Structural and melting studies of crosslinked linear polyethylenes

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The level of extractables, crystallinity, unit-cell parameters and X-ray line-broadening information have been obtained for linear polyethylene crosslinked using Vul-Cup R® in weight fractions ranging from 0.1 to 3.1%. Melting and crystallization studies have been carried out on the sol and gel fractions, as well as the unextracted crosslinked polymer. Melting and crystallization behaviour is dependent upon the level of extractables, crystallization temperature and crosslink density. The sol fraction is shown to influence the fraction of high-temperature-melting crystals, as well as their melting temperatures.

INTRODUCTION

Polyethylene (PE) is the most commonly used crystalline polymer today. Crosslinked polyethylene has several important uses, with crosslinked low-density polyethylene being used extensively as high-voltage insulation, while crosslinked linear polyethylene is used as hot-water piping. It is important to develop an understanding of the influence of crosslinking on the crystallization process in order to explore certain aspects of crystallization in general.

Many of the studies performed on crosslinked polyethylenes have been with polyethylenes crosslinked using radiation. Ungar and Keller[1] reported on the change in crystal structure for irradiated polyethylene, while Gielenz and Jungnickel[2] and Jager et al.[3] discussed the change in lamellar structure for linear polyethylene irradiated to varying levels. The work of Keller and Machin[4] and Hill and Keller[5,6] focused on crystallization under stress of linear polyethylene crosslinked by irradiation. However, it is known that the use of high-energy radiation produces crosslinks preferentially in the amorphous phase and at the fold surface, meaning that inhomogeneous cross-linked systems are formed[7]. In addition, differences are known to exist between systems crosslinked in the solid and melt states using radiation[2].

Crosslinking may also be carried out chemically, usually by the addition of peroxides, which produce crosslinks upon thermal decomposition. Manley and Qayyum[8] reported on the variation of the physical and mechanical properties of linear polyethylene crosslinked using di-t-butyl peroxide. Coxon and White[9] made measurements on the internal stresses in chemically crosslinked linear PE. Previously, the most extensive study of the effect of crosslinking on growth kinetics and morphology in any polymer is due to Andrews et al.[10]. They studied *cis*-polyisoprene crosslinked from the vapour phase and found that microstructural impurities, in the form of crosslinks, influence the rate of secondary

nucleation. This is analogous to the 'copolymer effect' referred to by Sanchez and Eby[11]. However, the work of Andrews et al. did not consider the effect of the presence of the non-crosslinked fraction on the crystallization of the crosslinked matrix. The most complete study of the effect of chemical crosslinking on the crystallization of polyethylene is due to Kao and Phillips[12], Phillips and Kao[13], Gohil and Phillips[14,15] and Phillips and Vatansever[16]. This work involved basic studies of the crystallization process, thermal and annealing behaviour, and crystal structure of crosslinked low-density poly-ethylene and its gel and sol fractions. Although this study produced considerable advances in understanding the crystallization behaviour of the crosslinked polymer, it was hampered by poor understanding of the behaviour of the basic polymer and the fine scale of the polymer morphology. Linear polyethylene has a better-understood morphology, which gives rise to much larger spherulites and thicker lamellae, thus permitting more thorough investigation. As a complication, however, the crystallization behaviour of crosslinked linear polyethylene is influenced by the copolymer effect, whereas for the low-density polymer the degree of branching exceeded the degree of crosslinking by a large factor, thus eliminating the copolymer effect as a serious perturbation of the system.

In this and in an ensuing paper[17], the effect of crosslinking on crystal structure, melting behaviour and the crystallization process of linear polyethylene will be examined. This paper will consider crystal structure and perfection, crystallinity and the melting behaviour of the crosslinked systems. The related paper[17] will deal with bulk crystallization kinetics and subsequent considerations for secondary nucleation theory.

