

Photocross-linking of Low-Density Polyethylene.

II. Structure and Morphology

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SYNOPSIS

Morphological structure and other properties of polyethylene photocross-linked in the melt (XLPE) have been studied by wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), density, and swelling measurements. The WAXD measurements show that the crystallinity of polyethylene decreases with increasing gel content in the XLPE samples and that the regularity and the size of crystals are affected by photocross-linking. DSC data confirm that photocross-linking occurs preferentially in the amorphous and interfacial regions and causes depression of the melting point and decreases the heat of fusion. The density of XLPE apparently decreases with increasing gel content, which is due to decreased crystallinity and lattice expansion. The cross-link density determined by the swelling measurements and evaluated using the Flory–Rehner equation correlates well with the changes in crystallinity and melting point. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, both low-density (LDPE) and high-density (HDPE) polyethylenes have been cross-linked (XLPE) and extensively used for high-voltage electrical insulation of wire and cable, heat-shrinkable tubing, film, and foam, and hot-water piping. Of particular interest are the effects of network, crystal, and morphological structures on the physical properties of XLPE materials.

Most studies in the past have been focused on the effects of high-energy irradiation^{1–6} and chemical cross-linking^{7–10} on crystalline morphology and structure. Recently, there have been important breakthroughs in the photoinitiated cross-linking of thick samples of PE.^{11–15} This paper describes changes in the physical properties and morphological structure of XLPE and the effects of the photoinitiated cross-linking on the size and perfection of the crystals when PE is photocross-linked in the melt.

It is well known that the properties of a polymer crystallized in bulk correlate well with the level of crystallinity, the resulting morphological structure of the lamellar crystallites, and the associated interfacial regions of the polymer. These parameters are influenced by the structure of the polymer chains, the cross-linking process, and the crystallization conditions. There are many methods available for the study of structure and properties of a crystalline polymer, such as wide-angle X-ray diffraction (WAXD), small-angle light-scattering (SALS), differential scanning calorimetry (DSC), density, and swelling measurements. The data can be applied to relate physical properties to molecular structure of PE before and after cross-linking. This paper, which is one of a series dealing with the photocross-linking of LDPE,^{13–16} presents new information on the relationship between morphological structure and thermodynamic properties of XLPE based on swelling, density, WAXD, and DSC measurements. Some corresponding data for HDPE are also presented for comparison. The study by SALS of the superstructure of XLPE will be described in Part III of this series.

Since previous studies emphasized the influence of crystallization conditions, particularly the crys-

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tallization temperature and rate, on the morphological properties and cross-linking efficiency of PE,^{4,17-20} the film samples in this study have been prepared in a manner similar to those used before¹⁵ in order to more easily compare the effects of photocross-linking on the properties and structure of XLPE.

EXPERIMENTAL

Sample Preparation

Materials

All samples used in this work were prepared from two kinds of PEs: low-density PE (DFDS 6600) from Neste Polyeten AB (Stenungsund, Sweden) and two high-density PEs (Lupolen 5261 z and Hostalen 412) from BASF and Hoechst AG, respectively.

All samples contain 1% by weight of 4-chlorobenzophenone (4-CBP) as photoinitiator and 1% by weight of triallyl cyanurate (TAC) as cross-linker. The properties of the samples before photocross-linking, e.g., density, crystallinity, and melting point, are reported in Table I.

To reduce the effects of sample preparation and photocross-linking processes on the resulting morphological properties of XLPE, a standardized procedure was used for mixing, hot pressing, UV irradiation, and cooling of the samples from the melt.

Mixing

Fifty grams of PE powder or granules with the desired amounts of additives were mixed for 10 min at 160–200°C in a Brabender Plasticorder, as described in Paper I of this series.¹⁵

Hot Pressing

The LDPE films were prepared in a Hotpress device. The sample was held in the molten condition at 160°C for 2–3 min and was then subjected to an appropriate pressure for 4–5 min. The sample was then rapidly cooled to room temperature in air. The

Table I The Properties of PE Samples Before Photocross-Linking

Samples	ρ (g cm ⁻³)	Crystallinity ^a (%)	T_m (°C)
LDPE	0.924	53	110
HDPE	0.961	77	135

^a Measured by X-ray diffraction.

sample thickness varied from 0.1 to 1 mm depending on the testing method. The HDPE samples were prepared in a similar manner at 180°C using the Hotpress.

