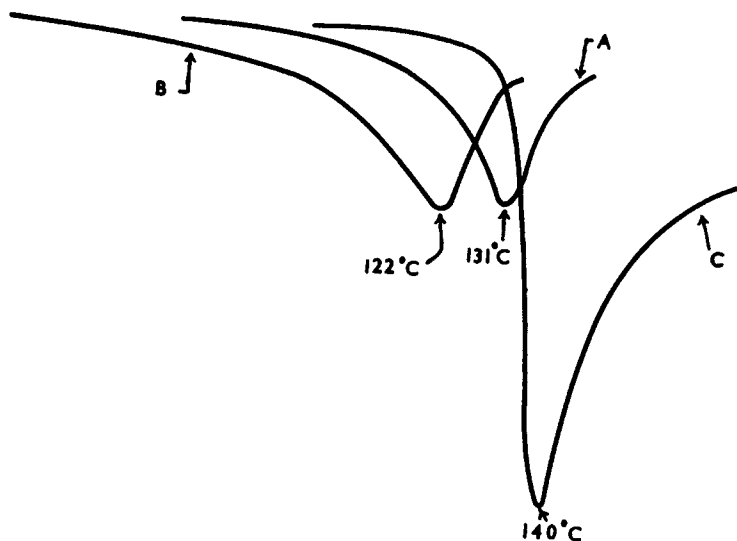

Fig. 2. DTA curves. Samples A, B, and C are shown on Fig. 1: (A) unmodified polyethylene [HDO3], HDT 100°C; (B) randomly crosslinked, HDT 93°C; (C) nonrandomly crosslinked, HDT 140°C.

points are above and below the annealing temperature. It was important to establish whether the same factors were responsible for the considerable elevation of melting points and HDTs described above. Accordingly, HDO3 and Rigidex 50 were taken through the same stepwise procedure, but without crosslinking, in a series of control experiments.

First, the effect of the annealing cycle alone, without any solvent, was investigated. Both types of polyethylene were given a series of annealing "treatments." Each treatment consisted of annealing for 18 hr at 120°C, followed by cooling down to room temperature and waiting for 6 hr before reannealing. For both polyethylenes the results were the same. There was no change at all in the HDT after five of these treatments. There was a slight change in the DTA curve after two treatments, with a slight sharpening of the shoulder, i.e., melting over a narrower range, and a small

elevation of the peak by about 3°C. There was no further change after subsequent treatments.

A second series of control experiments was performed to check whether the allyl methacrylate could have any effect on recrystallization. This time, a "treatment" consisted of carrying out the entire procedure as used when crosslinking, except that the peroxide was not present in the allyl methacrylate. Samples of HDO3 and Rigidex 50 were soaked in the allyl methacrylate for 5 hr at 60°C, and they were then annealed in sealed tubes at 120°C for 18 hr. The HDO3 tended to absorb increasingly larger amounts of allyl methacrylate, and the results were not meaningful. On the other hand, the Rigidex 50 had retained only a very small amount of allyl methacrylate, 0.3%, after the first treatment, and this amount did not increase in subsequent treatments. The results of these experiments on the Rigidex 50 were exactly the same as for annealing alone, i.e., sharpening and slight elevation of about 3°C of the DTA curves after two treatments, and no further change thereafter. There was no increase in HDT.

It could be argued, in the case of the Rigidex 50, that the allyl methacrylate does actually change the structure during annealing so as to raise the HDT and DTA peak stepwise towards 140°C, and that this would be evident if the residual solvent could be completely removed, this "removal" perhaps being what is achieved by the crosslinking when the peroxide is present. However, this is obviously highly improbable, since the 0.3% of residual solvent would have to depress the HDT to coincide exactly with the initial HDT for any number of treatments.

It can therefore be concluded that the large increases in HDT and melting points obtained by the nonrandom crosslinking were definitely real effects caused by the crosslink distribution, and not due to annealing either with or without the allyl methacrylate present. Additional support for this thesis is evident from Table II and Figure 1, where the HDT (nonrandom) is seen to be dependent on the amount of crosslinking agent only and not on the number of treatments. For instance, seven treatments of one sample of HDO3 produced the same HDT (135°C) as four treatments of another sample. (Presumably the difference must arise from slight variations in molding procedure.)

