

Thermal and Wide Angle X-ray Analysis of Chemically and Radiation-Crosslinked Low and High Density Polyethylenes

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ABSTRACT: Low and high density polyethylenes (PE) were crosslinked by two methods, namely, chemically by use of different amounts of *tert*-butyl cumyl peroxide (BCUP) and by irradiation with different doses of electron beam. A comparison between the effects of these two types of crosslinking on crystalline structure, crystallinity, crystallization, and melting behaviors of PE was made by wide angle X-ray diffraction and DSC techniques. Analysis of the DSC first heating cycle revealed that the chemically induced crosslinking, which took place at melt state, hindered the crystallization process and decreased the degree of crystallinity, as well as the size of crystals. Although the radiation-induced crosslinking, which took place at solid state, had no significant influence on crystalline region, rather, it only increased the melting temperature to some extent. However, during DSC cooling cycle, the crystallization temperature showed a prominent decrease with increasing irradiation

dose. The wide angle X-ray scattering analysis supported these findings. The crystallinity and crystallite size of chemically crosslinked PE decreased with increasing peroxide content, whereas the irradiation-crosslinked PE did not show any change in these parameters. As compared with HDPE, LDPE was more prone to crosslinking (more gel content) owing to the presence of tertiary carbon atoms and branching as well as owing to its being more amorphous in nature. HDPE, with its higher crystalline content, showed relatively less tendency toward crosslinking especially by way of irradiation at solid state. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3264–3271, 2006

Key words: polyethylene; thermal properties; wide angle X-ray scattering; chemical crosslinking; radiation crosslinking

INTRODUCTION

Polyethylene (PE) derives its mechanical properties from crystalline morphology. The loss of this crystal structure with increasing temperature limits material serviceability. Crosslinking is a means of modifying the structure of the base polymer.^{1,2} This can be accomplished either by irradiation with high-energy electron beams or through the use of chemical crosslinking additives.^{3,4} Chemical crosslinking is accomplished by incorporating organic peroxides, such as dicumyl peroxide or *tert*-butyl cumyl peroxide (BCUP), into PE, and subsequently by activating the peroxide that links the long-chain molecules into a three-dimensional network.^{5,6} This modification is manifested by changes in some properties of PE, such as mechanical, physical, and chemical properties. Crosslinking enables a thermoplastic polymer like PE

to exhibit a viscoelastic behavior, characteristic of an elastomer, at temperatures above the crystalline melting temperature of the thermoplastic. This valuable property is widely exploited commercially in the preparation of heat-shrinkable materials, wire and cable coating, hot water tubing and steam resistant food packaging, and so on.^{7–10} Irradiation of PE takes place normally in the solid state with a high-energy electron beam that results in crosslinking (together with some main-chain scission) whereas the chemical crosslinking takes place while the polymer is in the molten state (amorphous). The microstructure of PE chains treated in this fashion will be different. The crystallinity, crystal dimension, and crystal perfection are important microstructural parameters that control the macroscopic properties, including mechanical behavior and ultimate properties. Wide angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) are the most widely used methods for the study of crystal size, crystal orientation, and crystalline morphology of semicrystalline polymers.^{11–19} Many authors have reported comparable or contradictory results regarding crosslinking effect on crystalline structure of PE, using various crosslinking methods.^{20–26}

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Deviations have been attributed to the variety of PE types used and to the diversification of crosslinking processes (i.e., radiation or chemical techniques).