UV Irradiation

The samples were UV irradiated in a UV-CURE device as described before.¹⁵ The standard conditions were a high-pressure UV lamp (2 kW) held at a distance of 10 cm from the specimen that is in a nitrogen atmosphere. The standard irradiation temperatures were 140°C for LDPE and 150°C for HDPE. The irradiation time varied. The sample was kept in the cavity of the UV-CURE device for 3–5 min before irradiation to ensure temperature equilibrium and removal of oxygen. After UV irradiation, the molten sample was rapidly removed from the cavity of the UV-CURE device and cooled to room temperature. Some samples were UV-irradiated below the melting point, as indicated in the paper.

Analysis of Samples

Swelling Measurements

The degree of swelling was determined using the method reported by de Boer and Penning.²¹ After extraction of the cross-linked samples in boiling *p*-xylene for 48 h as previously described,^{12,15} the gel was transferred to fresh solvent (*p*-xylene) and allowed to equilibrate at 120°C for at least 2 h. The swollen gel was then picked up in a bag of a stainless-steel net, transferred quickly to a weighing glass with cover, and weighed. The data were recorded as the averages of five measurements. The mass of cross-linked sample was determined by weighing after drying at about 70°C in a vacuum desiccator overnight. The degree of swelling (q) was calculated according to the expression

$$q = \frac{\text{weight of swollen gel}}{\text{weight of dry gel}} \quad (1)$$

The network chain density (ν^* , mol/cm³ of dry gel) is calculated from the swelling data using the Flory–Rehner theory:

$$\nu^* = - \frac{\ln(1 - q^{-1}) + q^{-1} + \chi q^{-2}}{V_1(q^{-1/3} - 0.5q^{-1})} \quad (2)$$

where q is the degree of swelling; V_1 , the partial molar volume of the swelling solvent; and χ , the Flory–Huggins interaction parameter. For *p*-xylene

at 120°C in this study, $V_1 = 136$ mL/mol and $\chi = 0.37$ according to the literature.²¹

The molecular weight between cross-links M_c is calculated using the equation²²

$$1/M_c = \nu^* \cdot V \quad (3)$$

where V is the specific volume of XLPE equal to $1/\rho$, obtained from the density (ρ) of XLPE.

Wide-Angle X-ray Diffraction (WAXD)

Wide-angle X-ray measurements were carried out at room temperature in a Philips diffractometer equipped with a $\text{CuK}\alpha$ tube and Ni filter. The sample dimensions were $20 \times 10 \times 0.5$ mm. The diffraction patterns were determined over a range of diffraction angle $2\theta = 10^\circ$ – 30° . Typical patterns for the LDPE sample before photocross-linking are shown in Figure 1. The major characteristics of the patterns are the two principal crystalline reflection peaks at 2θ equal to about 21.4° and 23.7° , corresponding to the 110 and 200 lattice planes, respectively, and the amorphous scattering centered at 2θ equal to about 19.8° for uncross-linked LDPE. These values are only slightly different for uncross-linked HDPE. The calculation of crystallinity from X-ray diffraction spectra is based on the relative intensity of the three components.^{23,24} Interplanar distances in the

crystalline regions have been calculated using the Bragg equation.

Differential Scanning Calorimetry (DSC)

DSC thermograms were obtained by a Perkin-Elmer Model DSC-2 instrument, using a scanning rate of 10 K/min and a cooling rate of 30 K/min in the temperature range of 300–400 K. The melting point of a sample was taken as the temperature at the melt peak position. The heat of fusion was determined by comparing the area under the melting endotherm with the area of fusion of a standard indium sample having a known heat of fusion of 6.8 cal/g.²⁵

Density Measurement

Densities (ρ) were measured at $23 \pm 0.1^\circ\text{C}$, using an alcohol-water gradient column according to ASTM D1505-68. The density values are converted to crystallinity $(1 - \lambda)_\rho$ according to the equation

$$(1 - \lambda)_\rho = (1/\rho_a - 1/\rho)/(1/\rho_a - 1/\rho_c) \quad (4)$$

where ρ , ρ_a , and ρ_c are the measured densities of the whole sample and of amorphous and crystalline PE, respectively. The values $\rho_a = 0.851$ and $\rho_c = 1.00$ were taken from the literature.²⁶

