Crystallinity in chemically crosslinked low density polyethylenes: 1. Structural and fusion studies

Y. H. Kao and P. J. Phillips*
Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112, USA

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The level of extractables, crystallinity, unit cell parameters and other structural information have been obtained for low density polyethylene crosslinked using weight fractions of dicumyl peroxide from 0.9 to 6.8%. Since the presence of the extractable fraction influences the overall structure as well as the crystallization and melting behaviour studies have been carried out of the gel and sol fractions in addition to the as-crosslinked polymers. Evidence suggests that when crystallized above 100°C the sol fraction of the as-crosslinked polymer either self-crystallizes or selectively crystallizes with the most linear section of the gel network.

(Keywords: crystallization; polyethylene; structure; fusion studies; kinetics)

INTRODUCTION

Both high density and low density crosslinked polyethylenes have become commonly used industrial polymers in recent years. The effects of crosslinking on the crystallization process are of relevance to our understanding of crystallization in general. Of particular interest is the effect of a crosslinked network on the crystallization process through its influence on diffusional mobility and also on the probability of nucleation.

Most of the considerable effort expended in the past has been aimed at studying the influence of various types of radiation on crystalline morphology and structure[1]. The effects of β- and γ-radiation on linear polyethylene have received major attention; however, studies have generally considered irradiation of the solid state and crystallization studies of the crosslinked systems are generally lacking. Although details of the crosslinking mechanism remain matters of controversy, the overall effects on the solid state structure are well established. Low density polyethylene has received some attention but no extensive studies have been carried out[2].

Much of the interest in irradiation studies stemmed from the industrial importance of irradiation processing of manufactured items for dimensional stability as well as from interest in ageing effects on polyethylene electrical insulation in nuclear reactors. Over the past decade major technologies have developed involving the crosslinking of molten polymers followed by their subsequent crystallization on cooling. The major polymer of interest here is low density polyethylene, which is extensively used as high voltage insulation. Also high density polyethylene is used in melt crosslinked form as hot water piping. Recently there have been major technological advances in crosslinking of fibres immediately after extrusion and prior to solidification. All of these processes involve crosslinking of the polymers in the molten extruded state using chemical crosslinking agents. In practice there are two basic crosslinking processes in use at the present. The more usual involves crosslinking in the melt immediately after extrusion through the decomposition of dicumyl peroxide. Various forms of heat transfer are used to achieve decomposition of the crosslinking agent. Most often encountered is the use of steam at 410°F and 250–270 psi, whereby a layer of condensed water at *ca.* 400°F forms on the external surface of the extrudate. Another method is the use of thermal radiation from pipe surfaces at 700°F in the presence of an inert gas, typically nitrogen. Under these conditions crosslinking occurs in the melt, which may be oriented due to the extrusion conditions. A newer technique, the so-called Sioplas process, uses a silicone based crosslinking agent. Here the extruded product, already cooled to room temperature, is exposed to hot water, reaction of the silane with water serving to produce the crosslinking reagent. Of necessity this process involves a crystalline or partially molten polymer, dependent on the cure temperature and the melting curve of the polymer in question.

Recent research on crosslinking by irradiation of linear polyethylene has shown major differences between solid state and melt irradiation[3]. These differences were major in both wide angle and small-angle X-ray studies. Such effects should not be surprising since the influence of crosslinks on crystallization should be major. Studies of chemically crosslinked polyethylenes are few. Manley and Qayyum[4,5] have studied linear polyethylene crosslinked with ditertiary butyl peroxide but most attention was paid to mechanical property studies. As part of a larger programme concentrating on nuclear magnetic resonance studies of low density polyethylene crosslinked with various peroxides Kunert and coworkers[6] carried

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* To whom correspondence should be addressed; present address: Department of Materials Science and Engineering, University of Tennessee, Knoxville TN 37996-2200, USA.

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out some structural evaluations. The crystallization process has not been treated explicitly in any of the above mentioned research.

Much of the literature on the influence of crosslinking on crystallization has been aimed at crystallization under stress[7]. A large fraction of the research has been carried out on rubbers[8-10] or on linear polyethylene[11-13]. Generally, irradiation of various types, often carried out in the solid state, has been used as a means of producing the crosslinks. High energy radiation is known to produce crosslinks preferentially in the amorphous phase and in the fold surfaces[1] so that homogeneously crosslinked networks were not formed. Additionally irradiation crosslinking produces *ca.* 20% chain scission[14] whereas chemical crosslinking with dicumyl peroxide produces only 5% chain scission[15]. The most extensive studies of the influence of crosslink density on isotropic crystalline morphology and the kinetics of crystal growth are those of Andrews *et al.*[16] for cispolyisoprene chemically crosslinked from the vapour phase. The experimental procedures necessary to that research precluded extraction of the uncrosslinked molecules, whereas in many other cases extraction was not attempted or not essential for the studies being contemplated. It is, therefore, simply not known how an unstretched polymer network, devoid of soluble low molecular weight molecules, actually crystallizes. Many studies have not included an estimation of the crosslink density and those involving radiation have invariably quoted simply the radiation dose. The molecular weight distribution of the initial polymer is of critical importance in determining the level of extractables, yet the character of the extractable fraction of the crosslinked polymer has usually been ignored. The recent study by Gielenz and Jungnickel[3] of irradiation crosslinking in molten and solid linear polyethylene did consider both extracted and unextracted materials. However, none of the studies of crosslinked polyethylene have considered the determination of crystallization kinetics or the specification of the resultant morphologies.

The studies of Andrews *et al.*[16] showed that in the crosslinking of a linear polymer one of the effects of crosslinks was similar to that of isomerization. In other words the level of microstructural impurities influences crystallization through a copolymer effect[17]. Such effects are not due to the network, *per se*, and, whilst important, may obscure the true network effects. In low density polyethylenes the degree of branching is such that the number of branches greatly exceeds the number of crosslinks even for relatively high crosslink densities. Unlike linear polyethylene, therefore, low density polyethylene provides an opportunity for the unambiguous determination of the effects of a network on crystallization.

In this paper and its companions, studies of the effects of controlled crosslink density on many aspects of crystallization will be presented. Crystal structure, morphology, fusion, crystallization kinetics and annealing will all be considered for low density polyethylene crosslinked using dicumyl peroxide. It will be observed that many new and novel effects occur, some of which can be explained only in a tentative manner at the present time. The first four papers here published simultaneously, deal with the crystallization process. In this, the first paper, we will be concerned with aspects of essential crystallinity specification such as crystal structure, crystal perfection and melting points. The second paper will be concerned with bulk crystallization kinetics and the third and fourth papers with morphology. It will be demonstrated that crystallization from the melt of a randomly crosslinked network produces structures very different from those characteristic of irradiation of polyethylene in the solid state.

For the sake of clarity the following abbreviated nomenclature will be used throughout. OPE = original LDPE with dicup removed; NXLPE = loaded but uncured polyethylene, (e.g. NXLPE-2 is loaded with 2% w/w dicup); XLPE = crosslinked but unextracted polyethylene; SOL = extractable or sol fraction (e.g. SOL-2 is the extractable fraction from XLPE-2); GEL = crosslinked fraction, (e.g. GEL-2 is the crosslinked fraction from XLPE-2).

EXPERIMENTAL

Materials

The basic polymer was a crosslinkable low density polyethylene containing 2% dicumyl peroxide (Union Carbide HFDE 4201). It was used as provided and also as a base material following removal of the dicumyl peroxide. Values of M_w and M_n, determined using size exclusion chromatography, are 58 800 and 11 500 respectively. The average number of CH_3 units per 1000 carbons is 16 from infra-red spectroscopy.

