Crystallinity in chemically crosslinked low density polyethylenes: 2. Crystallization kinetics

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The bulk crystallization kinetics of low density polyethylene crosslinked to various levels by dicumyl peroxide and its gel and sol fractions have been determined. Analyses of the kinetics of gel fractions conform to Regime III analyses whereas the sol fractions and the original uncrosslinked polymers obey Regime II. Literal interpretations of Avrami coefficients suggest a sheaflike morphology which changes to a fibrillar morphology at high levels of crosslink density. Dicumyl peroxide serves as a nucleating agent for polyethylene.

(Keywords: crystallization; kinetics; polyethylene; morphology; crosslinking)

INTRODUCTION

As was discussed in the first paper in this series, crosslinked polyethylenes have become important industrial polymers in recent years but there have been few comprehensive investigations of their behaviour. In particular there have been no reports of the effect of crosslinking on the crystallization behaviour. Studies of the effects of crosslink density on crystallization in polymers has been restricted to rubbers in the past. Studies of bulk rubbers were carried out by Gent[1-3] and microkinetics by Andrews *et al.*[4]. Conclusions of both studies are similar, namely the effect of crosslinking was to reduce the rate of crystallization. The microkinetics study showed that the effect was approximately logarithmic (i.e. the rate of linear growth was reduced in a logarithmic manner by a linear increase in crosslink density).

Whereas such a relationship would not be unexpected on the basis of parallel studies of isomerization and later theories of crystallization in copolymers[5] it is surprising that the expected accompanying major limitation in diffusibility of the crystallizing sub-chains would not have produced more drastic effects. All of the above-mentioned studies considered polymers from which the noncrosslinked molecules had not been removed. Since extractable levels of 20% or more are not uncommon it is suggested that the presence of such more mobile species could have had an unduly large influence on the data acquired. Data presented in the first paper of this series[6] showed that considerable differences existed between extracted and unextracted polymers in their crystallization and fusion behaviour especially with regard to possible fractionation effects at low supercoolings.

Recent extensions of the theory of secondary nucleation in polymers to high supercoolings[7] assume a major influence of restricted mobility on crystallization kinetics over and above that of simply reducing the jump rate. Since in a crosslinked system there are few chain ends present and the majority of the crystallizing species are in fact subchains between junction points there should be a discontinuity in diffusional mobility caused by crosslinking, if recent approaches using reptation are valid[8]. Crosslinked chains simply cannot reptate since they have no chain ends. Their diffusional problems must be such that regime III should always be applicable. In this paper we will report bulk crystallization kinetics for the original polyethylene (OPE), loaded but not crosslinked polymers (NXLPE), crosslinked polymers (XLPE) and their GEL and SOL fractions. Secondary nucleation theory will be applied to half-time data and Avrami analyses will be performed in order to obtain an estimate of the morphologies present.

EXPERIMENTAL

Preparative and analytical procedures have already been discussed in detail[6] and will not be repeated here. Crystallization kinetics were obtained using the increase in transmitted light intensity[9-11] measured using a photomultiplier attached to the column of a Reichert Neovar-Pol polarizing microscope with an attached Mettler hot stage and temperature controller. When necessary a cooling attachment was used which consisted of a coil immersed in liquid nitrogen through which dry nitrogen gas was blown. This type of measurement did not appear to be sensitive to local melt strain provided specimens were well annealed prior to study, since the intensity in the melt was close to zero both before crystallization studies and again after subsequent melting. Baseline intensities were very low compared to even the lowest ultimate intensity points obtained in crystallization runs. A melt condition of 15 min at 145°C was used prior to all experiments. The required crystallization temperature was produced by a rapid

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quench from the melt and for all the data being reported was achieved prior to the onset of crystallization.

RESULTS

First we will consider the behaviour of the commercially available system and then of the materials prepared in the laboratory as a function of dicup loading.

XLPE-2 system

Characteristic light intensity traces as a function of crystallization time at various temperatures are shown in *Figure 1* for unextracted crosslinked polyethylene having a pre-cure concentration of 2% dicumyl peroxide (XLPE-2). The simplest method of analysis of such bulk crystallization kinetic data is to plot the reciprocal of the time for completion of 50% crystallization versus temperature. Such a plot is given in *Figure 2* for XLPE-2, its gel and sol fractions and the loaded polymer in its uncured state (NXLPE-2). It can be seen clearly that the crystallization rate of XLPE-2 is considerably slower than that of NXLPE-2. At 95°C the reciprocal half-time for XLPE-2 is one fifth the value for the uncrosslinked polymer. The crystallization half-time for the gel fraction is somewhat longer than that for the unextracted polymer. The sol fraction, however, crystallizes much more rapidly than the uncrosslinked polymer; indeed it can be crystallized at quite high temperatures for a low density polyethylene. It is also apparent that the sol fraction crystallizes in a quite different temperature range from the gel fraction. The two unseparated fractions would be expected to influence each other's crystallization behaviour and it remains to be seen whether or not any separation occurs during crystallization.

All crosslinked materials

Here data for a series of crosslinkable polyethylenes with 0.9, 3, 4, 5 and 6.8% dicumyl peroxide content will be reported (data were also obtained for 3% and 6% but are omitted for clarity in Figures). First the uncured materials were studied and it was found (*Figure 3*) that the dicumyl peroxide present had a significant effect on the growth rates. Clearly it is functioning as a nucleating agent, but it cannot be said at this stage whether the function was as a particulate nucleating centre or simply by being present as a dissolved impurity.