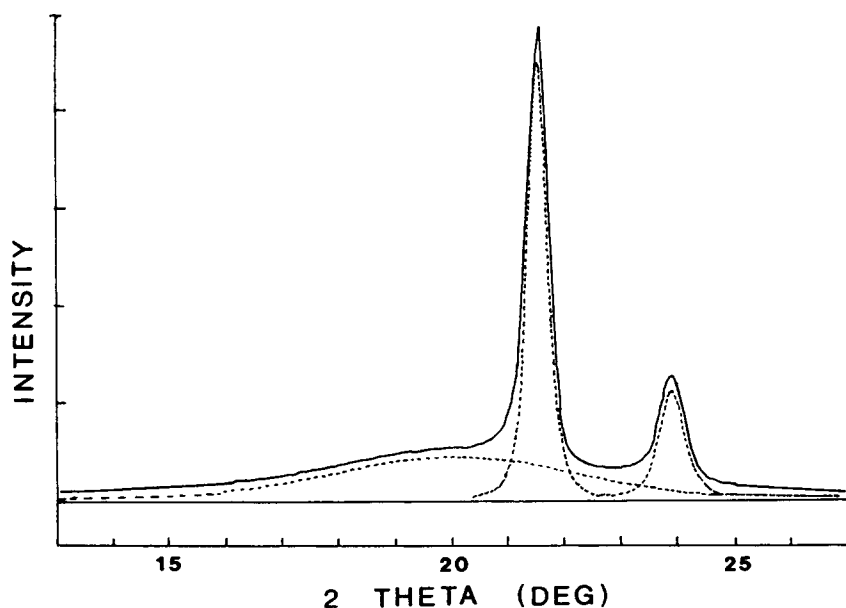


Figure 1 X-ray diffraction pattern of LDPE before photocross-linking at (—) room temperature and (---) resolved peaks.

Table II Swelling in Xylene at 120°C of LDPE Photocross-Linked in the Melt

Irradiation Time (s)	Gel Content (%)	Degree of Swelling (q)	$\nu^* \times 10^4$ (mol cm ⁻³)	$M_c \times 10^{-3}$ (g mol ⁻¹)
5	35.1	50.2	0.40	23.0
10	55.6	25.5	0.83	11.2
20	67.7	16.9	1.31	7.02
40	75.2	12.1	1.95	4.74
80	80.2	10.6	2.26	4.07
160	82.0	9.39	2.64	3.60
360	83.5	8.43	3.02	3.04

RESULTS AND DISCUSSION

Swelling Properties and Cross-link Density

The dependence of the degree of swelling (q), network chain density (ν^*), and the molecular weight between cross-links (M_c) on the gel content of photocross-linked LDPE networks is shown in Table II, together with the UV-irradiation time and corresponding gel content of XLPE samples.

Samples with a higher gel content clearly have a higher network chain density, a lower degree of swelling, and a lower molecular weight between cross-links M_c . The results of the swelling measurements in this study are in line with those obtained for PE cross-linked in solution.²¹

Density and Melting Behavior

Density (ρ), melting point (T_m), and heat of fusion (H_f) are important thermodynamic parameters of polymers since they are closely related to structure and physical properties such as crystallinity, permeability, mechanical strength, etc. The effects of the structure of cross-linked PE on its physical properties may be seen in the changes of these parameters.

Figure 2 shows the density and melting point of XLPE as a function of gel content. In both cases, monotonic decreases are observed as the gel content increases, which agrees with results reported in the literature.^{12,27} The density of LDPE drops from 0.924 g/cm³ before cross-linking to 0.920 g/cm³ after cross-linking to a gel content of 83.5%, whereas the melting point decreases from 383.0 to 378.5 K (cf. Tables II and III). The decrease in density can be attributed to the decrease of crystallinity and the crystal lattice expansion of PE photocross-linked in the melt, which is described later in this report.