The following nomenclature will be used throughout: OPE = original linear polyethylene, containing no peroxide; S-* = extractable or sol fraction from crosslinked sample of *wt% peroxide (S-0.1 is the sol fraction from the 0.1 wt% crosslinked sample) X-* = unextracted cross-linked PE produced from * loaded PE; G-* = crosslinked, extracted fraction produced from * loaded PE.

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EXPERIMENTAL

Materials

The material used in all experiments was Sclairlink, supplied by DuPont of Canada, a powdered high-density polyethylene containing the peroxide bis(t-butyl peroxy-isopropyl)benzene, which is commercially available under the tradename Vul-Cup R® (VCR) from Hercules Inc. Sclairlink was used as a base material following the removal of the VCR. Values of M_w and M_n, determined for us by Dr J. M. Lambert of the Beckton–Dickinson Corp. using gel permeation chromatography, are 42 000 and 12 700, respectively.

Polyethylenes containing varying concentrations of VCR were prepared by first dissolving a known weight of VCR in methanol. A known weight of polymer was then added to the VCR/methanol mixture and allowed to stir for 1 h to ensure the complete mixing of the VCR and polyethylene. The methanol was then evaporated and the VCR/PE mixtures dried to a constant weight under vacuum. Specimens were compression moulded at 140°C for 4 min without any applied pressure followed by 5 min with a ram pressure of 10 ton, and cured at 210°C for 5 min with no applied pressure.

Extraction and swelling studies

Solvet extraction was carried out on the crosslinked polyethylene (XLPE) sample using the boiling xylene method. Thin films of the XLPE of known weight were immersed in boiling xylene (138°C) in a stainless-steel basket for 72 h. Afterwards the remaining portion of the film, known as the gel, was transferred into a xylene-containing jar and held at 110°C for 24 h to allow for the swelling of the crosslink matrix. The samples were transferred to weighing bottles for weighing, before being vacuum dried to constant weight. Estimates of percentage of extractables were obtained using the weight loss of the XLPE. The molecular weight between crosslinks of the gel was estimated using the Flory–Rehner equation.

Sol specimen preparation

Upon extraction of XLPE, a low-molecular-weight, uncrosslinked fraction, known as the sol fraction, remained dissolved in the xylene. The sol fractions were collected by mixing the xylene solution with cold methanol. This mixture was suction filtered and the sol collected and rewashed. Complete xylene/methanol removal was carried out under vacuum. The molecular weights of the sol fractions were determined using gel permeation chromatography (g.p.c.) by Dr J. M. Lambert of the Beckton–Dickinson Corp.

Melting studies

Samples used in melting studies were isothermally crystallized by first placing the samples in a constant-temperature silicone oil bath for 30 min at 160°C, and then transferring them to another constant-temperature bath held at the specified crystallization temperature for 24 h.

All melting experiments were carried out using the Perkin–Elmer DSC-7, the instrument being calibrated using the melting onset and heat of fusion of standard materials. A scanning speed of $10°C min^{-1}$ was used throughout.

Structural studies

A Rigaku X-ray diffractometer was used to determine the unit-cell parameters, degrees of crystallinity and line-broadening effects of the XLPE and gel system.

RESULTS

Extraction studies

The level of percentage of extractables depends upon the amount of VCR present before crosslinking occurs, as seen in *Table 1*. All systems were crosslinked for a time corresponding to $>99.9\%$ decomposition of VCR according to the data of the Hercules Corp.[18] We can be certain that the levels of extractables are caused by a distribution in the molecular weight of the original polyethylene (OPE) and not by the incomplete reaction of the VCR. The level of extractables decreases from 18% to 3% as the initial peroxide content is increased, showing that a larger portion of the OPE is incorporated into the crosslinked matrix.

The molecular-weight between crosslinks was determined from swelling studies, estimated using the Flory–Rehner equation, and found to decrease as the initial VCR content increased, as expected (*Table 1*). The crosslinking mechanism and chemical structure of the sol and gel fractions will be discussed in detail in a later paper.