The cured but unextracted systems show a clear decrease in crystallization rate with crosslink density at a given crystallization temperature (*Figure 4*). Alternatively

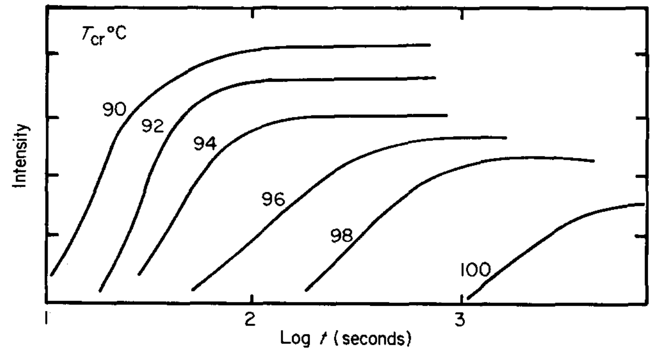

Figure 1 Light intensity (arbitrary scale) *versus* crystallization time for XLPE-2 at the temperatures indicated

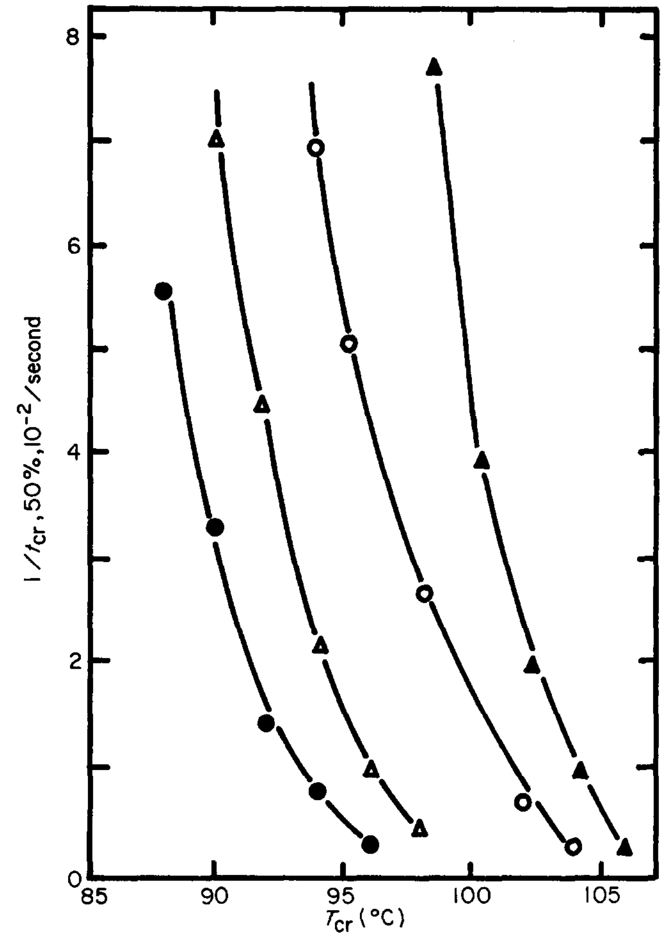

Figure 2 Reciprocal half-time *versus* crystallization temperature for XLPE-2 and its components (△, XLPE; ○, NXLPE; ▲, SOL; ●, GEL)

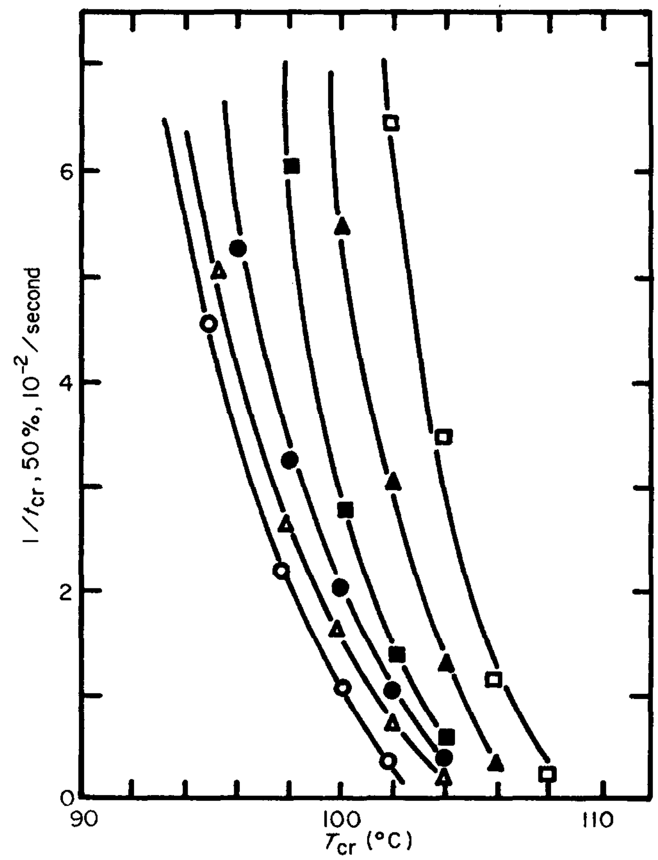

Figure 3 Reciprocal half-time *versus* crystallization temperature for uncured polyethylenes as a function of dicumyl peroxide loading (○, 0%; △, 0.9; ●, 2; ■, 4; ▲, 5; □, 6.8%)