Flory²⁸ suggested that the melting point depression associated with cross-linking was due to the

reduction in concentration of segments of a length suitable for crystallization. On the basis of Flory's theory, Akana and Stein²⁹ obtained an expression for the melting point depression of a cross-linked polymer system:

$$\frac{T_m^0 - T_m}{T_m^0 T_m} = \frac{R}{H_f} K M_0 \frac{1}{M_c} \quad (5)$$

where T_m^0 and T_m are the melting point temperatures of the uncross-linked and cross-linked polymer, respectively; R , the gas constant; H_f , the heat of fusion per monomer unit; K , the number of monomer units excluded from the crystals; M_0 , the molecular weight of the monomer unit; and M_c , the molecular weight between cross-links. Consequently, a plot of $(T_m^0 - T_m)/(T_m^0 \cdot T_m)$ against $1/M_c$ should give a straight line. Such a plot is given in Figure 3 according to the data in Tables II and III. As we can see, good linearity is obtained in the case of low cross-link density, but the data points at the higher cross-link density deviate from the straight line.

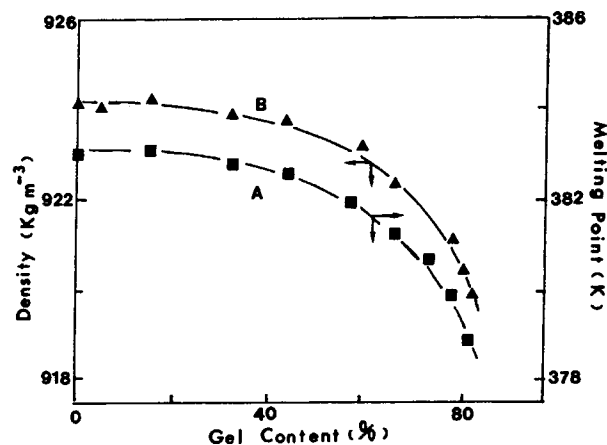


Figure 2 Density and melting point of photocross-linked LDPE as a function of gel content.

Table III Thermodynamic Parameters of Photocross-Linked LDPE

Irradiation Time (s)	T_m (K)	H_f (cal g ⁻¹)	ρ (g cm ⁻³)
0	383.0	26.7	0.9241
5	382.5	26.2	0.9236
10	381.8	25.4	0.9232
20	381.2	23.2	0.9225
40	380.5	18.2	0.9219
80	379.7	16.6	0.9210
160	378.5	15.5	0.9205

This can be interpreted as being due to the large decrease in the heat of fusion at an increased degree of cross-linking and the lattice expansions caused by higher cross-link density.

It is noteworthy that both the density and melting point of XLPE decrease rapidly near 60% gel content, which may mean that the morphological structure of XLPE is affected more pronouncedly when the cross-linking density reaches this value.

Other properties, such as the heat of fusion and the degree of crystallinity of XLPE, display similar features. Table III lists the heat of fusion (H_f) data obtained by DSC measurement, together with the two other thermodynamic parameters of melting point (T_m) and density (ρ). The change in heat of fusion due to photocross-linking is apparently quite large. H_f decreases from 26.7 to 15.5 cal/g when the gel content of cross-linked LDPE increases from 0 to about 82% (Table II). The decrease in heat of

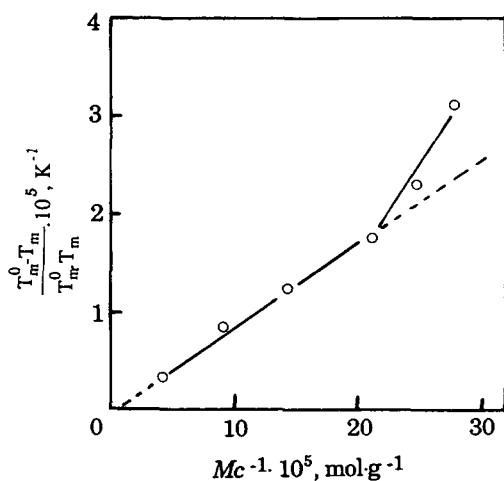


Figure 3 Plot of $(T_m^0 - T_m)/(T_m^0 \cdot T_m)$ vs. $1/M_c$ for photocross-linked LDPE according to the Flory-Rehner equation.

fusion of XLPE has been reported in the literature.^{2,3,7,9,30}

Essentially all properties are controlled by the molecular morphological structure. The changes in the melting point and the decreases in density and heat of fusion of XLPE must be primarily attributed to changes in the crystal morphological structure because cross-links produced by photocross-linking of PE influence the crystallization process and the degree of crystallinity when the polyethylene crystallizes from the melt. The following sections describe the use of the DSC method to study further the effects of chain structure changes caused by photocross-linking on crystal morphology and thermal behavior and the use of the WAXD method to determine quantitatively the changes in the degree of crystallinity of XLPE samples.

