The morphology of linear polyethylenes crosslinked in their melts. The structure of melt crystallized polymers in general

P. J. Hendra, A. J. Peacock and H. A. Willis
Department of Chemistry, The University, Southampton, SO9 5NH, UK

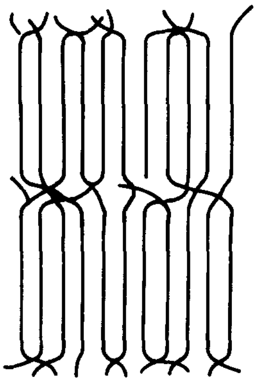
(Received 14 February 1986; revised 14 November 1986; accepted 20 November 1986)

A series of linear polyethylenes crosslinked at 180°C were prepared. They were extracted to remove non-crosslinked residues and then crystallized by rapid cooling. Studies on their crystallinity, melting point, lamellar core thickness and texture lead to the proposal that they crystallize by a mechanism similar to that proposed by Flory—the so-called crystallization model. It is then inferred that this model is closer to reality than its competitors in describing the crystallization of normal crosslinked linear polymers.

(Keywords: polyethylene; melt crosslinked; structure; morphology)

INTRODUCTION

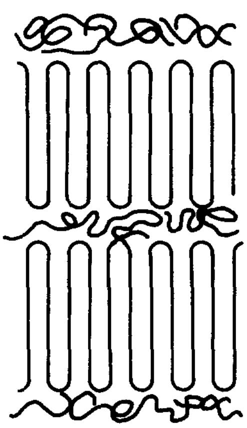
Over the last decade, controversy has raged over the detailed molecular level structure of lamellar melt-crystallized polymers such as linear polyethylene. Although there is no doubt that their morphology is lamellar in basic structural unit (see for example ref. 1) no comprehensive agreement exists on the manner in which the polymer molecules form their structural building blocks. Thus, one view favoured by Flory and many others[2,3] takes as its starting point the thesis that polymer melts are composed of randomly entangled species which on solidification form lamellae by a process which involves minimal movement of the chains during the crystallization process. The structure therefore proposed is composed of chains translating through lamellae in a random manner I.



I

The crystallization model of lamellar structure (Flory)

Others feel that the structural unit more typical of solution crystallized polymers, i.e. the chain folded free lamellar unit is present in melt crystallized material and hence model II is closer to the structure of these materials[4,5].



II

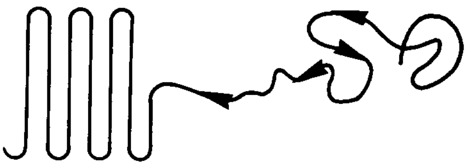
The 'chain folded' model of lamellar structure

Theoretical deduction based on crystallization kinetics and dynamics[6,7] and also on structural model predictions[8] tend to favour model II. The experimental evidence from neutron scattering and the morphology of quench cooled melts has been interpreted to support both or either proposal but it is clear that the weight of support available tends towards a structure lying between the two extremes[9-11]. Perhaps the most convincing evidence that a compromise position is more feasible[12,13] comes from infra-red spectroscopic studies on polyethylene/polyethylene D_4 mixtures[14]. However, doubts persist concerning the packing of chains at the surfaces of their cores in all but the chain folded model. It is clear that although few would now adopt a completely extremist view, none of the available evidence supports one view and refutes the others.

The basic argument of the protagonists of chain folded structures is that during crystallization, considerable mobility exists within the polymeric melt. This mobility permits a chain involved in the crystallization process to

0032-3861/87/050705-05$03.00

rapidly 'reel in' from the bulk to join the growing crystal front III[7].



III

Supporters of the crystallization model have found it hard to accept that the freedom of movement of the chains forming the crystallization front is such that 'reeling-in' and hence folding can be significant unless rates of crystallization are very slow indeed. Flory and Yoon discuss this point in detail[3]. In all real situations, the molecules are thought to have inadequate time to move before they are enveloped in the rapidly progressing solid/melt interface.