The HDT itself is a single-point test which may be criticized to some extent for its dependence on heating rate and the arbitrary angle chosen. However, it was found that the HDT correlated very well with the glass–rubber transition temperature for the crosslinked polyethylenes. This is demonstrated by Figures 3 and 4, which show the dynamic shear modulus as a function of temperature for the polyethylenes used and for two non-randomly crosslinked samples of each one. Also superimposed, with an arbitrary vertical scale, are the DTA thermograms, to show the melting range. The HDTs are indicated. It should be noted that the glass–rubber transitions are very sharp and that the shapes for each polyethylene are similar. The melting range shown by the DTA thermograms matches the transition range, which shows that softening commences at the beginning of
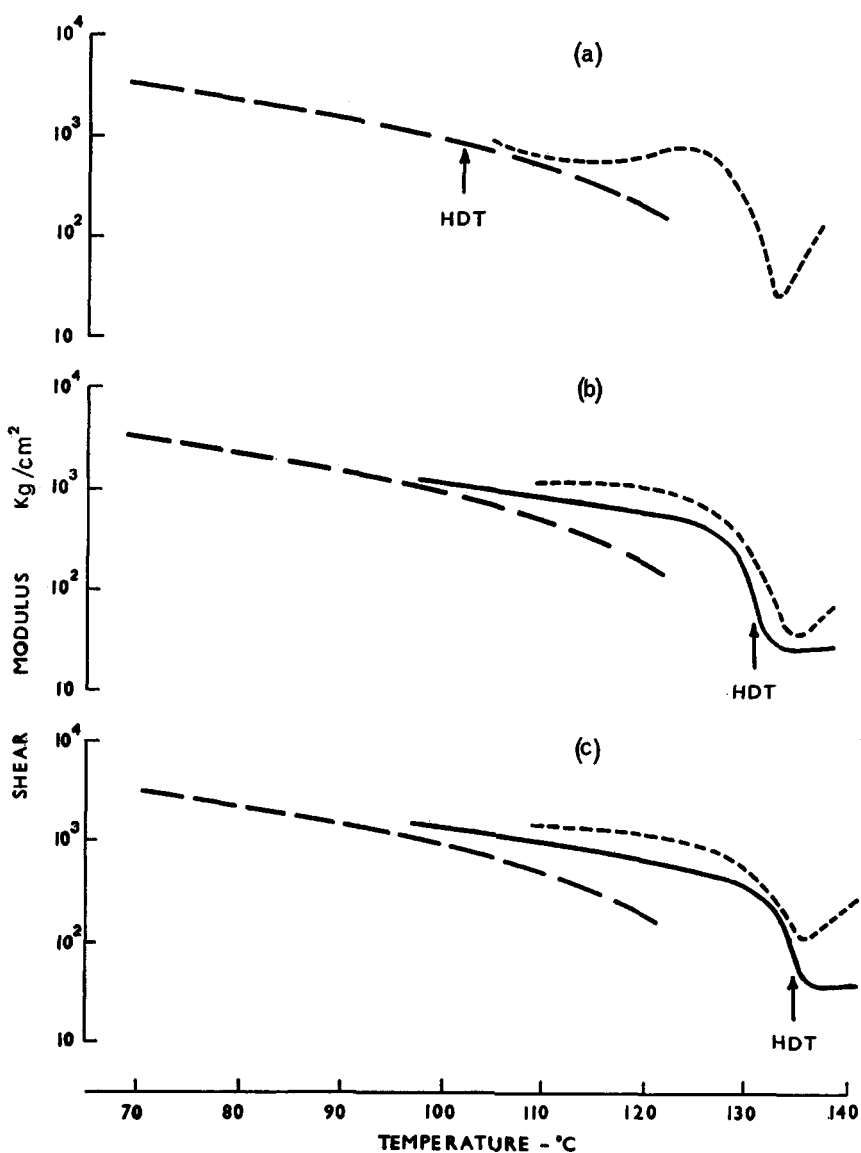
Fig. 3. Dynamic modulus and DTA curves of unmodified (a) and two different samples of nonrandomly crosslinked HDO3 (b,c), (DTA curves on arbitrary vertical scale.): (———) crosslinked modulus; (— —) unmodified modulus; (- - -) DTA curves.