The molecular weights of the sol fractions as determined through g.p.c. are presented in *Table 2*. They decrease with increasing VCR loading, as expected since increasing peroxide content results in increasingly shorter chains being incorporated into the crosslink matrix, meaning that only lower-molecular-weight molecules will remain uncrosslinked. However, the increase seen in M_w and M_z for the sol fractions of the highest VCR loadings may indicate that the percentage of the fractions due to highly branched, but still soluble, molecules is now greater than for lower levels of VCR.

Table 1 Percentage of extractables, molecular weight between crosslinks and average chain length between crosslinks as a function of VCR in pre-cured polymer

VCR (wt%)	Extractables (%)	MW between crosslinks $(\times 10^{-3})$	Average CH_2 units
0.1	17.9	17.3	1238
0.3	16.5	12.7	907
0.4	11.0	8.1	579
0.5	8.3	5.7	410
0.9	5.5	3.6	255
1.2	4.5	3.1	219
2.5	3.6	1.9	136
3.1	2.9	1.3	95

Table 2 Molecular-weight data of sol fractions

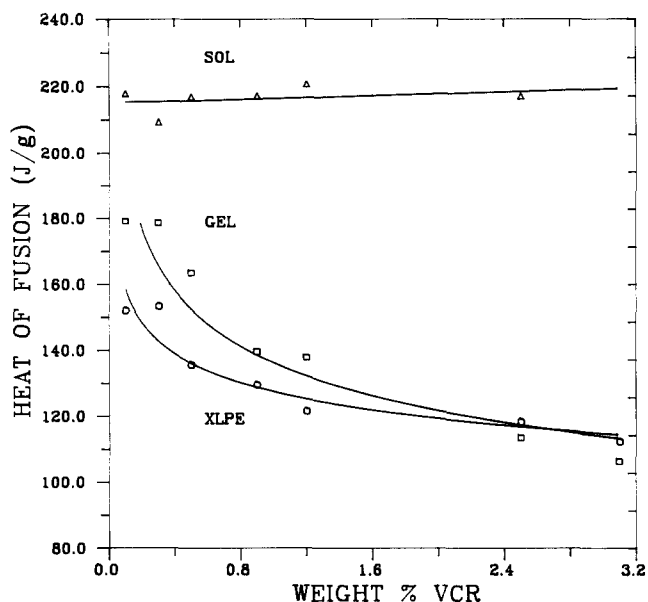| Sample	M_n	M_w	M_z	M_w/M_n
OPE	12 738	42 427	10 611	3.33
S-0.1	7 106	20 014	56 521	2.81
S-0.3	7 077	22 551	73 019	3.19
S-0.5	6 422	16 653	44 949	2.59
S-0.9	4 561	8 705	13 471	1.90
S-1.2	4 634	11 245	50 294	2.33
S-2.5	4 150	14 015	76 318	3.38

X-ray studies

The *a* and *b* lattice parameters of the unit cell show a small decrease with increasing crosslink density for the gel fractions, as shown in *Table 3*. Decreases in the *a* and *b* lattice parameters are most prominent for VCR loadings greater than 1.2%. This indicates that there is only a slight distortion in the crystal structure upon the introduction of crosslinks into the system, but it is not beginning to approach a hexagonal structure. Ungar and Keller[1] have reported the presence of a hexagonal phase in unextracted samples of linear polyethylene that have been exposed to high levels of radiation, but the chain lengths between crosslinks in that work are much shorter than those of our study (*Table 3*). Kao and Phillips[12] have reported a slight increase in the *a* and *b* parameters for quenched gel fractions of crosslinked low-density polyethylene (LDPE), while Kunert *et al.*[19] have observed considerable variation in the unit-cell parameters for crosslinking by several peroxides. The variations observed showed both increases and decreases in the *a* and *b* parameters depending on the thermal history of the system. Line-broadening studies may be used to estimate lateral crystal sizes. The accuracy of our methods are such that exact calculations may not be made; however, halfwidths give a qualitative impression of the lateral crystal sizes. *Table 3* shows that the halfwidth of the (1 1 0) peak is relatively constant for all gel fractions. Although the error may be quite high, it appears that no major distortion of the crystal structure has occurred upon the introduction of crosslinks into the system. Kao and Phillips[12] reported a large increase in broadening as crosslink density was increased in both XLPE and gel fractions of crosslinked LDPE. They suggested that this behaviour was due to the presence of branches in the low-density polyethylene, which control the lamellar thickness.