In this paper we report on results obtained where the mobility of chains is artificially restricted by crosslinking and hence attempt to provide further ammunition for one or other groups of protagonists mentioned above.

EXPERIMENTAL

Crosslinking of polyethylene

Crosslinking of linear polyethylene was carried out chemically using dicumyl peroxide. British Petroleum plc, grade Rigidex 006-60 was crosslinked to varying degrees in the melt phase at 180°C. Rigidex 006-60 is manufactured by a variant of the Phillips Process has an M_n value of 19500 and M_w of 130000 and less than 2 chain branches per 1000 carbon atoms. Each chain bears one terminal $HC{=}CH_2$ group. The dicumyl peroxide used was of general purpose reagent grade and was supplied by British Drug Houses Ltd. The purity as deduced by the method of Mair and Graupner[15] was 98.5 0.5%.

Crosslinking procedure

A weighed quantity of polymer (10 g) was dissolved in xylene (0.2 dm^3) at 125°C–130°C. This solution was cooled to 100°C to which was then added dicumyl peroxide in an accurately weighed portion. The resulting viscous solution was thoroughly stirred for 10 min. At 100°C the half-life of dicumyl peroxide is approximately 83 h. The mixture was placed in a preheated vacuum oven at 80°C to remove solvent to constant weight. This condition was typically attained after 48 h. At 80°C the half-life of dicumyl peroxide is approximately 1500 h. More than 90% of the solvent is removed within the first 4 h of evacuation.

Decomposition of the dicumyl peroxide to effect crosslinking was brought about by heating the polymer mix in a hot press at 180°C for 10 min after which time decomposition is calculated to be 99.9%.

Gel content analysis

To determine the gel content of samples, specimens were immersed in boiling xylene for 48 h. Specimen sizes were in the range 0.05 to 0.15 g. After extraction, specimens were dried in a vacuum oven at 80°C for 48 h by which time constant weight was achieved.

$$\text{Gel content}(\%)=\frac{\text{Mass of specimen after extraction}\times 100}{\text{Original mass of specimen}}$$

For each sample two completely separate determinations of gel content were made.

Gel equilibrium experiments

Fully crosslinked polyethylene does not dissolve, but rather will swell in appropriate solvents at elevated temperature to form a gel. The extent to which a specimen swells is determined by the average separation of crosslinks and the solvent/polymer interaction parameter.

The average separation of crosslinks may be calculated from the swelling ratio using the Flory–Rehner equation[16,17].

$$V=\frac{V_r+\mu V_r^2+\ln(1-V_r)}{V_0(V_r^{1/3}-V_r/2)}$$

where: V_r = volume fraction of polymer in gel; V = concentration of effective chains; μ = Huggins solvent/polymer interaction parameter[18,19]; V_0 = Molar volume of solvent; and where

$$V_r=\frac{1}{\dfrac{M_S\rho_P}{\rho_S M_P}+1}$$

and M_S = mass of solvent in gel; M_P = mass of polymer in gel; ρ_S = density of solvent; ρ_P = density of polymer. Further: $M_c=\rho_P/V$ where M_c = average molecular weight of effective chains with average separation of crosslinks.

The Flory–Rehner equation was developed from statistical mechanics and it fails to take into account network imperfections such as chain segments terminated by a crosslink at only one end. Flory proposed a modification to the equation to make allowance for such imperfections[20]:

$$M_c^1=\frac{M\times M_c}{M+2M_c}$$

where M_c^1 = true average molecular weight of effective chains; M = number-average of molecular weight of polymer prior to crosslinking.

This modification was used in our evaluation of average separation of crosslinks.

Experimentally, gel equilibrium measurement provides few difficulties, and is a tried and tested method for the rapid evaluation of crosslink density.

Gel equilibrium procedures

An accurately weighed specimen of crosslinked polyethylene which has previously had all soluble material extracted in hot xylene was immersed in boiling xylene for a minimum of 2 h. By this time the swelling equilibrium is achieved. The specimen was then removed and placed immediately in a pre-weighed airtight screw-top bottle. The bottle and solvent/polymer gel were then weighed to determine the uptake of solvent. The average separation of crosslinks can thus be calculated.