Phase Segregation and Morphological Structure

A most interesting result in the thermograms given by the DSC method is the double melting peak appearing at different irradiation times at 100°C, i.e., below the melting point of LDPE. These double melting peaks are shown in Figure 4, which also shows the following features:

1. The melting peak of the LDPE sample before photocross-linking is at 383 K, but after an irradiation time of only 5 s, a new endotherm peak 2 emerges from the original melting peak 1 on the low-temperature side. The main peak 1 does not change from its original position, but the new peak 2 appears at 380.2 K.

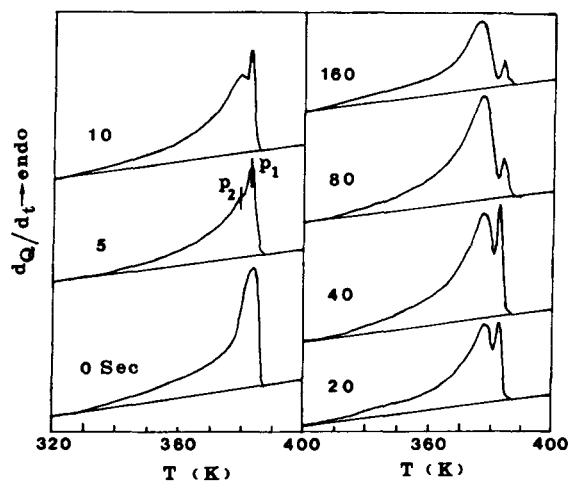


Figure 4 DSC thermograms for LDPE photocross-linked at 100°C with increasing irradiation times.

2. With increasing irradiation time, the intensity of peak 2 increases and moves gradually toward lower temperatures and becomes much broader. In contrast, the intensity and width of peak 1 decrease with increasing irradiation time, and the peak moves slowly toward higher temperatures.
3. If the material is scanned to a temperature of 410 K (above the melting point), cooled at a rate of 30 K/min back to 300 K, and then rescanned again, the double peaks disappear. Instead, a broad single melting peak is recorded (the thermogram is not shown here), which is almost the same as that obtained directly from a corresponding LDPE sample photocross-linked in the melt (140°C) and cooled quickly to room temperature. The detailed data behind these observations are listed in Table IV.

The double melting peaks below the melting point (100°C) brought about by photocross-linking are interpreted as being due to the fact that, below its melting point, cross-linking of a semicrystalline polymer such as PE preferentially occurs in the amorphous and interfacial regions, forming a cross-linked polymer as a second component. Crystallites formed when the cross-linked amorphous material is cooled from 100°C to room temperature are smaller and have a lower melting point than those that were originally in crystalline regions.

Peak 1, according to this hypothesis, represents the melting point of the original crystal regions, whereas peak 2 represents the melting point of the smaller crystallites in the cross-linked regions. It is expected that this phase segregation of the cross-

linked species will be further influenced by a longer irradiation time, i.e., by a higher degree of cross-linking. Photocross-linking of PE below the molten state therefore takes place primarily in the amorphous and interfacial regions, expands from the interface inward, and finally attacks the three-dimensional ordered crystal if the UV-irradiation continues. The broad melting behavior of peak 2 is related to different sizes of crystallites and imperfections in XLPE. Actually, the longer the irradiation time, the smaller and less perfectly ordered are the resultant crystals. These crystallites melt at a lower temperature because of a surface-free energy effect. The fact that photocross-linking alters the degree or perfection of crystallinity is described in detail in the next section.

The DSC data in Figure 4 and Table IV suggest that photocross-linking of PE below the melting point occurs preferentially in the amorphous and interfacial regions, as reported in the literature for cross-linking with high-energy radiation.^{4,20,31}

Crystallinity and Crystal Structure

It is accepted that the PE crystal structure at temperatures below the melting point may be divided into three main regions: lamellarlike three-dimensional ordered structures, diffuse and disordered interfacial regions, and liquidlike amorphous regions. The properties of bulk crystallized polymer correlate well with the level of crystallinity and the molecular structure of the lamellar crystallites and the associated interfacial and amorphous regions. These parameters are affected by the extent of chain branching and cross-linking and are also influenced by the rate of crystallization from the molten state. The relative amounts of amorphous and crystalline regions have an effect on mechanical and other physical properties. The quantitative determination of the degree of crystallinity in PE has therefore been the subject of many studies.^{8,23,24,26,32}