Preparation of polyethylenes containing dicumyl peroxide concentrations other than 2% was accomplished by first dissolving the polymer in xylene and precipitating in powder form. The powder was then dried in a vacuum oven and the dicumyl peroxide removed by extraction with methanol. The required amount of dicumyl peroxide was added as a methanolic solution to the polyethylene powder, which was stirred as the methanol evaporated to ensure a uniform distribution. Samples so prepared were then dried to constant weight in a vacuum oven. Uniformity of distribution of dicumyl peroxide as well as absence of methanol was confirmed through the use of Fourier transform infra-red spectroscopy (*FT*i.r.). Specimens were then compression moulded at 150°C for 3 min with a ram pressure of 300 psi and cured at 200°C for 3 min at 5000 psi.

Extraction studies

Several methods of solvent extraction have been used for crosslinked polyethylene, the boiling xylene method of Kunert *et al.*[6] appearing most effective. Studies were carried out on the effect of time of extraction for our thin films. It was found that constant weight was not approached until the extraction time neared 48 h.

We have therefore used a 72 h extraction in boiling xylene (138°C) rather than the 4 h extraction of Kunert *et al.*[6]. The recommended ASTM method[18] involves a 12 h extraction of the material in powder form in a Soxhlet and so is not appropriate for this study. A long dwell time at 138°C might have produced oxidation, however, *FT*i.r. studies did not detect carbonyl groups at concentrations higher than the very low initial levels of the starting material.

Crystallization procedures

Studies of crystallization kinetics will be described in detail in the following paper. Here we wish to report the effects of crosslink density on dynamic crystallization in the differential scanning calorimeter and the resultant melting behaviour. Also to be reported are the effects of crosslink density on unit cell parameters, X-ray line broadening, heat of fusion and crystallinity. Specimens for such experimentation were prepared by constant temperature crystallization in thermostatically controlled baths after holding the specimens in the molten state at 150°C for 15 min.

Differential scanning calorimetry

A Perkin Elmer DSC2 was used throughout and at a scanning speed of 10°C/min unless otherwise stated. Normal calibration procedures involving standard materials were used.

X-ray diffraction studies

A Diano X-ray generator was used in conjunction with a Diano automated diffractometer. Diffractometer traces were used in the estimation of crystallinity and unit cell parameters. The line broadening effects were also extracted from the diffractometry data.

RESULTS

Extraction studies

The percentage extractables (*Table 1*) depends very much on the level of dicumyl peroxide present. All samples were cured for an amount of time corresponding to better than 99.9% decomposition of dicumyl peroxide using the data of Harpell and Walrod[19]. We can, therefore, be confident that extractable levels are caused by the broad distribution of molecular weights in the original low density polyethylene (OPE) and not by incomplete reaction of the crosslinking agent. The highest extractable content (SOL fraction) occurs for the samples crosslinked with 0.9% dicup, as might be expected. As dicup content is increased the SOL fraction decreases rapidly up to 3% dicup after which point only a small decrease is observed, there being only a 2% difference in SOL fraction between the polymers produced using 3% and 6.8% dicup.

The molecular weights of the SOL fractions have been determined[15] using intrinsic viscosity and the molecular weight between crosslinks using linear swelling. The results are presented in *Table 1*, but will not be discussed in detail here since they will be the subject of another paper[15] dealing exclusively with the crosslinking mechanism and the detailed chemical structure of the SOL and GEL fractions produced as a function of dicup content.

Table 1 Extraction studies data

% Dicumyl peroxide	Sol fraction (%)	*MW*[a] of SOL	Swelling ratio in xylene at 100°C	*MW*[b] between crosslinks
0	—	31.4×10^3	—	—
0.9	39	—	17.8	110×10^3
2.0	18.3	8.38×10^3	13.3	36.2×10^3
3.0	9.0	—	12.8	32.09×10^3
4.0	8.8	6.18×10^3	6.2	9.35×10^3
5.0	7.0	—	5.7	7.76×10^3
6,8	6.0	3.85×10^3	3.9	3.53×10^2

[a] M_n from intrinsic viscosity using method of Harris, I. *J. Polym. Sci.* 1952, **8**, 353

[b] Calculated using $\chi = 0.33$ for linear polyethylene (Tung, L. H. *J. Polym. Sci.* 1957, **34**, 333)

X-ray studies

The *a* and *b* parameters of the unit cell both vary with the level of crosslinking. In *Figure 1* are presented data for quenched GEL fractions as a function of initial dicup loading. It can clearly be seen that the *a* parameter remains approximately constant except for the highest dicumyl peroxide loadings, where an increase of 0.15 Å can be detected. The *b* parameter behaves in a similar manner to the *a* parameter but shows about half the increase in *a* at high loading. The crystal structure is therefore distorted by the presence of crosslinks but is not yet approaching a hexagonal structure. Orth and Fischer[20] and later Ungar and Keller[21] have reported the presence of a hexagonal phase in unextracted samples of high density polyethylene that had been subjected to high levels of radiation damage. Although Gielenz and Jungnickel[3] carried out extensive X-ray studies of particle sizes from line broadening for melt irradiated polyethylene, they did not report the variations in unit cell parameters. There is no *a priori* reason for expecting the unit cell parameters of melt crosslinked polyethylene to mirror those of the solid state crosslinked polymer; however, the data shown in *Figure 2* follow the trends observed for irradiated linear polyethylene. Some data are available from the studies of Kunert *et al.*[6] where considerable variation in unit cell parameters was observed for crosslinking by several peroxides. Some of these variations were in the opposite direction to those reported here, especially when different thermal treatments were involved. We have also observed similar variations for isothermal crystallizations; however, it is difficult to make definitive statements for these low crystallinity polymers without conducting structure factor analyses. Gielenz and Jungnickel[3] reported decreases in the intensity of the (200)/(110) ratio, which presumably are related to setting angle changes. The more extensive experimentation necessary for structure factor analyses is currently underway and will be reported at a later date.

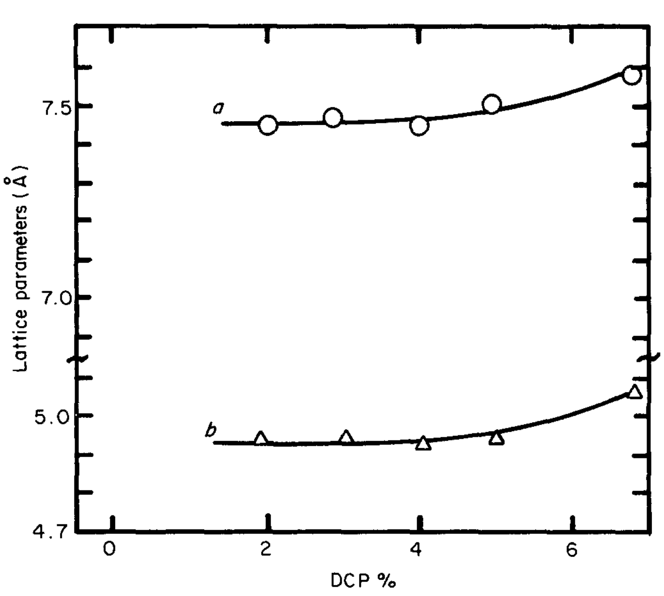

Figure 1 Unit cell parameters, *a* and *b*, of gel fractions (quenched) as a function of dicumyl peroxide concentration