The parameters used for solving the Flory–Rehner equation are $\mu=0.31$; $V_0=139.3\ \text{cm}^3$; $\rho_P=0.806\ \text{g cm}^{-3}$; $\rho_S=0.761\ \text{g cm}^{-3}$.

Errors in the evaluation of the average separation of crosslinks are thought to be around 10–15%.

Calculation of crosslink density from the quantity of crosslinking agent

From a knowledge of the efficiency of the crosslinking reaction and of the amount of dicumyl peroxide employed in reacting with terminal vinyl groups and thus producing chain extension (a reaction readily followed using *FT*i.r. methods) it is feasible to estimate the crosslink density in specimens of linear polyethylene. Now

$$\rho_c = \frac{M_d \times 100}{(O-F)E}$$

where: ρ_c = crosslink density expressed in molecular weight (M.wt) units; M_d = M.wt of dicumyl peroxide; O = wt % dicumyl peroxide added to polymer; F = wt % dicumyl peroxide added to polymer but used in chain extension; E = efficiency of crosslinking reaction.

The average separation of crosslinks is half the value of crosslink density for a heavily crosslinked sample.

Differential scanning calorimetry

Differential scanning calorimetry (d.s.c.) was carried out on a Perkin–Elmer model DSC-2 instrument. The instrument was calibrated with samples of pure lead and indium.

Samples of polymer had masses in the range 0.0080–0.0120 g. To ensure a known and repeatable thermal history, samples were heated to 180°C at which temperature they were held for 5 min, whence they were cooled to room temperature at 80°C min^{-1}.

The degree of crystallinity was calculated from the area under the melting endotherm and the melting point from the peak of the endotherm allowing for thermal lag. Errors in the degree of crystallinity are of the order of ±2% and of ±1°C for the melting point.

Determination of crystallite thickness

The average all *trans* stem length in crystallites was found by study of the Raman active longitudinal acoustic mode (LAM). The spectrometer used as a Coderg T800 employing a triple monochromator allowing spectra to be recorded to within a 5 cm^{-1} shift of the exciting frequency.

The most probable all *trans* stem length was calculated from the equation:

$$\Delta\nu = (E_c/\rho')^{1/2}(2CL)^{-1}$$

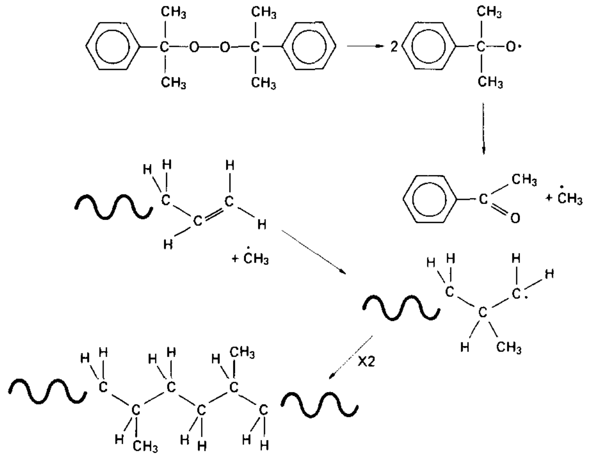
where: $\Delta\nu$ = shift of frequency, i.e. the LAM frequency; E_c = Young's modulus of the crystalline region; ρ' = density of the crystalline region; C = speed of light; L = stem length.

Although there is some doubt about the precise meaning of the values of L so calculated, it is clear that they are reliable as a method of indicating changes in lamellar core thickness in series of similar or related specimens.

RESULTS AND DISCUSSION

It is clear that reaction of dicumyl peroxide and linear polyethylene does indeed cause crosslinking because both the gel content and the swelling ratio of the products vary in the expected manner, i.e. they both respond progressively to crosslink agent concentration (see *Figure 1*). For our purpose we need to know the average separation between the crosslinks. In principle this is calculable from the Flory–Rehner equation (1) as discussed in the experimental section of this paper, however it has to be accepted that the equations were developed for structural situations very different from those encountered here. The values for the separation offered in *Figure 1* are based on the modified equation (3) discussed above but cannot be regarded as precise.