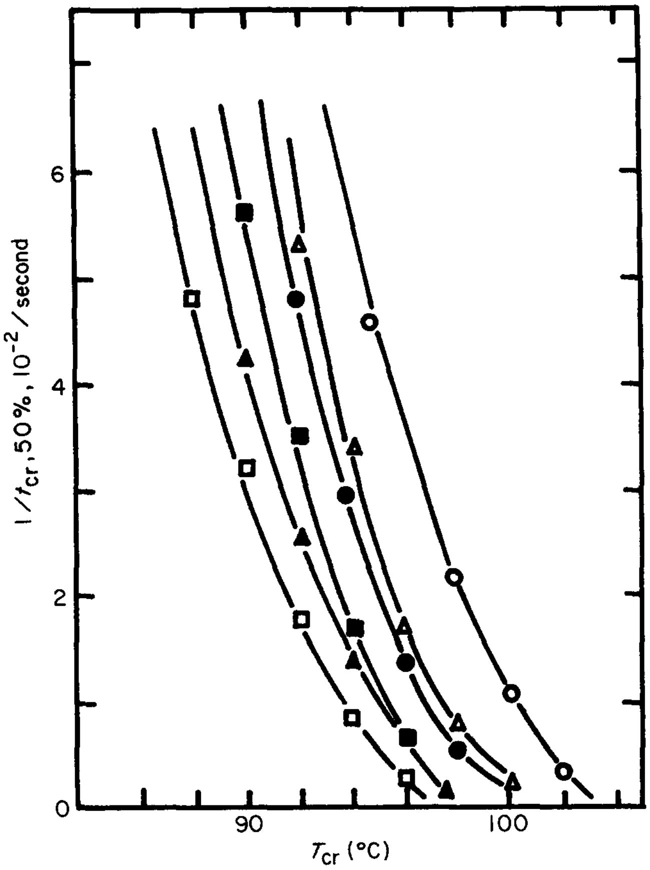

Figure 4 Reciprocal half-time *versus* crystallization temperature for crosslinked polyethylenes as a function of dicumyl peroxide loading (symbols as in *Figure 3*)

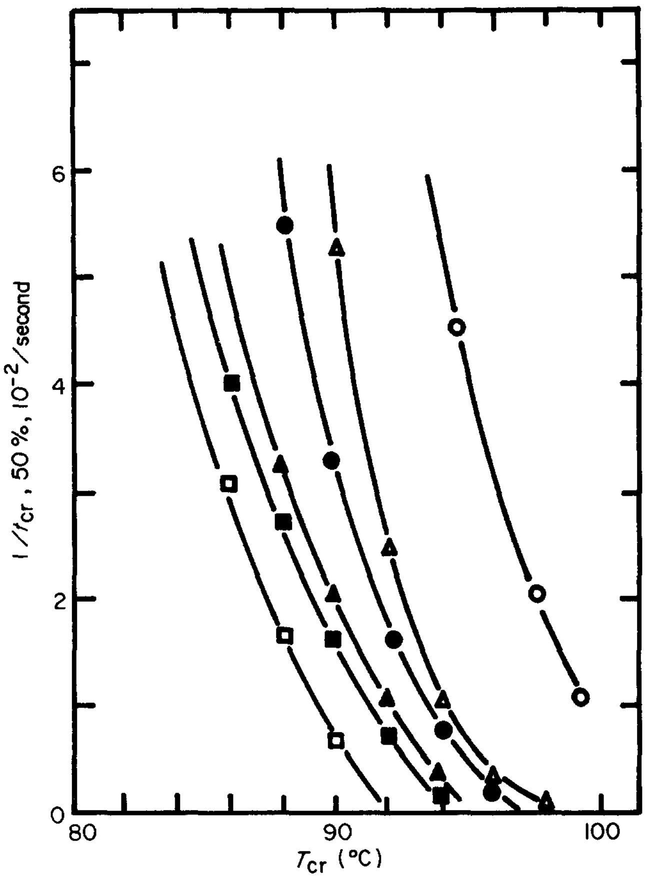

Figure 5 Reciprocal half-time *versus* crystallization temperature for the gel fractions as a function of dicumyl peroxide loading and OPE (symbols as in *Figure 3*)

the behaviour may be interpreted as a shift of the crystallization rate *versus* temperature curve to lower temperatures as crosslink density is increased. Similar but much more drastic effects are apparent for the gel fraction (*Figure 5*). It is, however, clear that the effect is not linear and that the gels of lowest crosslink density have been shifted by disproportionately large amounts.

In contrast to the above two classes of system, sol fractions have much higher rates of crystallization at any given temperature (*Figure 6*) and indeed crystallize at much higher temperatures and faster than the uncured systems. This occurrence was not unexpected since the crosslinking process would naturally favour the longer molecules thus leaving the sol fraction composition as predominantly lower molecular weight material. An additional factor may be a preference of free radicals for tertiary carbons (i.e. branch points) during the crosslinking process. This would tend to ensure that the sol molecules were also less branched than the 'average' initial molecule.

DISCUSSION

Crystallization kinetics

Bulk crystallization rates are not as simple to interpret as linear growth rates because of the combination of nucleation and growth phenomena. Reciprocal half-time data have been analysed in the past to give a reasonable indication of behaviour[12]. Here we have chosen to allow for the effect of mobility by using the U^* approach of Suzuki and Kovacs[13] which has been applied successfully to linear polyethylene by Hoffman *et al.*[14]. Data need to