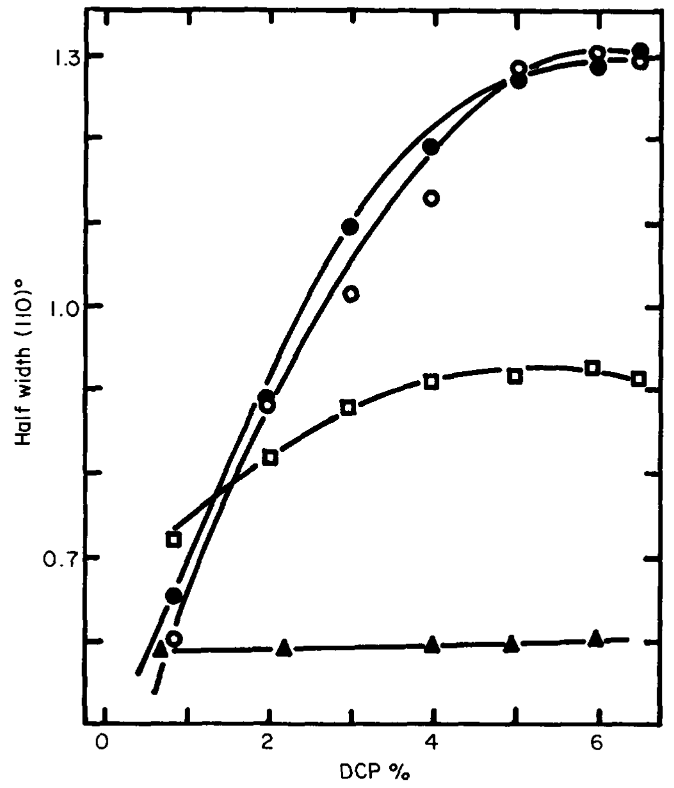

Figure 2 Half width of 2θ(110) for samples crystallized at 92°C (□, NXLPE; ○, XLPE; ▲, SOL; ●, GEL)

Our corrections are not sufficiently accurate to be able to calculate lateral crystal sizes from line broadening studies; however, half widths give a good qualitative impression of what is happening. In *Figure 2* can be seen the variation of half width *versus* initial dicup loading for NXLPE, XLPE, GEL and SOL. The SOL is well behaved showing no change in a relatively narrow peak. NXLPE shows some increase with loading. Both XLPE and GEL show a very large broadening as crosslink density is increased, which appears to become constant at about 4% dicup loading. These results show that the SOL forms thicker or more perfect crystals than even the original LDPE. The thickness or imperfection of crystals in the crosslinked polymers is determined largely by the GEL fraction for this temperature of crystallization. Although there is a respectable error involved, it appears that all materials show similar line broadenings at minimal levels of crosslinking.

The levels of crystallinity were determined from the intensity *versus* θ curve using standard methods[22], the results being summarized in graphical form in *Figure 3*. NXLPE and SOL both give levels independent of dicup loading, the SOL being slightly higher at 58%. Both the XLPE and GEL show a catastrophic decrease as dicup loading is increased up to 6%, the final level being at about 25% (i.e. half of that before crosslinking). This loss of crystallinity parallels the increase in line broadening and change in the unit cell parameters, indicating that less perfect crystals with increasingly distorted unit cells are produced as crosslink density increases. Gielenz and Jungnickel[3] reported a limiting crystallinity at a similar level in irradiated high density polyethylene. They interpreted their line broadening studies as a decrease in the lamellar thickness and also concluded that internal disorder increased, basing this on line broadening calculations. It therefore appears that one effect of crosslinking is that both LDPE and HDPE tend to the same level of crystallinity at high levels of crosslinking.

Heats of fusion

Integration of thermal analysis data is a commonly used technique for the estimation of crystallinity if the latent heat of fusion of a perfect crystal is known. For HDPE it is generally accepted that a value in the neighbourhood of 69 cal g^{-1} is appropriate. For LDPE the situation is not so clear since the presence of branches together with crystalline imperfections lead to values of the heat of fusion of crystals which are significantly lower than the value for the more perfect HDPE crystals. Measured values of the actual heats of fusion of NXLPE, XLPE, SOL and GEL are presented as a function of dicup loading in *Figure 4*, where it can be seen that the data tend to mirror the crystallinity data obtained using X-ray diffraction. Such values are virtually independent of crystallization temperature. Since values of crystallinity based on X-ray studies are known for the specimens, we have used our data to estimate the latent heats of fusion of the specimens as a function of crosslink density. Surprisingly, there is no significant dependence of the values on type of material or on crosslink density. The spread of values over all specimens is from 47.0 to 49.5 cal g^{-1}, the mean is 48.5 and the standard deviation is 0.6. All the specimens therefore, regardless of the amount of disorder produced by crosslinking, retain the latent heat of fusion characteristic of the original LDPE and presumably determined by the degree of short chain branching. The situation may not be the same in a linear polyethylene such as those studied by Gielenz and Jungnickel[3], where the number of crosslinks per 100 carbon atoms is not small compared to the number of branch points per 100 carbon atoms.

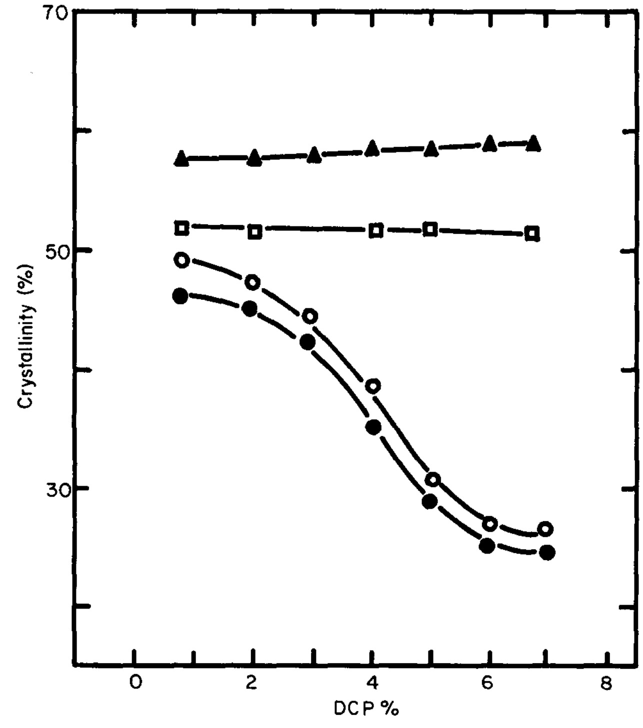

Figure 3 X-ray crystallinity as a function of dicumyl peroxide concentration (□, NXLPE; ○, XLPE; ▲, SOL; ●, GEL)

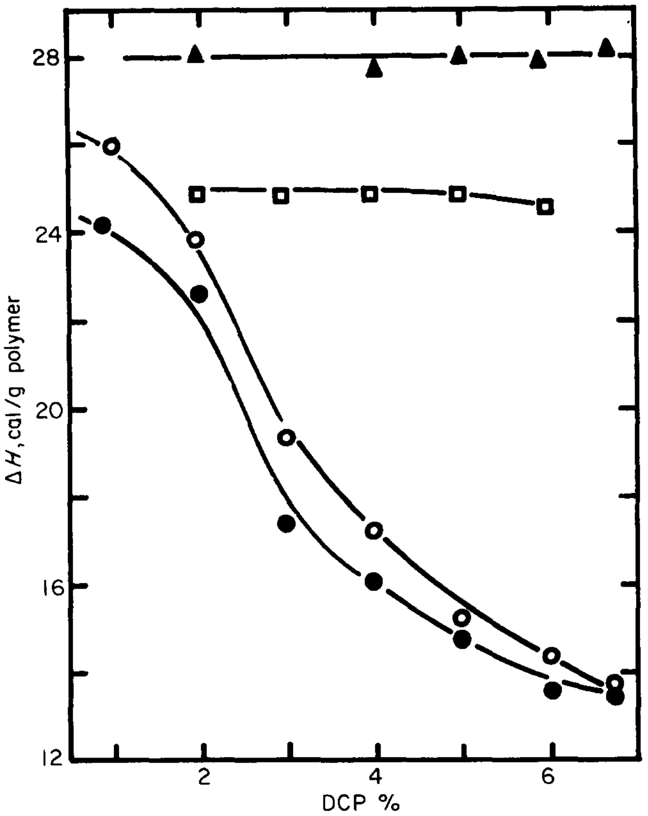

Figure 4 Measured heats of fusion of samples as a function of dicumyl peroxide concentration (□, NXLPE; ○, XLPE; ▲, SOL; ●, GEL)