In the present study, WAXD was used to determine the crystallinity of PE photocross-linked in the melt. The results are shown in Figure 5 and Table V. Figure 5 shows the degree of crystallinity and the corresponding gel content of samples cross-linked at different irradiation temperatures. Figure 5(A) applies to HDPE samples and Figure 5(B) to LDPE samples. It is clear that the crystallinity decreases with increasing gel content when the irradiation temperature is increased at constant irradiation time. The increase in gel content and the decrease in crystallinity exhibit almost symmetrical trends. The curves intersect near the melting point,

Table IV Comparison of Melt Peak Data of LDPE Photocross-Linked Below and Above Melting Point

Irradiation Time (s)	Photocross-Linking Below T_m			Above T_m Melt Peak (K)
	Peak 1 (K)	Peak 2 (K)	Rescan Peak (K)	
0	383.0	—	—	383.0
5	383.0	380.2	382.3	382.5
10	383.1	380.2	381.9	381.8
20	383.2	378.8	381.0	381.2
40	383.2	378.4	380.5	380.5
80	383.7	377.5	379.8	379.7
160	384.1	376.5	377.5	378.5

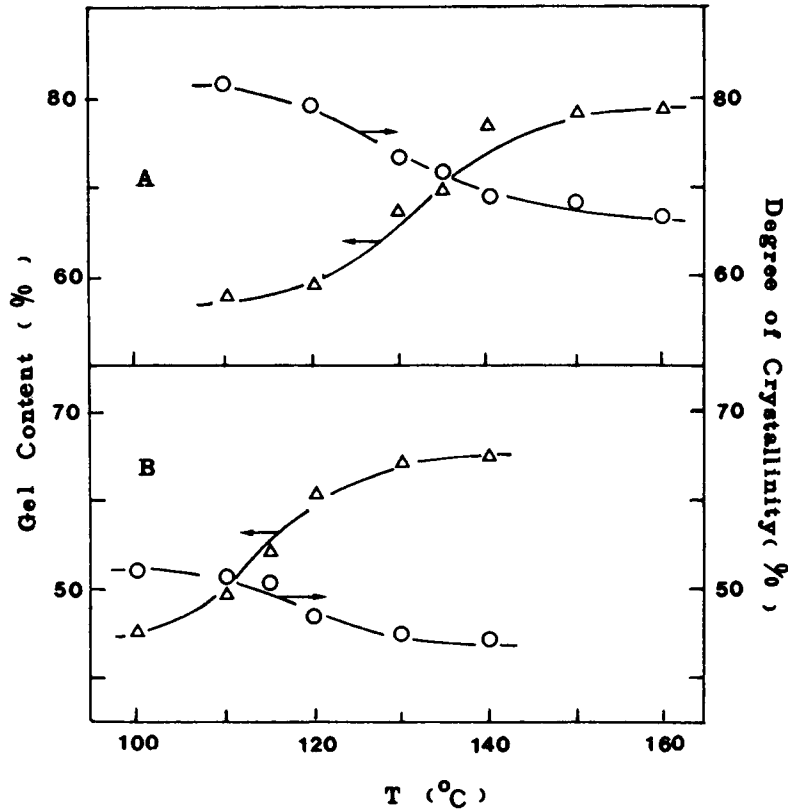


Figure 5 Degree of crystallinity and gel content as functions of irradiation temperature. Irradiation time, 15 s. (A) HDPE; (B) LDPE.

which is 110°C for LDPE and 135°C for HDPE. Both crystallinity and gel content change rapidly near the melting point in the case of both samples.

Table V Variation of the Degree of Crystallinity With Gel Content

Sample Type	Gel Content (%)	Crystallinity (%)	
		X-ray	Density
LDPE	—	53.2	53.3
	45.1	52.6	52.7
	50.2	51.8	52.6
	53.5	51.4	52.4
	61.1	49.8	52.3
	63.9	49.5	52.2
	65.0	49.0	51.9
	71.1	45.1	51.7
82.5	43.2	49.6	
HDPE	—	77.0	76.9
	80.4	64.5	68.9
	86.2	60.0	62.6
	91.3	58.6	62.2

The data in Table V show that the degree of crystallinity apparently decreases with increasing gel content of XLPE. The crystallinity of LDPE drops from 53.2% before cross-linking to 43.2% after a high degree of cross-linking (82.5%). The crystallinity of HDPE decreases from 77.0% before crosslinking to 58.6% at a gel content of 91.3%. The decrease in crystallinity with increasing degree of cross-linking is reasonable: Cross-linked polymer chains do not pack as easily into a crystal lattice as do uncross-linked chains when PE crystallizes from the melt and the cross-links are excluded from crystals,³¹ producing smaller crystals, or act as defects within a crystal.