In any attempt to crosslink a linear polyethylene, it has to be accepted that the reaction of the methylene group to form an interchain link is kinetically unattractive. Chain–chain addition using terminal vinyl group is a practicable alternative. If this were the sole reaction approximately 0.7% dicumyl peroxide would be absorbed in completing the process.



IV

Infra-red study of our specimens shows that the chain addition process occurs since the vinyl context of the polyethylene falls rapidly as small concentrations of crosslinking agent are added and cured. In fact, combining infra-red and gel content evidence, it is clear that until half the vinyl groups are used up, the chain–chain addition reaction overwhelmingly predominates, crosslinking becoming more prominent at high concentrations of dicumyl peroxide.

Turning now to the properties of the crosslinked material: small-angle light scattering confirms the spherulitic nature of the substances at room temperature. Further, although not utterly convincing, electron micrographs of the crosslinked materials show evidence of fine striation presumably due to the presence of lamellae.

The solidification of crosslinked melts and rubbers

The variously produced crosslinked materials were heated to above their melting (or softening) points (150°C) and then rapidly cooled (rates close to 80°C/min were used) to produce solids*. The polyolefine solids so produced were then studied by a variety of physical techniques to deduce their crystallinity, general state of order and lamellar thickness. In *Figure 2* we show the

---

* It is worth explaining that since the crosslinked specimens were dissolved, mixed with crosslink agent and evaporated prior to crosslinking and eventually extracted with solvent to remove non-crosslinked molecules, it is essential that the reference resin be treated in a similar way. This was achieved by solution, evaporation and vacuum backing prior to melting and cooling.

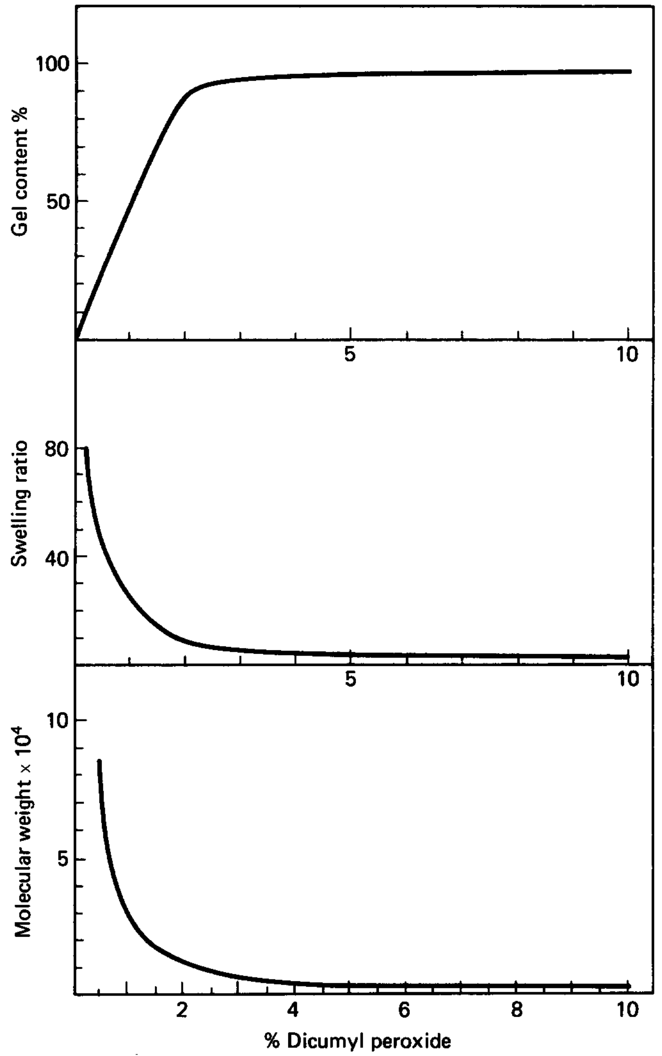


Figure 1 Characteristics of crosslinked linear polyethylenes vs. proportion of crosslinking agent

effect of crosslinking on the melting point of these materials and on their d.s.c.-derived degrees of crystallinity. It is clear that as the proportion of dicumyl peroxide is increased, the melting point falls and is paralleled by a slow diminution in the degree of crystallinity.