Nonisothermal crystallization behaviour

Here specimens were cooled at a rate of 10°C/min and the crystallization endotherms observed using the differential scanning calorimeter. The results, which can be seen in *Figure 5*, show that the recrystallization temperature decreases continuously as dicup level is increased. There is only one peak under these conditions, indicating a co-crystallization process between the GEL and SOL fractions. In *Figure 6* are plotted the crystallization temperature maxima of XLPE and GEL as a function of dicup content. Although the trends are the same it is clear that the presence of the more mobile SOL fraction permits the crystallization process of the XLPE to occur at a temperature 2 to 3°C higher than is possible in the GEL and with a dependence on the degree of crosslinking. In other words, the effect of the SOL on the recrystallization temperature is greatest for the more highly crosslinked systems even though the SOL fraction is smaller. If the elevation of the recrystallization temperature is normalized for SOL content then it is found that the effect for 6.8 % dicup is 9 times greater than it is for 0.9 % dicup (58.3°C cf. 6.4°C at SOL fraction = 1). It also has to be borne in mind that the crystallinity of the isolated SOL phase is 58 % whereas that of the GEL phase is 25 % in 6.8 GEL and 47 % in 0.9 GEL.

It can therefore be concluded from even this cursory study that the SOL fraction has considerable influence on the crystallization behaviour of an unextracted material and it cannot be assumed that studies of an unextracted polymer will be indicative of the behaviour of a crosslinked network.

Fusion studies

Specimens studied here have been crystallized isothermally to determine if multiple melting behaviour

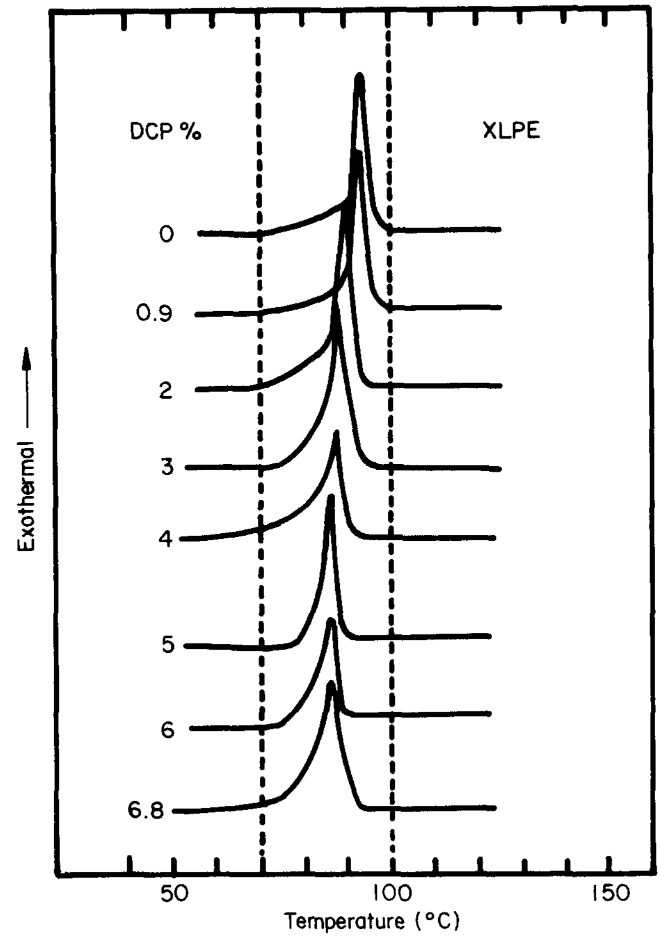

Figure 5 Nonisothermal crystallization kinetics of crosslinked polyethylene for various dicumyl peroxide concentrations (as directed)

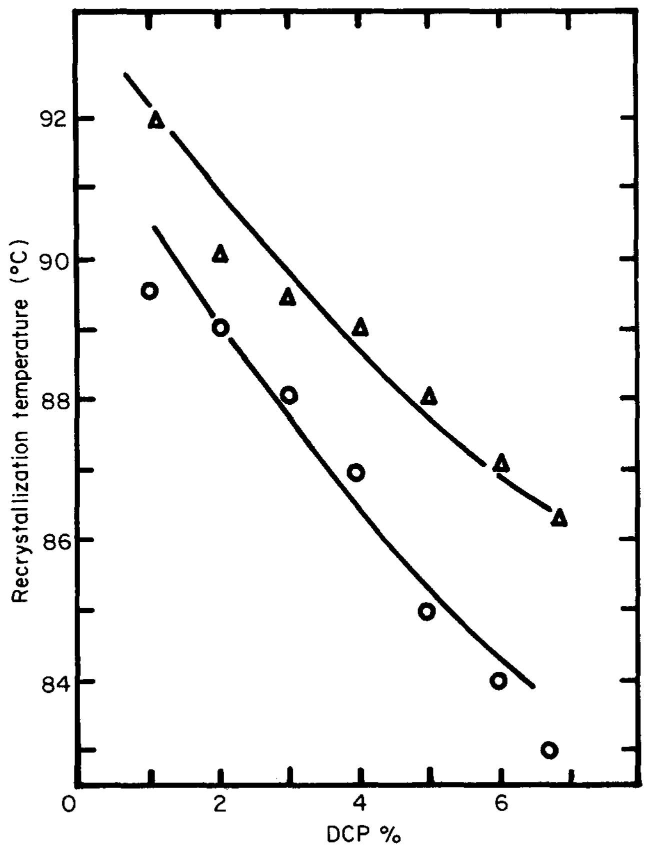

Figure 6 Recrystallization temperature maxima of XLPE and GEL as a function of dicumyl peroxide concentration (△, XLPE; ○, GEL)

occurs and also to estimate the equilibrium melting points of all materials and their component parts. That multiple melting can occur is beyond doubt as illustrated for XLPE-2 and its components in *Figure 7*. Clearly all but the GEL fraction show multiple peaks. This tends to indicate that the original polyethylene itself has a large range of molecular structures present. In order to understand the effects occurring all specimens have been studied at a series of crystallization temperatures. The behaviour of OPE is shown in *Figure 8*, the crystallization temperatures being indicated on the melting endotherms by vertical arrows. It can be seen that a pair of overlapping peaks is the norm, in contrast to nonisothermal crystallization, where a single peak always resulted. At crystallization temperatures in excess of 98°C a low temperature broad peak occurs, being in the vicinity of 80°C for a crystallization temperature of 98°C. As the crystallization temperature increases this peak becomes more prominent and moves to higher temperatures. At the same time the higher peak tends to lose its bimodality and become much sharper. This means that as the crystallization temperature is increased above 98°C an increasingly large fraction of the material is unable to crystallize and hence does so on cooling to ambient. The behaviour is influenced by the presence of dicup as can be seen in *Figure 9* where the behaviour of NXLPE-2 is shown. As will be seen in the following paper dicup acts as a nucleating agent even though it is present in solute form at the crystallization temperatures used. Again the changes occurs most prominently at temperatures of 98°C and above. A comparison of the curves in *Figures 8* and *9* for temperatures of 98 and 102°C perhaps best illustrates the effect. Dwell times in the melt for the NXLPE samples