At low degrees of cross-linking, the crystallinity data estimated from density measurements are in good agreement with those given by the WAXD method. At high degrees of cross-linking, however, the crystallinities given by the density method are appreciably higher than those given by the WAXD method. This difference is probably associated with cross-linking of the interfacial regions, which may be included in the degree of crystallinity given by the density method. Cross-linking of the interfacial

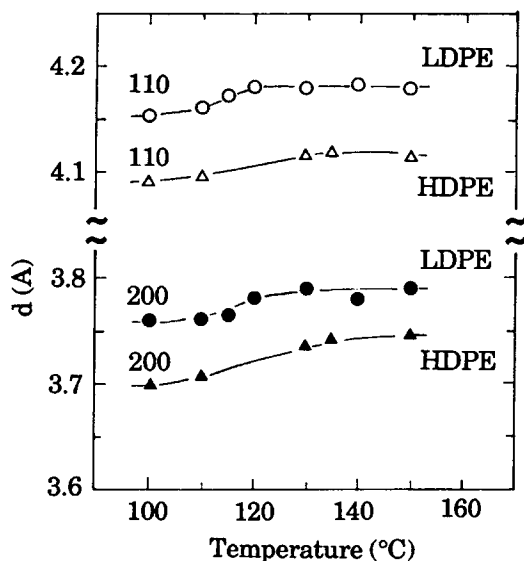


Figure 6 Variation in lattice interplanar distance with irradiation temperature for photocross-linked XLPE. Irradiation time: 15 s for LDPE; 80 s for HDPE.

regions could reduce the size of the crystalline regions as indicated by the decrease in X-ray diffraction from the crystals.

The phenomenon of lattice expansion, i.e., a slight increase in the interplanar distance [d (Å)] for 110 and 200 planes in crystalline XLPE with increasing irradiation temperature, is shown in Figure 6. The decrease in density is here considered to be the result of lattice expansion because cross-links decrease the order of the crystalline regions and affect the compactness of lamellar packing after photocross-linking of PE in the melt. Lattice expansion in γ -irradiated PE has been reported in the literature.^{1,3}

The widths of the crystal peaks (110 and 200) in the WAXD crystallograms also indicate increasing

disorder or decreasing order due to photocross-linking at increasing temperature. Data obtained after photocross-linking below and above the melting point are presented in Table VI for both HDPE and LDPE. The cross-linked PE samples show wider peaks than those of uncross-linked ones, especially above T_m . Since the width is inversely related to the crystallite breadth perpendicular to the crystalline plane in question,³³ the effect of cross-linking is a decrease in the average size of the crystallites. These changes in the crystal structure are in good agreement with the results obtained by the DSC method.

CONCLUSIONS

The principal effects of photocross-linking on the thermodynamic properties and the crystal morphological structure observed in the present work can be summarized as follows:

1. Photocross-linking of PE in the melt leads to a lowering of the melting point and to a decrease in density and heat of fusion. These changes in the properties of XLPE are attributed to the effects of cross-linking on the crystal and morphological structures.
2. The degree of crystallinity decreases with increasing gel content because the cross-links affect the packing of the crystal lattice and result in smaller, less perfectly ordered crystallites.
3. Cross-links occur preferentially in noncrystalline regions. Photocross-linking of PE in the melt can therefore produce a homogeneous network.

Table VI Change of WAXD Peak Width With Temperature of Photocross-Linking^a

Sample Type	UV-Irradiation Temp (°C)	Relative Width of 110 Peak (mm)	Relative Width of 200 Peak (mm)
LDPE	—	7.3	13.3
	100	8.5	15.4
	110	9.0	16.0
	140	9.0	16.0
HDPE	—	5.5	6.8
	130	5.6	7.2
	135	6.2	8.2
	150	6.2	8.2

^a The irradiation conditions: 4-CBP 1%, TAC 1%; t , 15 s.

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