(1) There seems little reason to feel that linear polyethylenes when melt crosslinked crystallize differently from their parent materials.

(2) As the crosslinked density is raised and hence the average crosslink–crosslink separation is reduced, the lamellar core thickness of the solids changes little until the separation falls to values close to the core thicknesses themselves, i.e. closer than a separation of 150C atoms.

(3) Relatively widely spaced crosslinks appear to lower the crystallinity and hence melting point of these materials.

If one subscribes to the folded chain structure of lamellar crystallization it is in turn consequent that 'reeling in' of the chain must occur during the growth of individual lamellae. This is quite out of the question in the work described here. All chains present one part of three dimensional networks—free uncrosslinked chains have all been illuted. Further, it is difficult to rationalize the second observation above within the chain folded model. Flory's view of the lamellar structure and its formation would, however, predict the behaviour we observe.

Taking each of our observations in turn: the fact that chains were incapable of large scale movement relative to their neighbours would not influence the Flory mechanism since no large scale movement is envisaged during crystallization. The lamellar thickness of the solid crosslinked material would be that of the non crosslinked equivalent. If, however, the level of crosslinking were such that the intercrosslink distance was close to or less than the lamellar thickness of the non crosslinked material these very crosslinks would restrict growth of the crystallites along their chain axes and hence our second observation would be expected. This lack of freedom would also produce observation number three.

If one persists in supporting models *close* to the chain folded structure but incorporating a significant element of interlamellar randomness arising from intercore linking chains a further dilemma arises. In all the experiments reported here, non crosslinked polymer was deliberately extracted *prior* to crystallization, i.e. the subject of our studies was always close to a 'free' crosslinked network. It must be emphasized that extraction was not carried out *after* crystallization but rather *before* melting and hence 'free' chains were not present to influence the structural outcome. A parallel series of experiments were then completed where no extraction was attempted, i.e. the specimens were intimate mixtures of crosslinked network and non-crosslinked polymer. One might well have anticipated, if one supports a structural view involving significant degrees of chain folding, that these would behave on crystallization, differently from their extracted brethren. Clearly, the difference in behaviour is not the case; curves for extracted, i.e. 'pure' network polymers are indistinguishable from their non-extracted equivalents. See also, to emphasize the point, *Figure 3*.

To conclude: we offer these experiments as further subjective evidence to support a structural description of melt crystallized polymers closer to Flory's view than to the chain folded description.

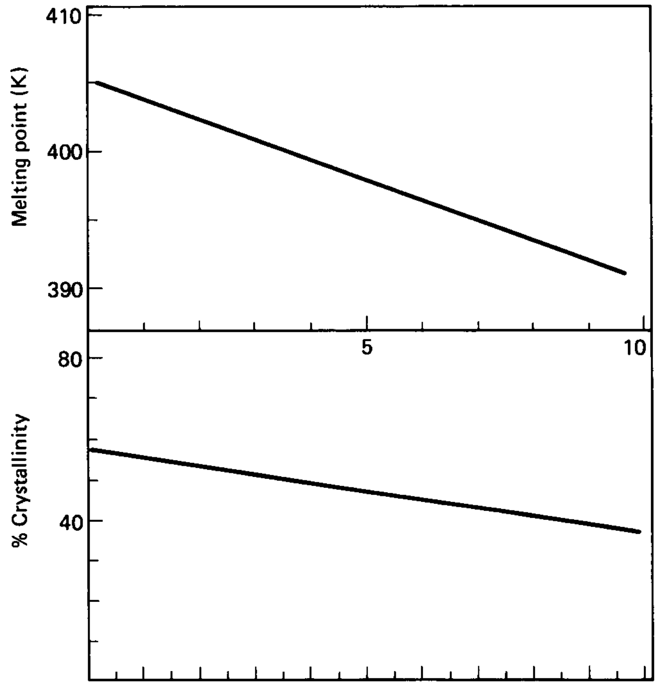


Figure 2 Melting point and per cent crystallinity of crosslinked linear polyethylenes vs. proportion of crosslinking agent