The degrees of crystallinity were determined from 2θ scans using the method of Nichols[20]. Crystallinity decreases as crosslink density increases, the decrease being most prominent for the higher-crosslink-density systems of the gel fractions, as seen in *Table 3*. Kunert *et al.*[19] found the crystallinity of their original LDPE to be 42% and of the crosslinked PE to be 40% when chemically crosslinked using dicumyl peroxide (DCP) with loadings ranging from 0.5 to 2.5%. Kao and Phillips[12] similarly found that the crystallinity of chemically crosslinked LDPE did not change very much (approximately 47%) for DCP loadings below 3%. However, as the DCP content was increased beyond this point, the crystallinity decreased drastically. They attributed this behaviour to a distortion in the crystal structure due to the increase in the crosslink density. Gielenz and Jungnickel[2] reported a limiting crystallinity

Figure 1 Heats of fusion of sol, XLPE and gel fractions *versus* weight per cent VCR in pre-cured polymer

in irradiated linear polyethylene at a similar level to that of Kao and Phillips[12]. Thus, while the above studies suggest that the same level of crystallinity is reached at high levels of crosslinking for both low-density and linear polyethylene, such high levels of crosslinking were not reached in this study. The high levels of crystallinity parallel the constant values found in line broadening in that a relatively high level of crystal perfection is maintained. It is only at the highest levels of crosslinking, where the molecular length between crosslinks approaches lamellar thickness values, that crystallinity begins to decrease rapidly and approach the values reported above. Thus it appears that even higher levels of crosslinking are necessary than those generated here in order to reach the reported low levels of crystallinity in other studies.

Heats of fusion

The heats of fusion of the sol, XLPE and gel fractions were estimated by integration of d.s.c. endotherms. The heat of fusion of a crystalline polymer depends upon its crystallinity, as well as its crystal perfection. The heats of fusion of the sol, XLPE and gel fractions are plotted in *Figure 1* as a function of the initial VCR loading. A decrease in the heats of fusion of the crosslinked systems indicates a reduction in the crystallinity, and presumably a lowering of the crystal perfection. It is possible to determine the latent heat of fusion of a perfect crystal since both the crystallinity and the heat of fusion are known. For linear polyethylene, it is generally accepted that the latent heat of fusion of a perfect crystal is 289 J g^{-1}. The latent heats of fusion of the gel fractions were found to decrease from 243 to 178 J g^{-1} with increasing crosslink density. A reduction in the latent heat of fusion suggests that chain defects may be included within the lamellar crystalline lattice, or higher-than-normal surface free energies are active.

Non-isothermal crystalline behaviour

Qualitative information on crystallization behaviour may easily be obtained through non-isothermal crystallization studies. In this study all samples were held at
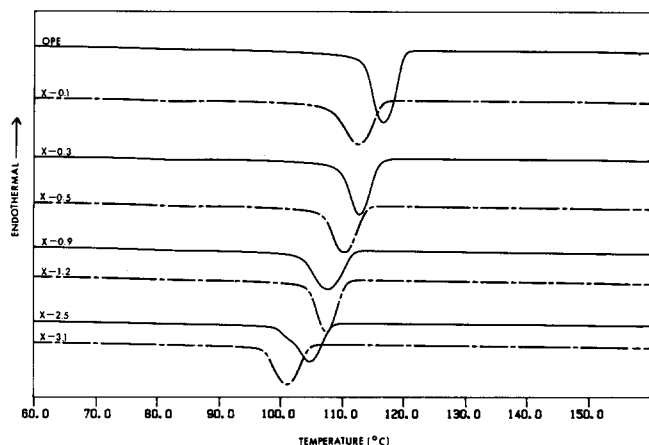
Table 3 Crystallinity, halfwidth and lattice constants of crosslinked systems