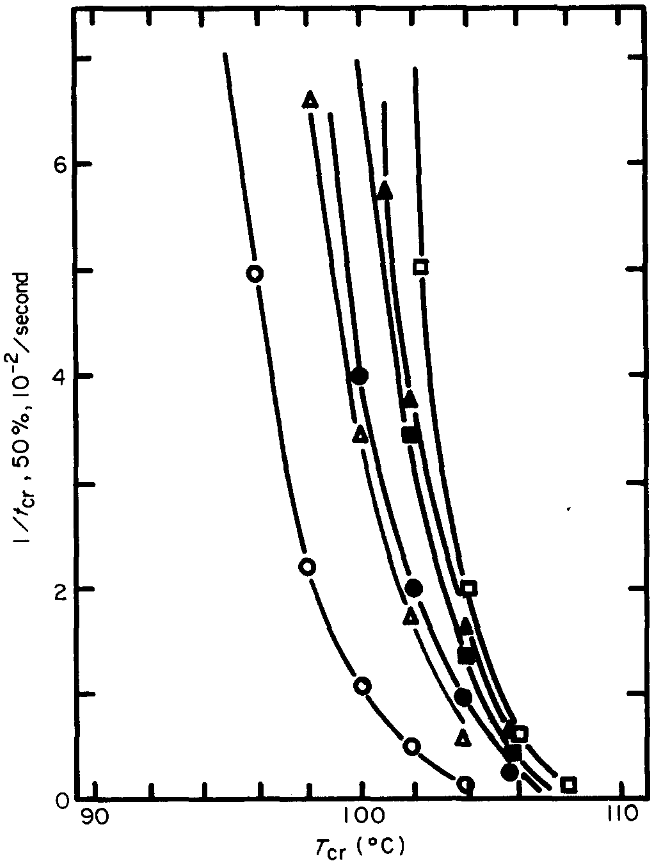

Figure 6 Reciprocal half-time *versus* crystallization temperature for the sol fractions as a function of dicumyl peroxide loading (symbols as in *Figure 3*)

be analysed using one of two assumptions: (1) heterogeneous nucleation dominates and the data are therefore a reflection of the linear growth; or (2) homogeneous nucleation dominates. The two assumptions lead to different analytical equations since for case (1) an inverse dependence on supercooling occurs whereas for case (2) the inverse dependence is on the square of the supercooling.

Calculations of latent heat of fusion[6] showed that it was independent of crosslinking at the value typical of low density polyethylene. Studies of the unit cell parameters showed also that no major changes occurred. Estimations of equilibrium melting point showed that extrapolations of the non-crosslinked and crosslinked systems and the sol fractions led to values in the neighbourhood of 140°C–145°C. However, extrapolations of gel fraction melting points were not possible since the observed melting points were independent of crystallization temperature. In order to carry out a first approximation analysis of the kinetics, it has been assumed that one equilibrium melting point is not a major function of crosslink density. Since we are dealing with supercoolings in the range 40°C–60°C the actual melting point is not as critical a variable as in analyses of linear polyethylenes.

The assumption of homogeneous nucleation leads to the plot:

$$\log(1/t_{1/2}) + U^{*}1/2.3R(T-T_{\infty}) \textit{ versus } 1/T(\Delta T)^{2}f^{2}$$

where f is a factor which corrects for the change in heat of fusion as temperature falls below the equilibrium melting point. The value of f was taken as $2T(T_{m}^{\circ}+T)$ and T_{m}° as 414 K.

Another problem lies in the choice of values of U^{*} and T_{∞}. We have used the values found to be appropriate for linear polyethylene by Suzuki and Kovacs[13], i.e. $U^{*}=1500\,\mathrm{cal\,mol^{-1}}$ and $T_{\infty} \simeq T_{g}-30°\mathrm{C}$, where $T_{g}=-40°\mathrm{C}$[16]. Although it might be argued that the value of T_{g} should be 20°C higher for a low density polyethylene, recent results of Boyd[15] have clearly shown several previous estimates of the T_{g} of linear polyethylene to be in error and the correct value to be in the neighbourhood of −60°C. The chosen value for the T_{g} of low density polyethylene should therefore be in the region of −40°C, as used here.

Curved plots result for all systems indicating that the influence of homogeneous nucleation is of secondary importance. More detailed analyses have therefore been carried out using the assumption of dominant heterogeneous nucleation and a temperature dependence of kinetics dominated by the linear growth rate. The plot to be made is therefore

$$\log(1/t_{1/2}) + U^{*}/2.3R(T-T_{\infty}) \textit{ versus } 1/T(\Delta T)f$$

It was found that significant variations in U^{*} and T_{∞} produced only small changes in the slope, K_{g}. Values of $\sigma\sigma_{e}$ have therefore been extracted from the values of K_{g} using either

$$K_{g}\,(\mathrm{II}) = \frac{2b\sigma\sigma_{e}T_{m}^{\circ}}{\Delta hf.k}$$

$$\text{or } K_{g}\,(\mathrm{III}) = \frac{4b\sigma\sigma_{e}T_{m}^{\circ}}{\Delta hf.k}$$

where Δhf values were in the range 1.81 to $1.94\times10^{9}\,\mathrm{erg\,cm^{-3}}$ as determined for each material and as described in ref. 6. The values of b were also known from the same study.

The non-crosslinked polyethylenes and the sol fractions were first analysed since the behaviour was relatively well established and major discrepancies in values of $\sigma\sigma_{e}$ from those known for linear polyethylene[14] were not expected. Specimen plots are shown in *Figures 7* and *8*, where it can be seen that linear plots resulted which, when analysed using regime II, gave values of $\sigma\sigma_{e}$ comparable to those in the literature (*Table 1*), confirming the validity of the analysis. Similar plots for gel fractions also resulted in linear behaviour (*Figure 9*) but gave values of $\sigma\sigma_{e}$ in a reasonable range only when regime III was assumed. Although the crosslinked polymer (*Figure 10*) also gave linear plots, the assignment of regime was difficult.