the melting range. For both polyethylenes, the HDT occurs around the end of the transition and close to the DTA peak. The sharpness of the transitions, their similarity, the match with the DTA thermograms, and the correspondence of the HDTs certainly support the use of the HDT as a property related to the transition. This is very advantageous, since obtaining shear modulus curves is very time consuming.
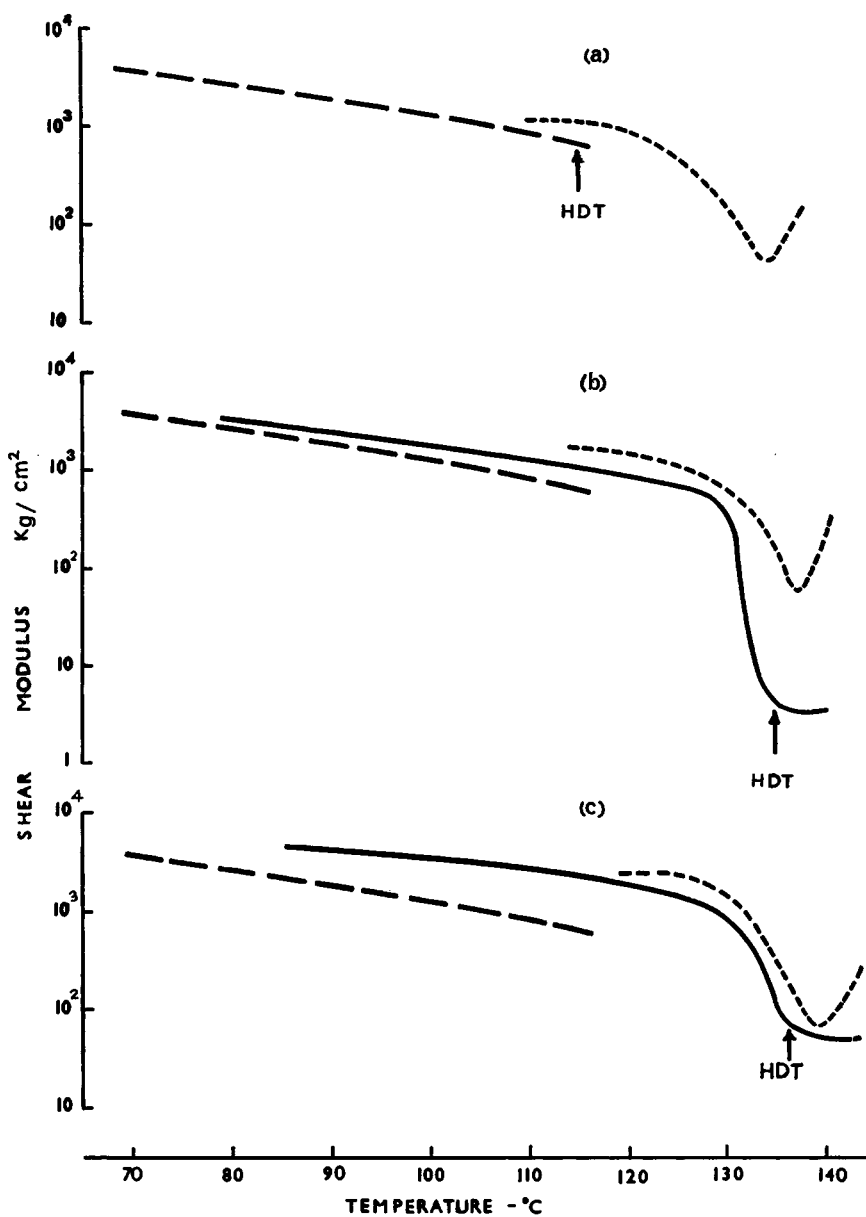
Fig. 4. Dynamic modulus and DTA curves of unmodified (a) and two different samples of nonrandomly crosslinked Rigidex 50 (b,c) (DTA curves on arbitrary vertical scale.): (———) crosslinked modulus; (— — —) unmodified modulus; (- - - - - -) DTA curves.