Sample	Crystallinity (%)	Halfwidth (1 1 0) (deg)	*a* (Å)	*b* (Å)
G-0.1	73.8	0.488	7.28	4.86
G-0.3	79.9	0.650	7.39	4.94
G-0.5	80.9	0.463	7.41	4.97
G-0.9	74.6	0.488	7.27	4.85
G-1.2	75.2	0.506	7.31	4.86
G-2.5	65.3	0.450	7.28	4.92
G-3.1	59.9	0.606	7.24	4.78

Figure 2 Non-isothermal crystallization behaviour of XLPE

Table 4 Crystallization peak temperatures of crosslinked systems

VCR (%)	T_c (°C)	
	XLPE	Gel
0.1	112.47	112.30
0.3	112.71	112.84
0.5	110.19	110.42
0.9	107.71	108.29
1.2	107.36	107.68
2.5	104.65	103.28
3.1	101.03	99.40

160°C for 5 min before being cooled at a rate of 10°C min^{-1}. Exotherms obtained for various VCR loadings of the XLPE may be seen in *Figure 2*. Similar behaviour is followed in the non-isothermal crystallization of the gel fractions. The peak temperature decreases from 116.5°C for OPE to 101°C for X-3.1 (molecular weight between crosslinks of 1300). The overall behaviour reflects two phenomena: (a) an increase in the imperfections present in the system, and (b) a decrease in the crystallinity of the system. There is only one peak under these conditions, indicating co-crystallization of the sol and gel fractions. *Table 4* lists the crystallization maxima for both the XLPE and gel fractions, it being apparent that the presence of the sol fraction affects the crystallization process of the gel fraction. For VCR loadings of 1.2% or less (molecular weight between crosslinks of 3100), the sol has no apparent effect on the recrystallization temperature of the XLPE by comparison with that of the gel. However, at higher levels of crosslinking, crystallization of XLPE occurs at temperatures 1 to 2°C higher than is possible in the gel fraction. Although the sol content is only about 3% for VCR loadings greater than 1.2, the sol is able to raise the crystallization temperature of XLPE by several degrees. At lower crosslink densities, the sol fraction has quite a different effect on the crystallization temperature. It would be expected that the presence of greater amounts of the sol molecules would result in the crystallization of XLPE occurring several degrees higher than is possible in the gel fraction. This is not the case, as the higher levels of extractables inhibit the crystallization process of the crosslinked matrix, and thus show no apparent effect on the crystallization temperature of XLPE.

Melting studies

Isothermal crystallization may be used to determine whether or not multiple melting is possible in polymeric systems. Multiple melting in OPE and the sol fractions is to be expected since the mobility of the chains is not restricted. The occurrence of multiple melting in the crosslinked systems may be due to a naturally occurring distribution of crosslinks in the material, but it also indicates that molecular rearrangement is possible in these systems. Multiple melting in the gel fractions of crosslinked LDPE was not observed by Kao and Phillips[12]. Gohil and Phillips[14,15] found that the lamellar thickness of their original linear PE was limited to approximately 140 Å by the branching levels, so it is possible that the effect of crosslinking was to limit further the maximum thickness attainable so that thickening is not possible.