A closer look at the behaviour of the gels shows that there is a considerable variation in the value of $\sigma\sigma_{e}$ with crosslink density. It is clear that for the highest levels of crosslink density only a Regime III analysis gives reasonable values whereas for the lower levels a mixed II–III transition region might be more appropriate. Since for GEL-0.9 and GEL-2 the length of chain between crosslinks is quite high this might not be unreasonable. For the crosslinked polymers regime II clearly gives results that are much too high whereas regime III generally tends to give low results for all but the highest crosslink densities.

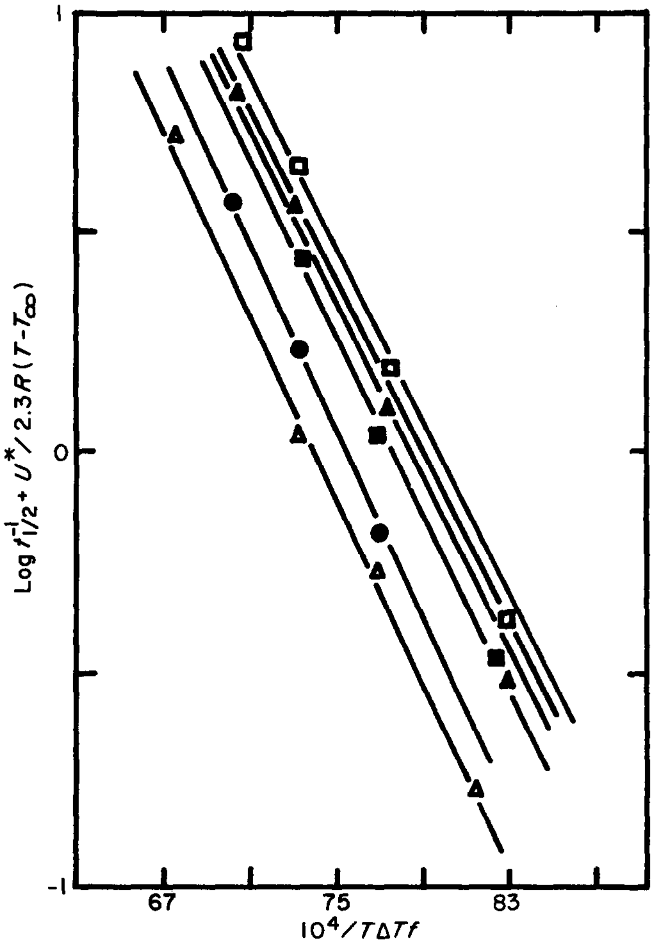

Figure 7 Plots of log $t_{1/2}^{-1}+U^{*}/2.3R(T-T_{\infty})$ *versus* $10^{4}/T\Delta Tf$ for uncured polyethylenes as a function of dicumyl peroxide concentration (symbols as in *Figure 3*)

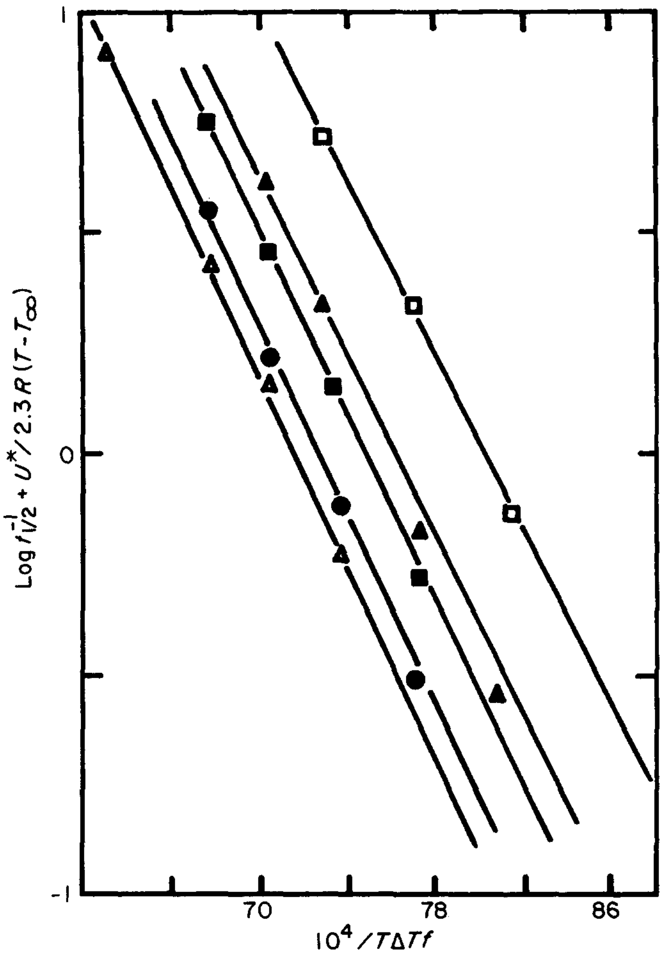

Figure 8 Plots of log $t_{1/2}^{-1} + U^*/2.3R(T-T_\infty)$ *versus* $10^4/T\Delta Tf$ for sol fractions as a function of dicumyl peroxide concentration (symbols as in *Figure 3*)

It seems clear therefore that the behaviour of the crosslinked polymers is a compromise between the sol and gel fractions.