It is significant that the HDTs appear to asymptote to a value of a little above 140°C and that the maximum DTA nominal melting point is also at this level. Flory has shown that the theoretical melting point of an infinite crystal of polyethylene is 145.5°C,[4] although Wunderlich thinks that a

lower value of about 142°C is more correct.[9]   Melting points of about 140°C have been obtained before, although it has usually been necessary to use either high-pressure and high-temperature crystallization conditions[9-11] or narrow molecular weight fractions.[12,13]   Hoashi and Mochizuki obtained 142.4°C as the higher of two DTA peaks after isothermal crystallization at 128°C.[8]   Intercrystalline crosslinking would tend to weld lamellae faces together to form a pseudoinfinite crystal, which could explain why the melting temperature asymptotes to about 140°C.

Alternatively, it could be argued that such an increase is in agreement with the predictions of Flory[4] in terms of a reduced configurational melt entropy caused by the addition of crosslinks to an ordered structure, as mentioned earlier.   In an analogous case, Mandelkern crosslinked a stretched rubber and measured the melting points after relaxation and cooling.[14]   Although there was a reduction and not an increase in melting point compared with the original material, this reduction was slight compared to the reduction obtained by normal crosslinking and was due to the crosslinks impeding the crystallization process.

These arguments would also explain why there is such a good correspondence between the HDT and the melting points for the crosslinked polyethylenes shown in Figures 3 and 4.   As mentioned before, the HDT should tend to correspond with the beginning of the melting range, since the melting of only a small number of crystallites should cause the cantilever beam to deform under load.   This is exemplified in Figures 3 and 4 by the HDTs of the unmodified polyethylenes, which are seen to be considerably below the peaks of the thermograms.   Joining the crystallites together into a pseudoinfinite crystal should therefore give a much narrower size range of crystallites and much sharper melting, as indeed occurs.   The increase in the sharpness of melting can be seen from sample C in Figure 2.   (Although annealing alone gives sharper melting, it produces no increase in HDT, so that a considerable amount of smaller crystallites must still be present.)   Sample B, which had been randomly crosslinked, had an even broader melting range, and it can clearly be seen why the HDT is 93°C even though the peak of the thermogram, the nominal melting temperature, is 122°C.

TABLE III
Elongation and Modulus after Nonrandom Crosslinking
with Allyl Methacrylate

Sample	HDT, °C	Modulus,[a] psi	Elongation, %
Rigidex 50	115	68,900	600[b]
Rigidex 50 crosslinked	142	175,000	2
with allyl meth-	138		
acrylate		113,600	14
Rigidex 50 irradiated			
with 100 Mrads	125	189,600	6

[a] Speed of 2 in./min for 1-in. gauge.
[b] Mostly cold draw.

Surprisingly, x-ray diffraction photographs show little difference between any of the three samples in Figure 2, although sample C does appear to have sharper lines and possibly greater crystallinity than the unmodified polyethylene, while sample B may have slightly less perfection.