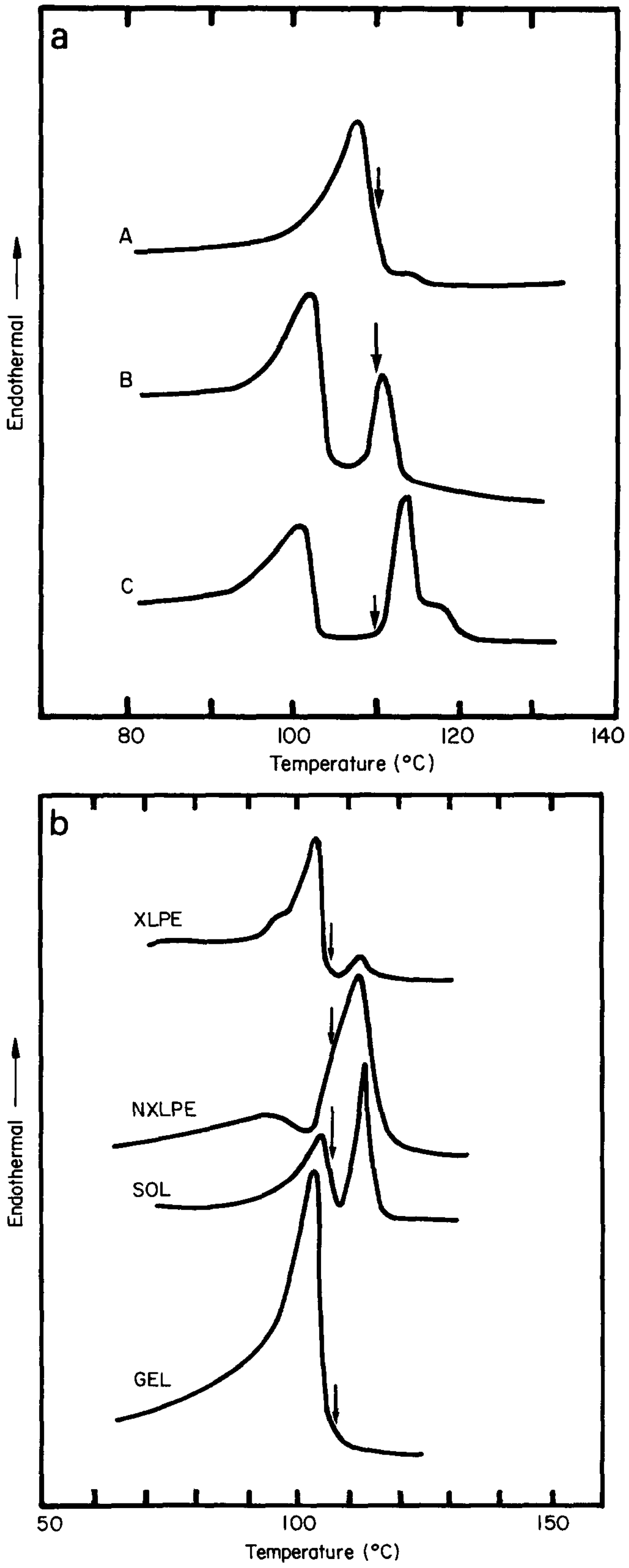

Figure 7 (a) Melting behaviour of OPE crystallized at 110° for (A) one hour, (B) eleven days, (C) 21 days. (b) Melting curves for XLPE-2 and its components when crystallized at 106°C

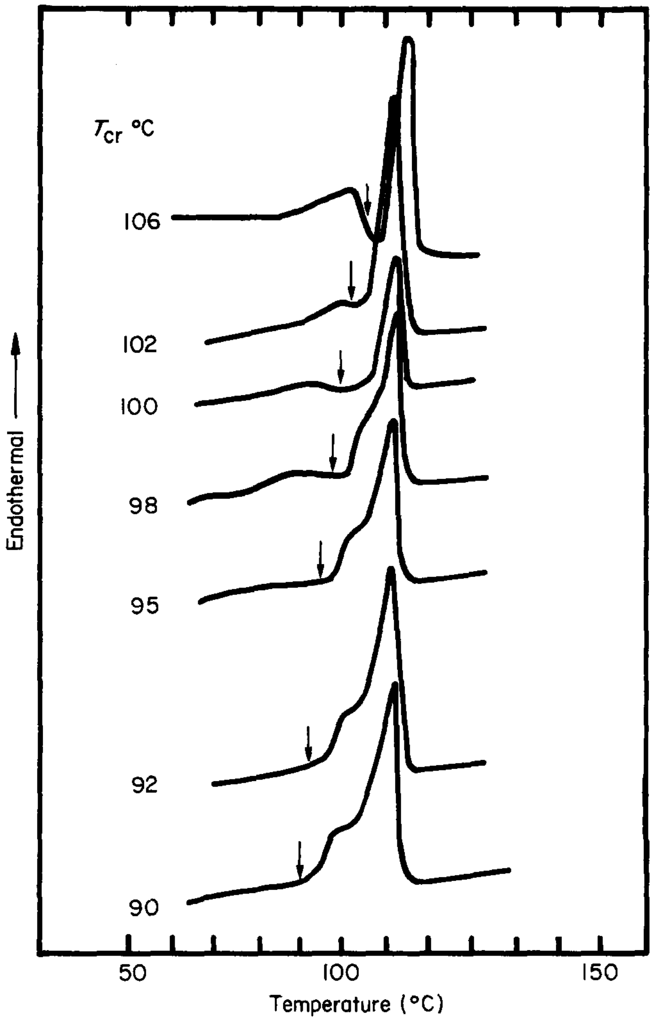

Figure 8 Melting curves for OPE crystallized isothermally at the temperatures indicated

were minimized so as to limit decomposition of the dicup. Specimens remained completely soluble after treatment so that no crosslinking network had been produced.

When crosslinks are introduced major effects occur, the most prominent being a reduction in the highest temperature at which crystallization can occur. In order to discuss the effects of crosslinking in detail we will first consider XLPE-2 and its components. Being commercially available it was chosen as the yardstick to permit easy confirmation of our data and further research by others. Melting curves as a function of crystallization temperature are shown in *Figure 10* for XLPE-2, *Figure 11* for GEL-2 and *Figure 12* for SOL-2. A comparison of *Figures 9* and *10* shows that the crosslinked material begins to produce the low temperature peak at lower supercoolings than OPE, but that at temperatures in excess of 100°C very little of the polymer crystallizes at the crystallization temperature, the majority crystallizing on cooling. Also the melting point of the material that does crystallize at temperatures in excess of 100°C is *ca.* 2°C higher than for lower crystallization temperatures. The GEL (*Figure 11*) shows very little tendency to give multiple melting points. A hump can be seen in the vicinity of 90°C for crystallization temperatures between 95°C and 102°C. Above 102°C virtually no crystallization at the crystallization temperature can be detected although a small hump can be seen at 110°C for the specimen which was crystallized at 104°C. It does, however, appear that SOL needs to be present for significant multiple melting behaviour to be observed.