Since the analyses are not particularly sensitive to reasonable variations in U^* and T_∞, unlike *cis*-polyisoprene[17], poly(ethylene terephthalate)[18] or polystyrene[19] and the supercoolings are so large that reasonable variations of equilibrium melting point have a quite minor influence on the data, certain conclusions can be drawn safely. The most important of these is that crosslinked systems from which solubles have been extracted obey regime III kinetics. It is necessary to note that equivalent analyses on non-crosslinked materials and the sol fractions obeyed regime II. It is difficult to decide whether unextracted crosslinked systems show a regime II–III transition region or a mixture of both types of behaviour at the same time. Since the data are uniformly closer to regime III than to regime II the latter might be the case. If so it would imply that mixed crystallization is not occurring at the growth front. There could be both regime II and regime III lamellae growing concurrently or a given crystal could switch from regime II to regime III if the supply of the more mobile sol molecules near the growth front were exhausted.

Avrami analyses

In order further to analyse the crystallization kinetics, the Avrami approach has been utilized[20]. To do this we have plotted

$$-\log\left(\frac{I_\infty - I_t}{I_\infty - I_0}\right) \textit{ versus } \log \text{ time (seconds)}$$

This procedure was found to be quite accurate since both the intensities at infinite time and zero time were known. The Avrami coefficients were obtained as the slope of the linear region. Actual Avrami plots are too numerous to present and so only a representative fraction will be given. Typical examples for a gel fraction and a sol fraction are presented in *Figures 11* and *12*. The Avrami exponents obtained are to be found in *Table 2*. It can be seen clearly that crosslinked polymers and the sol fractions show exponents typical of spherulitic systems, the values for the sol fractions being generally close to three. The crosslinked polymers have values between five and six, which according to the Avrami derivations are typical of sheaves. Morphological studies using transmission electron microscopy of replicas of permanganic etched surfaces support these conclusions[21].

Most fascinating is the behaviour of the gel fractions. As can be seen from *Figure 13*, there is a very clear transition in behaviour for the gel crosslinked with 4% dicumyl peroxide (GEL-4) where the Avrami exponent clearly drops from over four to two. GEL-6.8 shows a constant Avrami value near two, which is

Table 1 Analysis of kinetic data

		Slope $\times 10^5$	$\sigma\sigma_e$ (erg^2 cm^{-4})	σ_e (erg cm^{-2})	Regime assumed
GEL	0.9	16.82	1426	98.4	
	2	16.85	1430	98.6	
	3	18.8	1595	110	
	4	20.8	1766	121.8	III
	5	22	1866	128.6	
	6	23.5	1994	137.5	
	6.8	27.638	2295	161.7	
XLPE	0.9	14.5	2460, 1640, 1230	169.6, 113.1, 84.8	
	2	16	2715, 1810, 1357	187.2, 124.8, 98.6	
	3	17	2884, 1923, 1442	198.9, 132.6, 100	II*,
	4	18	3054, 2036, 1527	210.6, 140.4, 105	(II, III),
	5	19	3223, 2149, 1612	222.2, 148.2, 111	III
	6	19	3223, 2149, 1612	222, 148, 111	
	6.8	20.8	3529, 2353, 1764	243, 162, 121	
SOL	0.9	11.6	1968	135.7	
	2	11.6	1968	135.7	
	3	11.8	2022	138.1	
	4	11.9	2019	139.2	II
	5	11.9	2019	139.2	
	6	11.9	2019	139.2	
	6.8	12.0	2036	140.4	
NXLPE	0	11.15	1892	130.4	
	0.9	11.1	1883	129.8	
	2	11.1	1883	129.8	
	3	11.0	1883	128.7	II
	4	11.0	1866	128.7	
	5	11.1	1883	129.8	
	6.8	11.2	1900	131	

* Left to right across columns

Input data:

$b^\circ = 4.15 \times 10^{-8}$ cm $\quad \sigma = 14.5$ erg cm^{-2} $\quad T_\infty = 203.2$ K

$T_g = 233.3$ K $\quad U^* = 1500$ cal mol^{-1}

$T_m^\circ = 413$ K is assumed for all gel

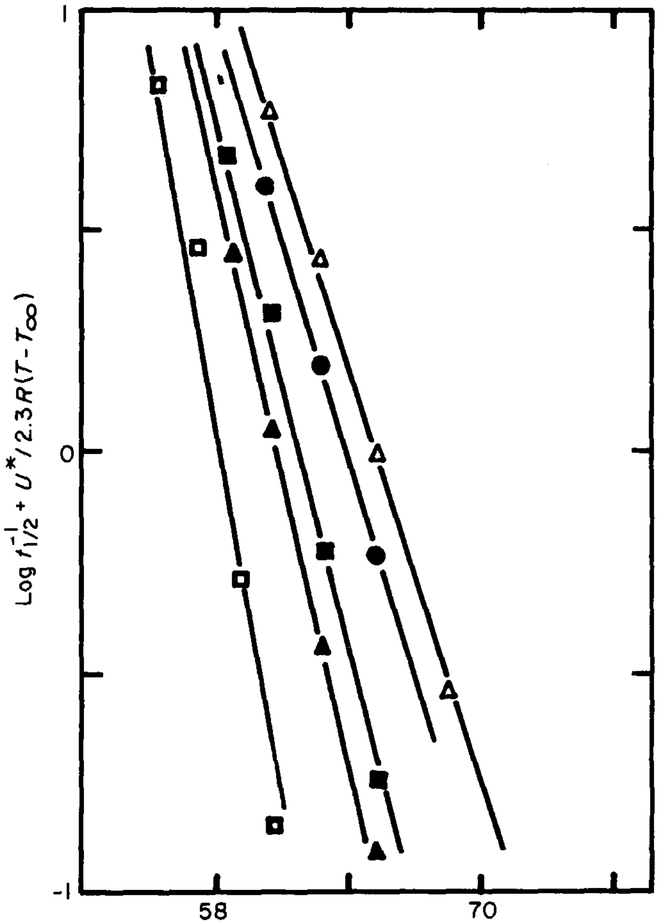

Figure 9 Plots of log $t_{1/2}^{-1} + U^*/2.3R(T - T_\infty)$ *versus* $10^4/T\Delta Tf$ for gel fractions as a function of dicumyl peroxide concentration (symbols as in *Figure 3*)

independent of crystallization temperature. It can also be seen that GEL-5 and GEL-6 show part of the transition. The effect can also be seen for the unextracted crosslinked polymers, but the decrease in exponent value is lower (*Figure 14*). Avrami exponents in the region of one to two are regarded as typical of fibrillar crystallization. Although there must be fundamental packing problems in both sheaf-like and fibrillar crystallization which might negate the theoretical assumption of random directionality, because of non-spherical symmetry, the experimental Avrami exponents are themselves quite clear.