The most significant mechanical property change that occurs when the intercrystalline areas are crosslinked and a high HDT is produced is a considerable reduction in elongation at break. This also occurs with irradiated polyethylene. Some results are given in Table III. It is interesting to note that the elongation tends to a very low value as the maximum HDT of about 140°C of the pseudoinfinite crystal is approached. A perfect crystal would be quite brittle. For instance, it has been shown that polyethylene crystallized at very high pressures crystallizes in extended chains, and the material crumbles in the fingers.[15]

Dicumyl Peroxide Alone

As a check on the contribution of the allyl methacrylate, it was decided to crosslink the intercrystalline areas with dicumyl peroxide only. This was done by swelling Rigidex 50 in a dicumyl peroxide–xylene solution at 90°C, evaporating the xylene, which should leave the peroxide situated in the amorphous areas, and decomposing the peroxide both above and below the polyethylene crystal melting point. The polyethylene swelled by 15% in xylene at 90°C, and since it was not possible to work with a much more concentrated solution of peroxide than 50%, the maximum amount of peroxide in the polyethylene was 7.0%. The HDTs obtained are given in Table IV, the control for uncrosslinked Rigidex 50 being 115°C. The results are similar in kind to those obtained with the allyl methacrylate; the HDT increases with increasing nonrandom crosslinking and decreases with increasing random crosslinking. These results suggest that the allyl methacrylate acts as an effective "cement" to weld the crystallites together, since it produces much higher HDTs.

TABLE IV
HDTs of Rigidex 50 Crosslinked with Dicumyl Peroxide Alone

	HDT, °C	
Dicumyl peroxide, %	Crosslinking at 120°C (nonrandom)	Crosslinking at 160°C (random)
1.5	115	104
2.9	117	100
4.3	118	100
5.7	121	99
7.0	124	90

Gel Swelling

The gel swelling for randomly crosslinked samples is higher than that for nonrandomly crosslinked samples having the same gel content. The

difference depends on the degree of randomness, or, in other words, the crosslink distribution. This is shown by Figures 5 and 6, where the results have been separated into two groups for clarity, the allyl methacrylate samples in Figure 5 and the dicumyl peroxide alone and the irradiated samples in Figure 6. The allyl methacrylate results are also shown in Figure 6 as broken lines for comparison. The crosslink distribution appears
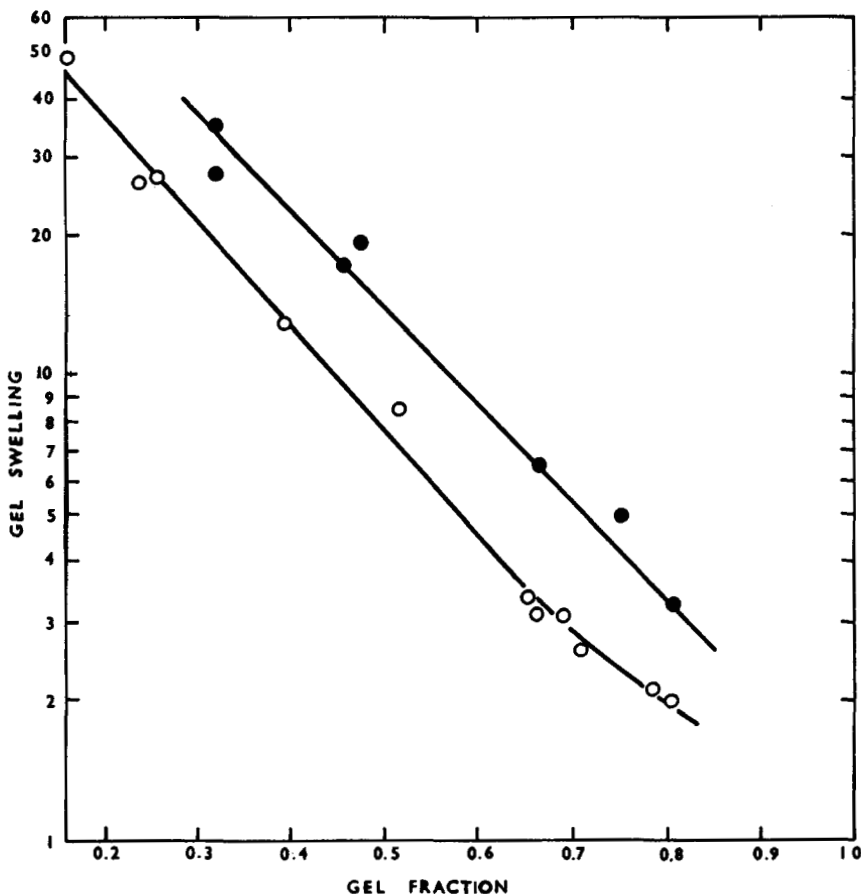