The behaviour of the SOL fraction is quite different. As can be seen in *Figure 12* complicated melting curves are the norm rather than the exception. Even at the lowest temperatures of crystallization sizeable low melting shouders or peaks can be observed. At the highest

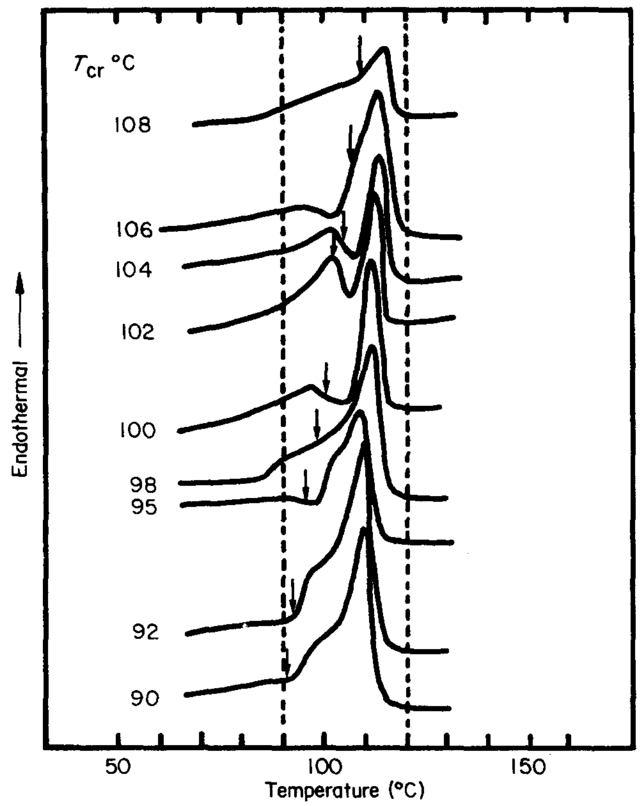

Figure 9 Melting behaviour NXLPE-2 crystallized isothermally at the temperatures indicated

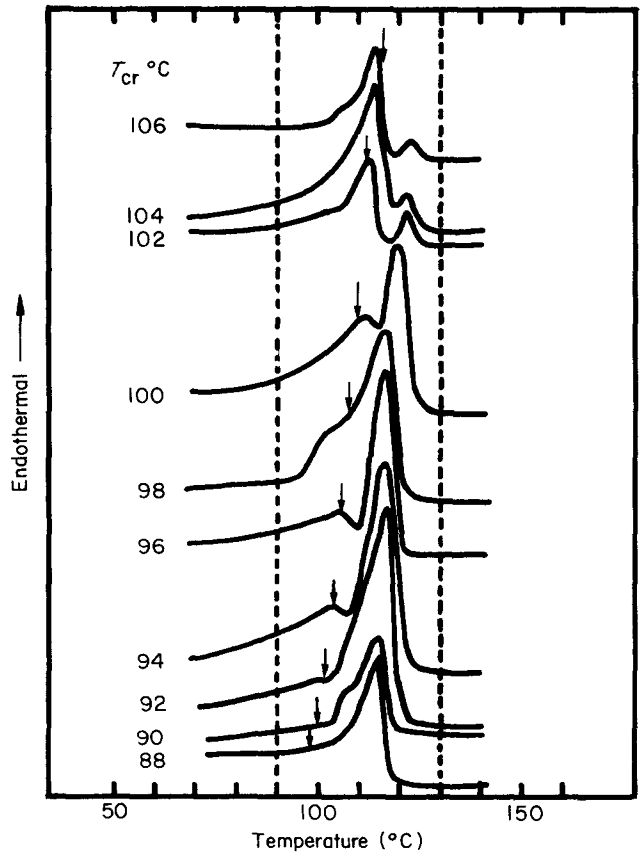

Figure 10 Melting curves for XLPE-2 crystallized isothermally at the temperatures indicated

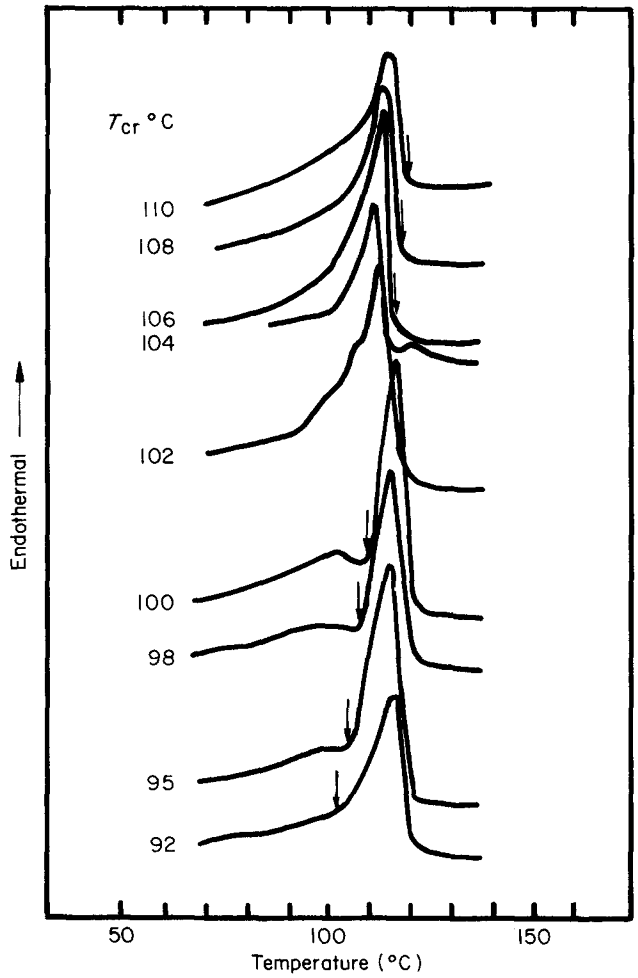

Figure 11 Melting curves for GEL-2 crystallized isothermally at the temperatures indicated

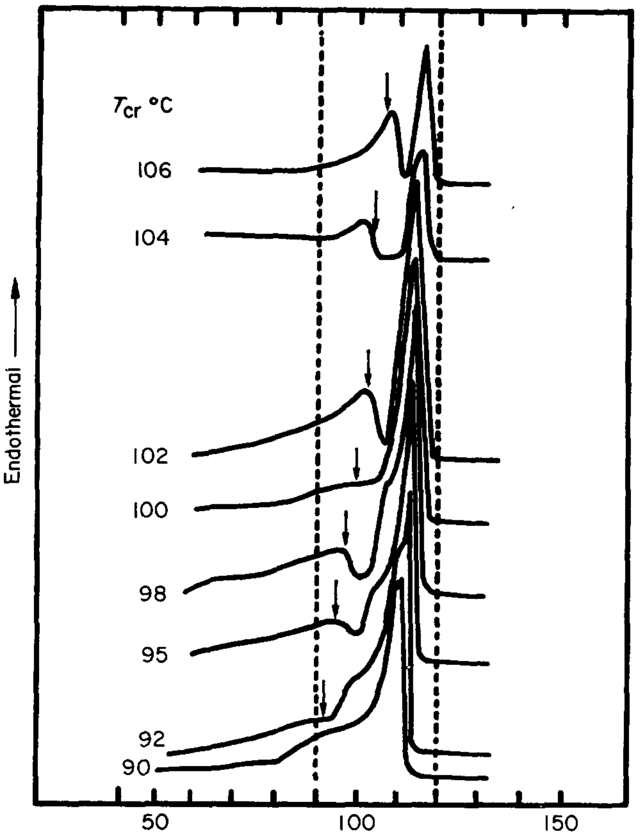

Figure 12 Melting curves for SOL-2 crystallized isothermally at the temperatures indicated