Most interesting in these melting studies was the effect of the sol fraction on the crystallization process of the gel fraction in XLPE. The melting points of the sol, XLPE and gel fractions of the 0.1 loaded systems are centred about 131°C when crystallized at 115°C (*Figure 3*) and at 132.5°C when crystallized at 121°C (*Figure 4*). Thus the sol fraction does not influence the melting temperature of X-0.1 (molecular weight between crosslinks of 17 300), and the small number of crosslinks does not significantly reduce the melting temperature of the gel.
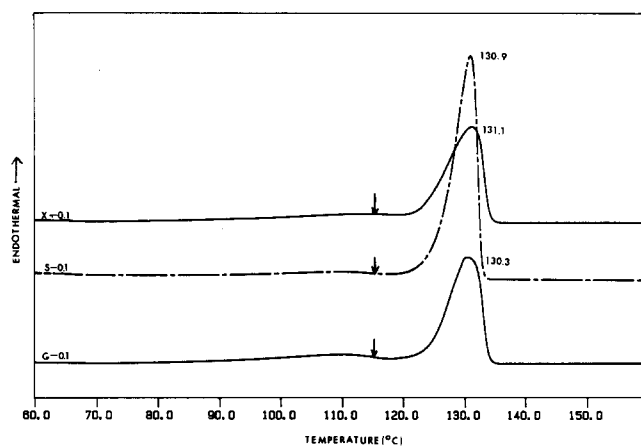

Figure 3 Melting behaviour of 0.1 systems isothermally crystallized at 115°C ($MW_x = 17\,300$)
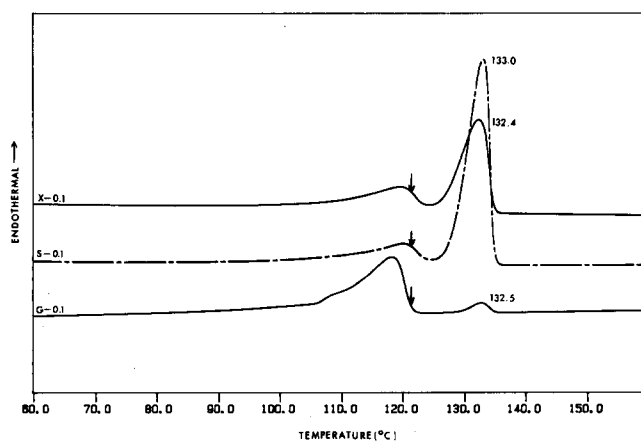

Figure 4 Melting behaviour of 0.1 systems isothermally crystallized at 121°C ($MW_x = 17\,300$)

However, the relative heights of these peaks vary with the crystallization temperature, suggesting that the portion of the gel incorporated into the crystals is a function of the crystallization temperature. The larger melting peak of X-0.1 at 121°C is due to the presence of the sol fraction, as the sol may act as a nucleating agent for the gel, resulting in an increase in the amount of crosslinked material that is able to crystallize at this temperature.