Fig. 5. Gel swellings of high-density polyethylene crosslinked with an allyl methacrylate–dicumyl peroxide mixture: (O) crosslinked at 120°C (nonrandom); (●) crosslinked at 160°C (random).

to depend on the amount of preswelling undergone by the polyethylene before crosslinking; the higher the swelling the more random the distribution. When dicumyl peroxide alone was used, the swelling in p-xylene was 15%, and this explains why the gel swellings from these samples are higher. In this case, the nonrandomly crosslinked samples appear to have crosslink distributions close to those of the randomly crosslinked allyl methacrylate samples.

Although the effects of crosslink distribution on gel swelling would hardly have been predicted a priori, a tentative explanation can be offered. Assume that a certain number of random crosslinks form a specified amount of gel. If additional crosslinks are added adjacent to these to form bunches, the number of crosslinks may be increased without increasing the amount of gel. However, the additional crosslinks can reduce the swelling
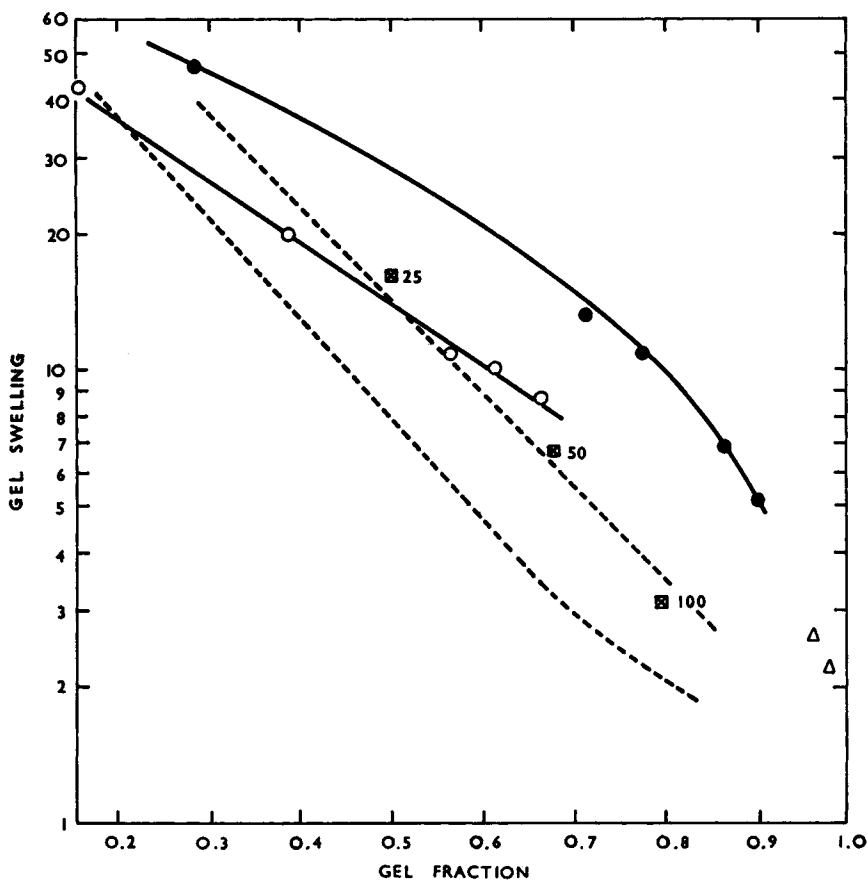

Fig. 6. Gel swellings of high-density polyethylene crosslinked with dicumyl peroxide alone: (O) crosslinked at 120°C (nonrandom); (●) crosslinked at 160°C (random); (⊠q) irradiated by q Mrads; (△) crosslinked by Luperco 130XL (random); (- - - - -) allyl methacrylate results from Fig. 5.