temperatures of crystallization at least two-thirds of the material is able to crystallize. The major melting occurs in the vicinity of 110°C–112°C and the peaks are relatively sharp. It therefore appears that the high melting peaks of XLPE-2 are closely related to the presence of SOL in the material. The melting point of the GEL is generally centred around 105°C as also is the melting point of XLPE-2 crystallized at temperatures below 100°C. As the crystallization temperature reaches the range characteristic of still rapid SOL crystallization but very slow GEL crystallization the melting peak of the resultant crystals begins to approach but not reach the melting point of the isolated SOL fraction. One inference from the data might therefore be that the proportion of GEL incorporated in the crystals is a function of the crystallization temperature. It seems likely that the small high melting peaks found in XLPE-2 at crystallization temperatures in excess of 100°C are caused only by the SOL fraction. For XLPE-2 a separation of SOL from GEL during crystallization at low supercoolings appears to be a definite occurrence. In order to look at the effect of increasing crosslink density let us now look at the behaviour of XLPE-0.9 (*Figure 13*) and XLPE-6.8 (*Figure 14*). The behaviour of XLPE-0.9 is clearly intermediate between that of OPE and XLPE-2, as might have been expected. At low temperatures of crystallization a pair of overlapping curves are obtained whereas at crystallization temperatures in excess of 98°C a low temperature peak indicative of crystallization on quenching again appears. The fraction of material crystallizing at the crystallization temperature is greater than for XLPE-2. The melting temperature is again found at 110°C–112°C for high crystallization temperatures. It will be recalled that the SOL fraction of this material is close to 40% (i.e. double that of XLPE-2). XLPE-6.8 shows behaviour quite different from that of both XLPE-2 and XLPE-0.9 (*Figure 14*). At low temperatures of crystallization all of the material crystallizes at the crystallization temperature and produces a melting peak

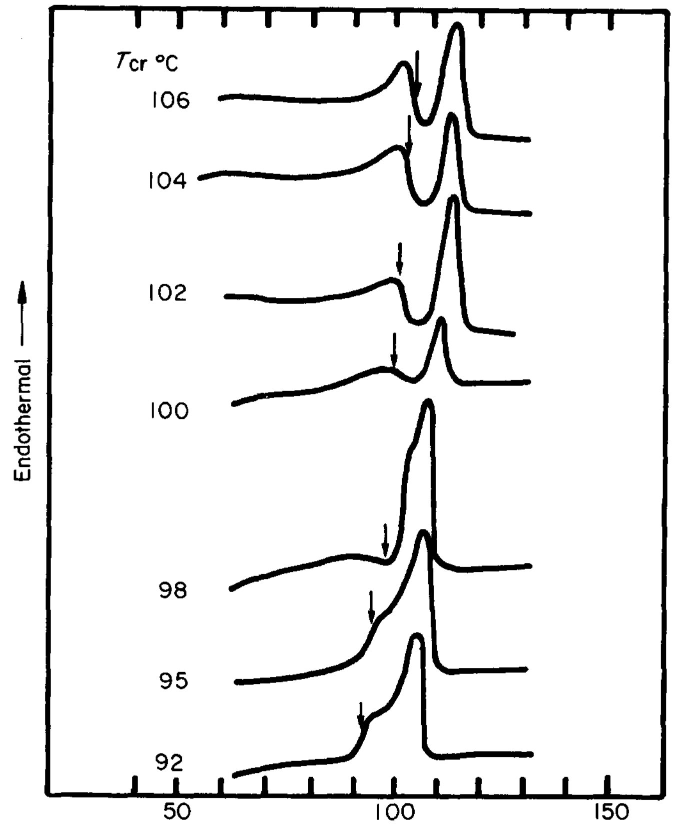

Figure 13 Melting curves for XLPE-0.9 crystallized isothermally at the temperatures indicated

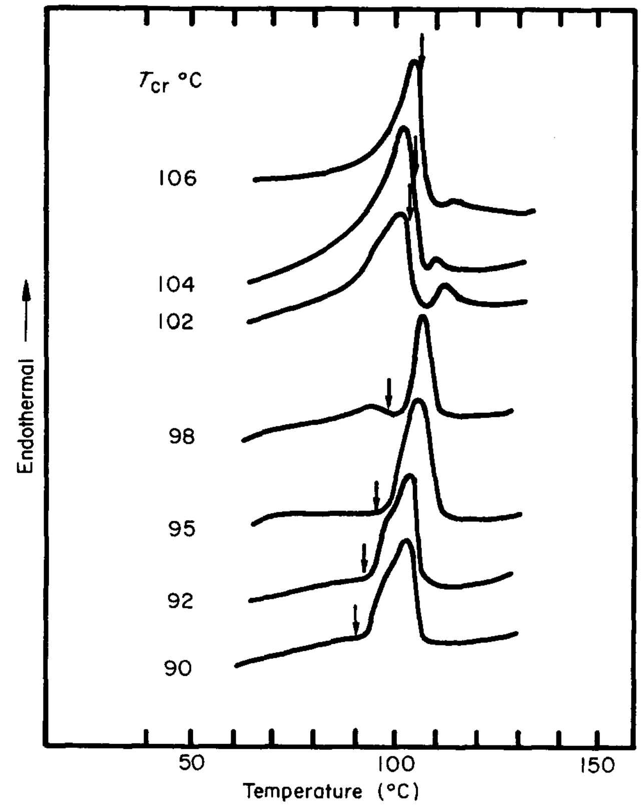

Figure 14 Melting curves for XLPE-6.8 crystallized isothermally at the temperatures indicated

which increases slightly with crystallization temperature. At temperatures in excess of 98°C very little of the polymer crystallizes at the crystallization temperature. There does, however, remain a small melting peak at 110°C. The SOL fraction here was only 6%.

It therefore appears that all of the unextracted polymers produce a high temperature melting peak in the vicinity of 110°C (i.e. the melting point of isolated SOL) if crystallized at temperatures generally in excess of 100°C. Moreover the relative size of this high temperature peak is clearly related to the SOL content.

DISCUSSION

The most important general point to be made is that the presence of the sol fraction has a significant influence on the crystallization and melting behaviour of crosslinked polyethylenes. The influence is greatest for materials of low crosslink density and is quite major for the only polymer available commercially, XLPE-2. There is very clear evidence for its separation during crystallization at temperatures in excess of 100°C. The amount of high temperature melting crystals is closely dependent on the sol fraction present. Whether this effect is thermodynamic or kinetic in origin remains to be explored. It is possible that the equilibrium melting points of the sol and gel phases are different and as a result different supercoolings are effective for the same temperature of crystallization. It is possible that the greater mobility of the sol phase, which will have an activation energy dependence, is so much greater than that of the gel that the result is self-crystallization. It is also possible that the sol and gel phases are no longer compatible with one another at temperatures in excess of 100°C and so will phase-separate in the molten state resulting in separate crystallization regimes. Since the sol is of low molecular weight (*ca.* 7000) all of the above possibilities could in fact be occurring.