This possible problem in interpretation of the exponents may be purely hypothetical since studies of crystallinity levels in the gel fraction using X-ray diffraction[6] indicate a lower level (25–46%) than for either the crosslinked or noncrosslinked XLPE-2. The sol fraction showed an enhanced crystallinity (*ca.* 57%). Transmission electron microscopy studies of the materials will be reported in the following papers[21,22].

CONCLUSIONS

The bulk crystallization kinetics of the gel fractions of crosslinked polyethylene are considerably different from those of a noncrosslinked system. Analyses of the crystallization kinetics of crosslinked polymers and their gel fractions show that they give values of $\sigma\sigma_e$ comparable with those obtained for linear polyethylene when analysed using Regime III kinetics. Similar analyses using identical thermodynamic parameters for noncrosslinked polymers and sol fractions alone gave reasonable values of $\sigma\sigma_e$ when Regime II was assumed. Literal interpretation of the Avrami exponents indicates a sheaf-like morphology for low levels of crosslinking which

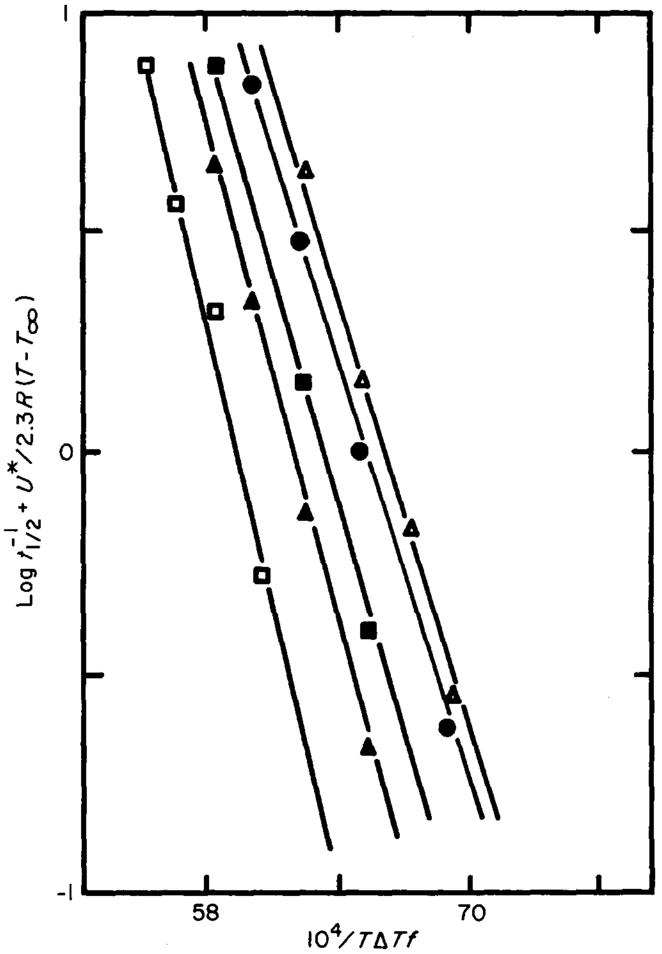

Figure 10 Plots of log $t_{1/2}^{-1} + U^*/2.3R(T - T_\infty)$ *versus* $10^4/T\Delta Tf$ for crosslinked polymers as a function of dicumyl peroxide concentration (symbols as in *Figure 3*)

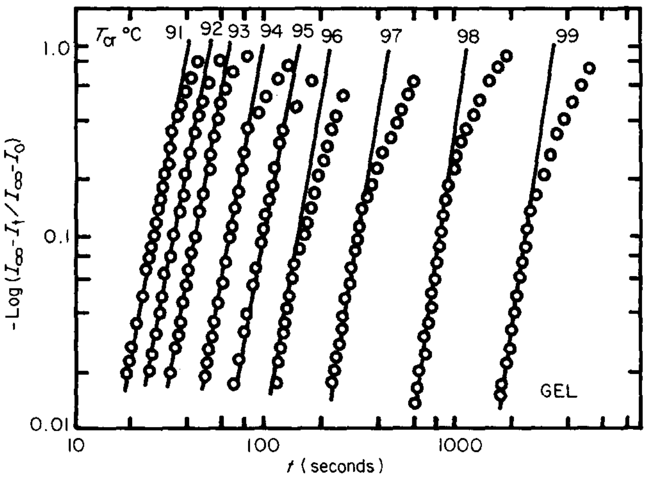

Figure 11 Avrami plots for GEL-2 as a function of crystallization temperature

changes to fibrillar as crosslink density is increased. At intermediate levels of crosslinking the morphology is dependent on crystallization temperature. The sol fraction behaves conventionally, crystallizing as spherulites but with enhanced growth rates and crystallinity levels over that of the original polymer. Unextracted crosslinked polymers exhibit a crystallization behaviour which is strongly influenced by the sol fraction. This is a result of the higher crystallinity levels of the sol despite its small volume percentage (i.e. <20%). Studies of unextracted crosslinked polymers cannot accurately reflect the crystallization behaviour of the crosslinked material.