of this gel. An effect caused by different crosslink distributions was found by Mandelkern, who showed that oriented Marlex 50 had a higher gel content than the unoriented polymer for the same radiation dose.[16] It has also been found by Salovey that quenched high molecular weight polyethylene has a gel content approximately twice that of the unquenched polymer, for the same radiation dose.[17]

It would appear that the position on the gel swelling map is an indication of the HDT.   Figure 7 shows that, with few exceptions, the more non-random the crosslinking and the more the original crystallites are preserved by minimizing the distortion during swelling, the higher the HDT.   Gel swelling is therefore a valuable tool for indicating the location of crosslinks and their effect on HDT.
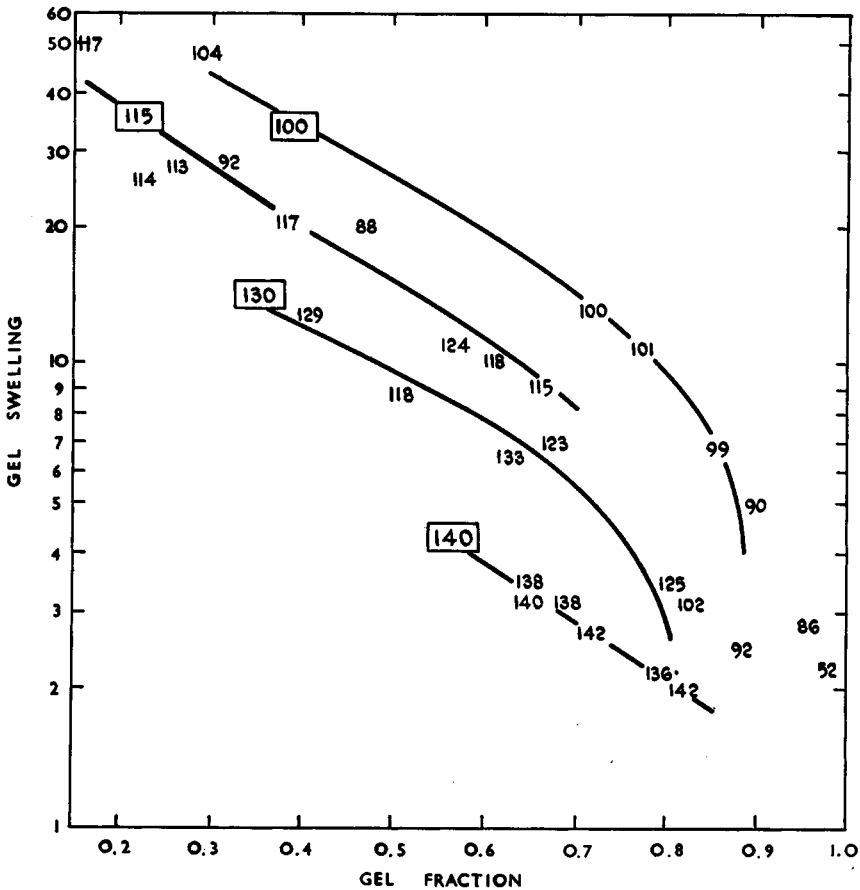

Fig. 7. Heat distortion temperatures (°C) as a function of gel swelling for all samples, random and nonrandom. (Each line is drawn to give the HDT in the box).

After a nonrandomly crosslinked sample having a HDT of 140°C had been heated at 160°C for 30 min and cooled, its HDT was reduced to 113°C, even though gel swelling measurements showed that there was no change in crosslink distribution.   Presumably the crystal perfection must be reduced in some way by heating above the HDT, and this emphasizes the dependence of the HDT on this property.   The HDT map in Figure 7 can only be used for the first heating.