The melting behaviour of the 0.9 loaded systems differs from that of the 0.1 systems. The most prominent effect of increased crosslinking is a reduction in the highest temperature at which crystallization can occur. A comparison of the melting temperatures of the crosslinked systems shows that the melting peak of X-0.9 (molecular weight between crosslinks of 3600) is 1 to 2°C higher than that of G-0.9 for all crystallization temperatures, being intermediate between the peak temperatures of S-0.9 and G-0.9 (*Figures 5* and *6*). The higher melting temperature of X-0.9 is due to the presence of the sol fraction. For crystallization temperatures between 109 and 116°C (*Figure 5*), the peak heights of X-0.9 and G-0.9 are similar, implying that melting in X-0.9 is due largely to the gel fraction. This suggests that it is possible for a large portion of the gel to be incorporated into the crystals for crystallization temperatures in this range. At 119°C (*Figure 6*), the large melting peak of X-0.9 is due
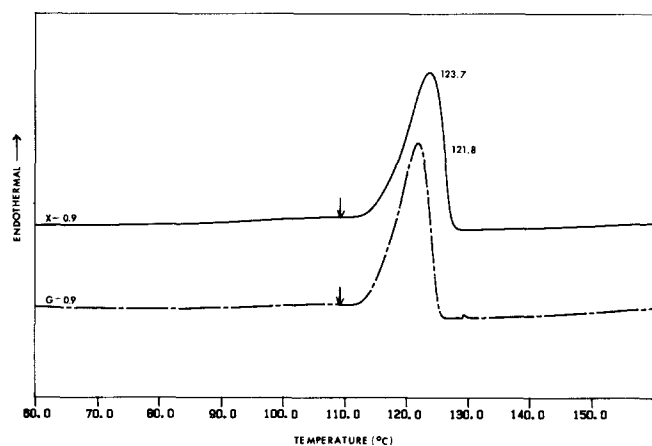
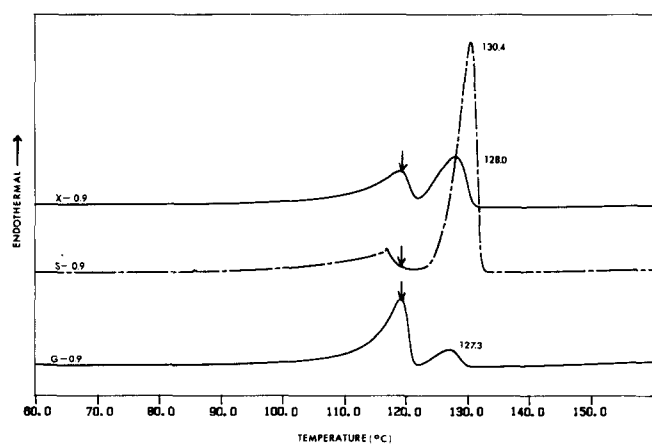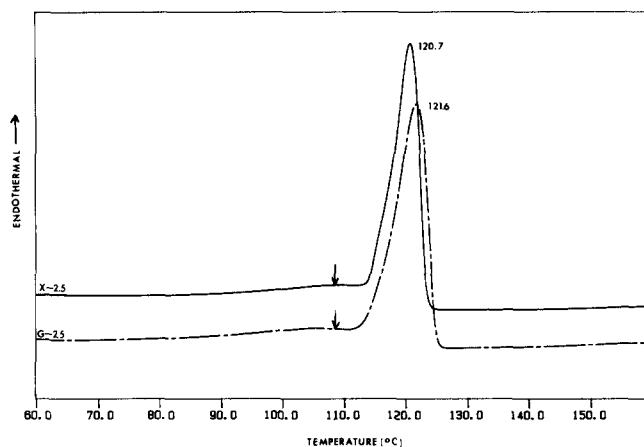**Figure 7** Melting behaviour of 2.5 systems isothermally crystallized at 108°C ($MW_x = 1900$)

Figure 8 Melting behaviour of 2.5 systems isothermally crystallized at 116°C ($MW_x = 1900$)

Figure 5 Melting behaviour of 0.9 systems isothermally crystallized at 109°C ($MW_x = 3600$)
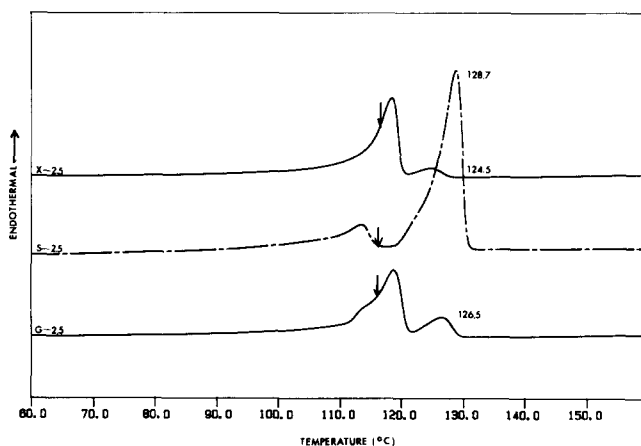
Figure 6 Melting behaviour of 0.9 systems isothermally crystallized at 119°C ($MW_x = 3600$)

to the presence of the sol fraction. It is in this crystallization temperature range (117 to 120°C) that rapid sol and slow gel crystallization occur[20,21], again suggesting that the sol may act as a nucleating agent for the gel.