Since only the first possibility can be explored now, an attempt has been made to obtain equilibrium melting points using the common method of extrapolating data obtained as a function of crystallization temperature to the point at which the crystallization and melting temperatures are the same. There is no doubt that data for XLPE can be extrapolated, despite the limited number of points available, to an intersection in the vicinity of 140°C. The same intersection is obtained regardless of the level of crosslinking present. For the XLPE-2 system similar extrapolations were obtained for OPE, XLPE-2 and SOL-2, the extrapolation for the sol fraction being of high accuracy. However, the melting point of the gel showed no temperature dependence that was greater than experimental error. This occurrence may not be too surprising in view of the influence of the sol component on the melting temperature as discussed above. It therefore appears that such extrapolations for unextracted materials are indicative of the equilibrium melting point of the sol fraction in the presence of a crosslinked matrix. The insensitivity of the crystals in the gel to supercooling could be indicative of three effects. First it is possible that the lamellar thickness is insensitive to crystallization temperature. This possibility is currently being explored using Ramam LAM and small-angle X-ray scattering studies. Since we are dealing with a polymer which before crosslinking forms thin crystals because of its high degree of branching, it is possible that the effect of the introduction of crosslinks, still in amounts smaller than the branches, could further limit the maximum thickness attainable to a dimension such that no thickening is possible following the initial attachment of the polymer chain to the growing crystal. Another possibility is that the incorporation of crosslinks into the system results in the production of a stress along the crystallizing chain such as to oppose the incorporation of additional members of the same chain, thereby limiting the initial length of chain that can be incorporated into the crystal and/or the extent of the thickening process. One quite different and less realistic possibility is that the surface free energy has become so great that only the δL term of the equation derived from secondary nucleation theory[16] is operational. Either way the question remains to be answered as to what is the equilibrium melting point of a crosslinked polymer and how it varies with crosslink density. The fact that the latent heat of fusion was invariant for all samples studied and was essentially controlled by the degree of branching suggests that any change in the equilibrium melting point must be caused by a change in the entropy of fusion. That such a variation can occur must be beyond question; the problem lies in deciding how large the effect might be. Should there be a change in the entropy of fusion with crosslinking, and if the lamellar thickness is also invariant with crosslinking, any change in the measured melting point with the level of crosslinking may be ascribed to a change in entropy of fusion. The melting temperature of the gel does indeed vary with crosslinking as can be seen in *Figure 15*, where data for GEL and also XLPE (determined two ways) are presented. The melting peak of OPE crystallized under identical conditions was found to be 112°C. The creation of even a lightly crosslinked network such as that present in GEL-0.9 produces a depression of 5°C whereas for the densest network, that of GEL-6.8, the depression is 9°C. Clearly a nonlinear dependence is operative. Although we cannot calculate the entropy of melting at the equilibrium melting point it is possible to calculate the change in

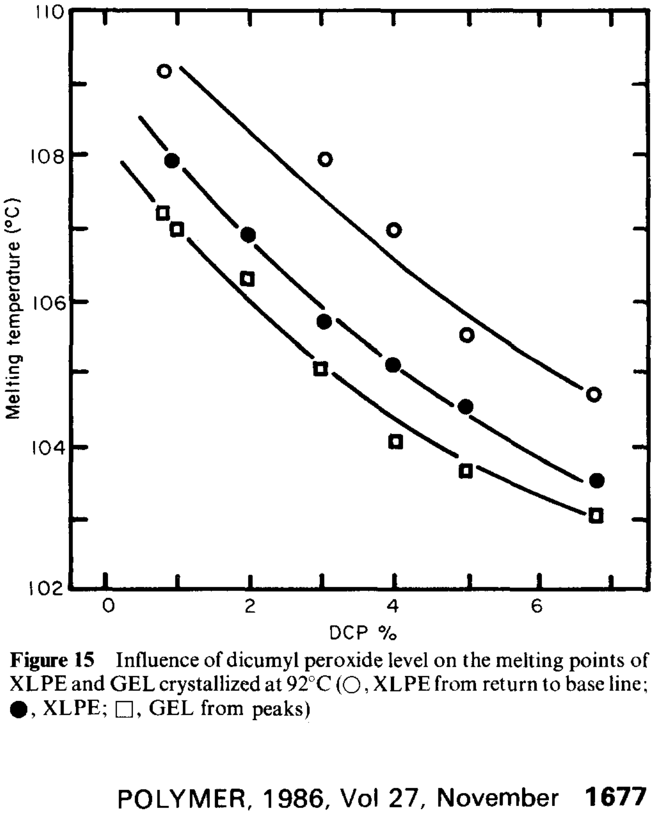

Figure 15 Influence of dicumyl peroxide level on the melting points of XLPE and GEL crystallized at 92°C (○, XLPE from return to base line; ●, XLPE; □, GEL from peaks)

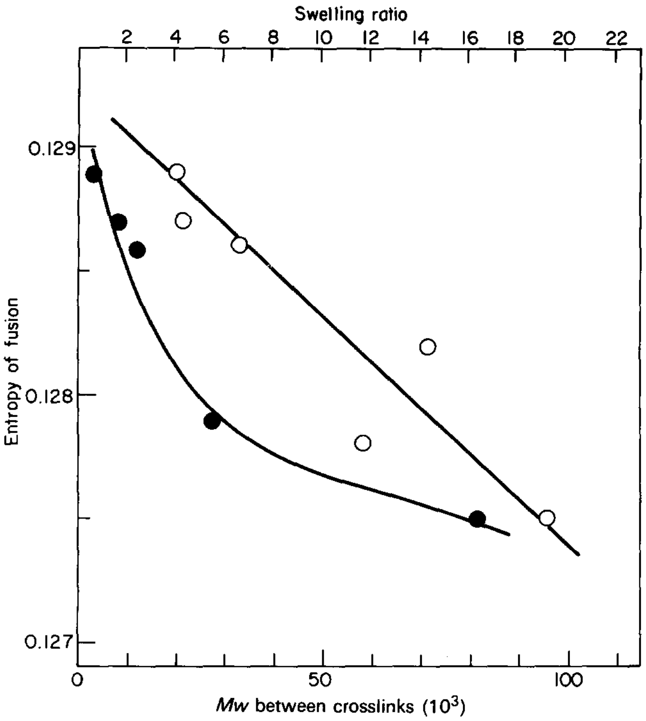

Figure 16 Entropy of fusion *versus* (○) swelling ratio (●) molecular weight between crosslinks

entropy of melting at the observed melting points. Results are plotted in *Figure 16* as a function of both the swelling ratio of the gel and the molecular weight between crosslinks[15]. It is clear that there is an inverse relation between the entropy of fusion and the crosslink density. The change is relatively small (*ca.* 1%) but there is also a discontinuity of approximately the same size between the noncrosslinked polymer and the most lightly crosslinked system. Crosslink density would be expected to reduce the entropy of fusion and hence increase the melting point were enthalpy of fusion unaffected. The observed trend is, therefore, the opposite of what might be expected. However, since equilibrium melting points are not being considered, for reasons already discussed, the observed trend might be caused by decreasing lamellar thickness and misleading in an absolute sense. Direct estimations of lamellar thickness are necessary before any definite conclusions can be made in this regard.

CONCLUSIONS

The presence of extractables, even at low percentages, exerts a significant effect on the crystallization and melting behaviour of a crosslinked system. Extractables must be removed prior to study if definitive experimentation on the behaviour of crystallizable crosslinked networks is to be obtained. The level of extractables present is inversely proportional to crosslinking agent concentration but is ultimately determined by the extent of chain scission occurring for high crosslink densities.

Crystallization at temperatures of 100°C and above suggests either the self crystallization of SOL or the selective crystallization of SOL with the more linear sections of the gel network. No definitive statement can yet be made on the reasons for this behaviour.

The melting point of the gel crystals is insensitive to supercooling and the equilibrium melting point cannot be determined in the usual manner.

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