Irradiated Polyethylene

Rigidex 50 irradiated by 100 Mrads from a ^{60}Co source had a HDT of 125°C, compared with 115°C for the original material. This increase agrees with previous literature values.[2] Figure 6 shows that the gel swellings lie roughly midway between the most nonrandom samples obtained by using allyl methacrylate and the most random samples obtained by using dicumyl peroxide alone.   There has been some controversy in the literature as to whether radiation crosslinking takes place preferentially in the inter-crystalline[18] regions or in a uniform fashion including the crystal regions.[19] These gel swelling results suggest an intermediate view, which is compatible with the work of Kawai and co-workers.[20]   They propose that free radicals formed by radiation in the crystals migrate to the surface of the lamellae and there form either intra- or intermolecular crosslinks.   This means that crosslinks are produced in the intercrystalline regions only, but that there must be a gradual breakdown of the crystallites.   This reduction in crystallinity becomes quite significant above a radiation dose of about 100 Mrads.[1] The crosslinks will therefore be more randomly distributed than if they were confined to the original intercrystalline regions alone.   The difference between high- and low-density polyethylene should be borne in mind, however, and it seems reasonable that the crosslink distribution will be less random in the high-density case where the crystallinity is higher.

Conventional Peroxide Crosslinking

The results of milling Luperco 130 XL into the HDO3 and crosslinking during molding above the crystal melting point (190°C) are given in Table V.   It can be seen that the effect of increasing amounts of peroxide used

TABLE V
Properties of High-Density Polyethylene (HDO3)
Crosslinked by Luperco 130 XL at 190°C

Luperco 130 XL (as peroxide), %	Elongation, %	HDT, °C
0	600	103
2	800	102
4	520	101
6	450	88
10	270	70

in this way is to lower the HDT rather than raise it.   This agrees with the above conclusions that random crosslinking breaks up the crystallinity and increases the range of crystallite size, thus lowering the HDT.   A reduction in elongation has been observed by other workers and presumably arises from a reduced relative molecular movement.

Carbon Black-Filled Polyethylene

It was found that Rigidex 50 filled with carbon black (Kosmos 60 HAF) also exhibited an increase in HDT and a decrease in elongation at break, as shown in Table VI. The fact that carbon black does raise the HDT, and the similarity between the mechanical properties of polyethylene having a high HDT which has been filled with carbon black and those of polyethylene having a high HDT which has been nonrandomly crosslinked with allyl methacrylate, suggest that carbon black similarly "crosslinks" the intercrystalline regions (although DTA shows no increase in crystal melting point for the sample containing 50% carbon black). Crosslinking by carbon black has been suggested as a mechanism for the reinforcement of rubbers.[21] Such a mechanism might explain the curious fact that brittle carbon black-filled polyethylene is toughened by crosslinking in the conventional way with peroxide[22]—the peroxide crosslinking would break down the crystallites and regenerate amorphous regions thus providing the ability for elongation to occur.

TABLE VI
Properties of Carbon Black-Loaded Rigidex 50

Carbon black, %	HDT, °C	Initial modulus,[a] psi	Elongation, %
0.5	117	146,000	185
1.0	118	159,000	101
3.0	121	151,000	13
30.0	124	197,000	3
40.0	128	200,000	2
50.0	133	202,000	2

[a] Speed of 2 in./min for 1-in. gauge.

CONCLUSIONS

Nonrandom crosslinking of polyethylene where the crosslinks are confined to the amorphous or intercrystalline regions raises the HDT and crystal melting point; in contrast, these properties are lowered by random crosslinking. Nonrandom crosslinking also produces a narrower melting range. This increase in HDT appears to be due to the formation of a "pseudoinfinite" crystal, and removal of the amorphous regions tends to lead to a low elongation at break. The degree of gel swelling is sensitive to the crosslink distribution, and a correlation of the gel swelling with gel content provides a valuable diagnostic tool for studying the distribution. It appears that the distortion of the crystallites during crosslinking has to be kept to a minimum in order to obtain a high HDT. A few results on irradiated polyethylene seem to suggest that it is more heavily crosslinked in the amorphous than the crystalline areas. Carbon black also raises the HDT and, by analogy, might be said to similarly "crosslink" the amorphous areas.

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