The melting behaviour of the 2.5 loaded systems (molecular weight between crosslinks of 1900) differs from the behaviours observed for the 0.1 and 0.9 systems. *Figures 7* and *8* show that the melting peaks of G-2.5 are about 1 to 2°C higher than the melting peaks of X-2.5 when crystallized at 108 and 116°C, respectively. This behaviour is true at all crystallization temperatures. The relative heights of the peaks of X-2.5 and G-2.5 are similar at 108°C, indicating that the sol fraction is not as effective a nucleating agent for the gel fraction, as it was in other specimens. It is possible that the sol fraction acts to reduce the observed melting point of X-2.5, or that the sol fraction inhibits the crystallization process of the gel.

DISCUSSION

X-ray diffraction and subsequent analyses of the results demonstrate several important points about the crosslinked systems. It is important that the introduction of crosslinks does not radically decrease the crystallinity of the system until high values of crosslink density are achieved. This may be a result of the crosslinks limiting

the lamellar thickness but also generating more crystals through branching mechanisms. It is interesting to note that the percentage crystallinity of G-3.1 has a value approaching that of low-density polyethylene. This is not surprising when considering that the number of methylene units between crosslinks (95 CH_2 units) in G-3.1 is close to the number of methylene units between branch points in low-density polyethylene (63 CH_2 units)[12]. As mentioned earlier, Gohil and Phillips[14] found the lamellar thickness of low-density polyethylene to be limited by the branching levels in the polyethylene. It is possible that the crosslinks in linear polyethylene function similarly to branches in low-density polyethylene in controlling the lamellar thickness. Thus the high crystallinity values can be understood in terms of the molecular length between crosslinks that is able to crystallize. Studies are currently being performed to determine the variation of lamellar thickness with crosslink density.

Halfwidth and lattice-parameter calculations show that there are no large-scale crystal distortions in the gel fractions. Decreases in the *a* and *b* parameters of the unit cell are most prominent at the highest crosslink densities, where the degree of crystallinity begins to decrease. The most prominent crystal distortions would be expected to occur at higher crosslink densities. D.s.c. studies support this behaviour from the sharpness of the melting endotherms, while transmission electron microscopy does not reveal any large-scale orientation[21].

It is apparent that the sol fraction has quite a significant influence on the crystallization and melting behaviour of crosslinked linear PE. As seen from melting studies of isothermally crystallized systems, the melting behaviour of XLPE has a complex dependence on the crystallization temperature, sol content and crosslink density of the system. Kinetic data, which are presented in a separate paper[17], show that the rate of crystallization of the sol is 100 times greater than that of the gel at 121°C for the 0.1 loaded systems. A similar comparison of rates for higher crosslink densities shows an even higher ratio of rates. The mobility of the sol fraction, which is much greater than that of the gel, results in its self-crystallization. It is clear that the sol crystallizes separately from the gel at higher crystallization temperatures, thus influencing the number of high-temperature-melting crystals, as well as their melting temperatures. Calculation of the equilibrium melting points of the sol and gel fractions is not an easy task. But using standard plots of T_m versus T_c leads to an estimate of the melting point of the sol to be approximately 3°C higher than that of the gel (144°C compared to 141°C). As a result, two different supercoolings are effective at the same crystallization temperature, thus providing further support for self-crystallization of the sol.

CONCLUSIONS

The level of extractables and chain length between crosslinks are inversely proportional to the amount of crosslinking agent used.

Relatively high values of crystallinity are maintained by the crosslinked systems, with the most prominent decrease in crystallinity occurring for the highest crosslink densities. High degrees of crystal perfection have been inferred from halfwidth and lattice-parameter calculations.

The melting behaviour of isothermally crystallized samples is dependent on the level of extractables, crosslink density and crystallization temperature. Multiple melting is observed in the crosslinked systems.

The chain length between crosslinks is believed to have a major influence on crystallinity, crystal perfection and melting behaviour.

ACKNOWLEDGEMENTS

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