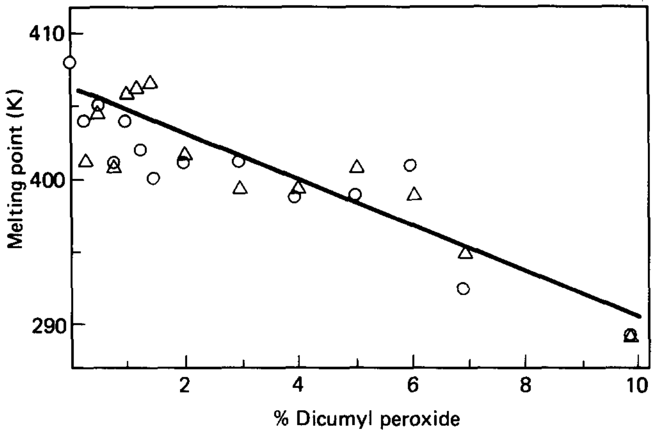


Figure 3 Comparison of extracted and unextracted crosslinked polyethylenes vs. proportion of crosslinking agent: (○) whole polymer; (△) extracted

ACKNOWLEDGEMENTS

The authors wish to thank the Science and Engineering Research Council Polymer Engineering Directorate for a postgraduate award for one of them (AJP) and the Office of Naval Research of the US Navy for generous financial assistance.

REFERENCES

1 Bassett, D. C. and Hodge, A. M. *Proc. Roy. Soc. Lond.* 1981, **A377**, 25
2 Flory, P. J. *J. Am. Chem. Soc.* 1962, **84**, 2857
3 Yoon, D. Y. and Flory, P. J. *Faraday Disc. Chem. Soc.* 1979, **68**, 288 and *Nature* 1978, **272**, 226
4 Geil, P. H., Anderson, F. R., Wunderlich, B. and Arakawa, T. *J. Polym. Sci.* 1964, **A2**, 3707
5 Hoffman, J. D., Guttmann, C. M. and DiMarzio, E. A. *Faraday Disc. Chem. Soc.* 1979, **68**, 177
6 Hoffmann, J. D. *Polymer* 1982, **23**, 656
7 De Gennes, P. G. *J. Chem. Phys.* 1971, **55**, 572
8 DiMarzio, E. A. and Guttmann, C. M. *Polymer* 1980, **21**, 733
9 Schelten, J. S., Ballard, D. G. H., Wignall, G. D., Longmann, G. and Schmatz, W. *Polymer* 1976, **17**, 751
10 Yoon, D. Y. and Flory, P. J. *Polymer* 1977, **18**, 509
11 Yoon, D. Y. *J. Appl. Cryst.* 1978, **11**, 531
12 Guttmann, C. M., Dimarzio, E. A. and Hoffman, J. D. *Polymer* 1981, **22**, 597
13 Guttmann, G. M., DiMarzio, E. A. and Hoffman, J. D. *Polymer* 1981, **22**, 1466
14 Scherer, J. R., Snyder, R. G. and Krause, S. J. *J. Phys. Chem.* 1979, **83**, 626
15 Mair, R. D. and Graupner, A. J. *Anal. Chem.* 1964, **36**, 194
16 Flory, P. J. and Rehner, J. *J. Chem. Phys.* 1943, **11**, 572
17 Flory, P. J. *J. Chem. Phys.* 1950, **18**, 108
18 Trementozzi, Q. A. *J. Polym. Sci.* 1957, **23**, 887
19 Tung, L. H. *J. Polym. Sci.* 1957, **24**, 333
20 Flory, P. J. *Ind. Eng. Chem.* 1946, **38**, 417
21 Strobl, G. R. and Eckel, R. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 913