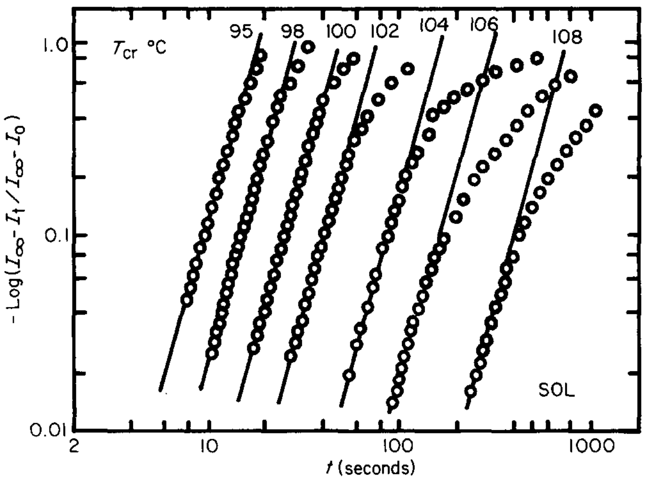

Figure 12 Avrami plots for SOL-2 as a function of crystallization temperature

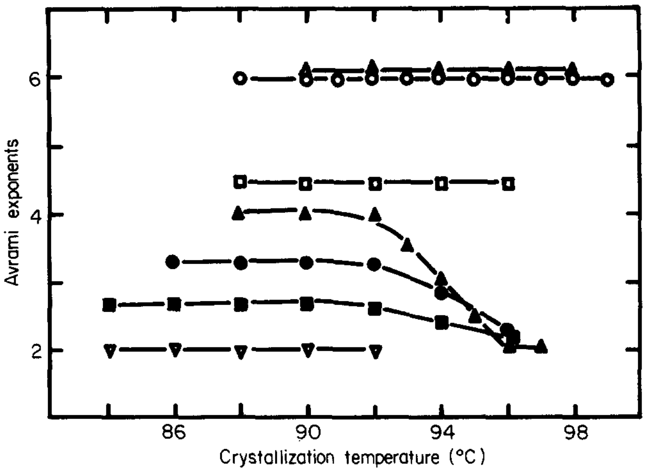

Figure 13 Plots of Avrami exponents *versus* crystallization temperature for GEL fractions (△, 0.9; ○, 2; □, 3; ▲, 4; ●, 5; ■, 6; ▽, 6.8)

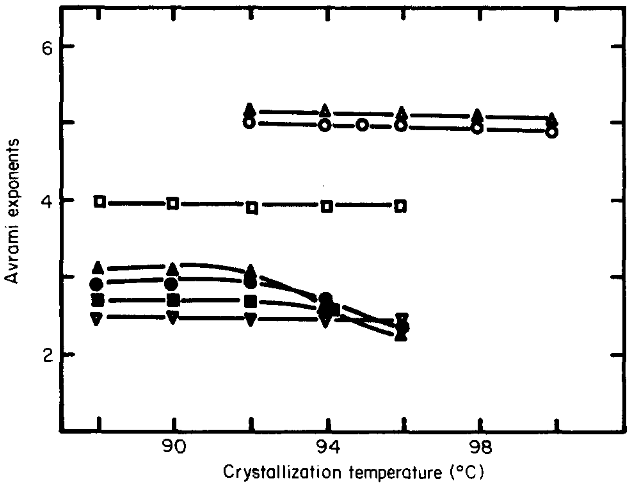

Figure 14 Plots of Avrami exponents *versus* crystallization temperature for crosslinked polymers (symbols as in *Figure 13*)

Table 2 Avrami exponents

	T (°C)	86	88	90	92	93	94	95	96	97	98	100	102	104	106	108
XLPE	0.9			5.0	5.02		5.0		5.0							
	2			5.0	4.8		5.0		5.16		5.16					
	3		4.01	4.02	4.01		4.02									
	4		3.02	3.05	3.07		2.68		2.38							
	5		2.88	2.8	2.6		2.5		2.4							
	6		2.64	2.64	2.6		2.6		2.5							
	6.8		2.52	2.52	2.52		2.56		2.54							
GEL	0.9			6.01	6.01		6.02		5.98		6.00					
	2			5.98	6.00		6.02		6.04							
	3			4.4	4.3		4.34		4.3							
	4			4.2	4.2	3.63	3.0	2.5	2.05	2						
	5	3.2	3.2	3.25	3.23		2.8		2.46							
	6	2.8	2.8	2.8	2.78		2.4		2.2							
	6.8	2.1	2.1	2.0	2.0											
SOL	0.9								3.5		3.5		3.5			
	2								3.6		3.61	3.61	3.63	3.61	3.6	
	3								3.62		3.62	3.6	3.61	3.65	3.64	
	4										3.65	3.7	3.7	3.69	3.7	
	5										3.68	3.71	3.7	3.69	3.72	
	6										3.67	3.72	3.74	3.73	3.72	
	6.8										3.68	3.73	3.75	3.76	3.76	
LDPE	0.9										3.2	3.1	3.2	3.1	3.15	
	2										3.2	3.2	3.1	3.2	3.2	
	4										3.21	3.23	3.2	3.16	3.15	
	5										3.17	3.16	3.14	3.1	3.1	
	6.8												2.61	2.62	2.6	2.6

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