Radiation-induced crystallinity changes in pressure-crystallized ultra-high molecular weight PEs (UHMWPE) are reported by Bhateja, and it is stated that irradiation of UHMWPE at ambient conditions causes an increase in the degree of crystallinity.²⁰ On the other hand, Lazar et al.,²¹ have reported that chemical crosslinking of polyolefins reduces the crystallinity. Kitamaru et al.,²⁴ reported that a highly transparent, irradiation-crosslinked, linear PE films have very high melting temperatures and a highly ordered stable crystalline phase, but a rather low degree of crystallinity. Ungar and Keller have studied the effect of radiation on crystals of PEs and paraffins. They reported a destruction of crystalline structure of PE above a certain dose, where the radiation temperature approaches the temperature of orthorhombic-hexagonal transition.²⁷

To understand the effect of crosslinking on crystalline structure of PE, we have selected two different types of PE (HDPE and LDPE). These PEs were crosslinked by two methods, namely chemical crosslinking at molten state and by radiation crosslinking at solid state. Comparison between these two methods of crosslinking on the crystalline structure was made. For this purpose, thermal and WAXS investigations of chemically crosslinked LDPE and HDPE with different peroxide content as well as irradiated LDPE and HDPE with various irradiation doses were done.

EXPERIMENTAL

Materials

LDPE of grade LD 00BW, with a MFI of 2 g/(10 min) and a density of 0.923 g/cm³, was kindly supplied by Exxon Mobile Co., Germany. HDPE of grade MG7547A, with a MFI of 4 g/(10 min) and a density of 0.954 g/cm³, was obtained from Borealis group, Denmark. BCUP, with a purity of 96% and a density of 0.96 g/cm³, was provided by Peroxid-Chemie GmbH, Germany.

Sample preparation

The LDPE and HDPE, with different peroxide contents, were melt-mixed at 150°C in an internal mixer (PlastiCorder, Model PL 2000, BRABENDER), with a speed of 50 rpm for 5 min. Then the samples were compression-molded to flat sheets using Fontune 400 KN laboratory (Holland) hot press, operated at 190°C for 5 min under 10 MPa pressure, and thereafter the sheets were cooled at a cooling rate of 15 K/min to ambient temperature.

The irradiation of LDPE and HDPE sheets (dimensions: 120 × 120 × 1.5 mm³) were carried out using an electron accelerator ELV-2, INP Novosibirsk (Russia), with the energy of 1 MeV under various irradiation conditions (doses from 0 to 300 kGy) in air atmosphere.

Gel measurement

The gel content of the crosslinked PE was determined gravimetrically, according to ASTM D 2765, using a 16-h soxhlet extraction cycle, with *p*-xylene as the solvent at 140°C. About 0.5 wt % Irganox 1010 was added to inhibit polymer degradation during the extraction process. Approximately 0.3 g of the crosslinked polymer sample was cut into small pieces and placed in a preweighted stainless steel, fine wire mesh. After the extraction cycle, the sample was washed with acetone and vacuum-dried to a constant weight. The gel fraction was calculated as the percentage ratio of the final weight of the polymer to its initial weight.

Thermal analysis

The DSC tests were performed on a DSC Q 1000 of TA (USA), with samples of about 5 mg sealed in aluminum pans, under nitrogen atmosphere in a temperature range between -60 to 180°C, at a heating rate of 10 K/min. The melting and crystallization enthalpy and melting temperature of the samples were determined. The degree of crystallinity was calculated via the total enthalpy method, according to the following eq. (1):

$$X_c = \frac{\Delta H_m}{\Delta H_m^+} \quad (1)$$

where X_c is the degree of crystallinity, ΔH_m the specific enthalpy of melting, and ΔH_m^+ is the specific melting enthalpy for 100% crystalline PE. We used a ΔH_m^+ value of 288 J/g.^{28,29}

WAXS analysis

The overall percent of crystallinity and crystallite size of chemically and irradiation-induced crosslinked samples were determined by WAXS. X-ray measurements were carried out on a Siemens 4-circle diffractometer with a HiStar area detector, using Cu K α radiation, at a wavelength of $\lambda = 0.1542$ nm in transmission technique.

The degree of the crystallinity was estimated from the wide-angle data recorded on the area detector as the ratio of the scattering from the crystalline regions, I_{cr} , to the total sample scattering, $I_{cr} + I_{amr}$, (using a simple peak area method in an angular range of 2θ

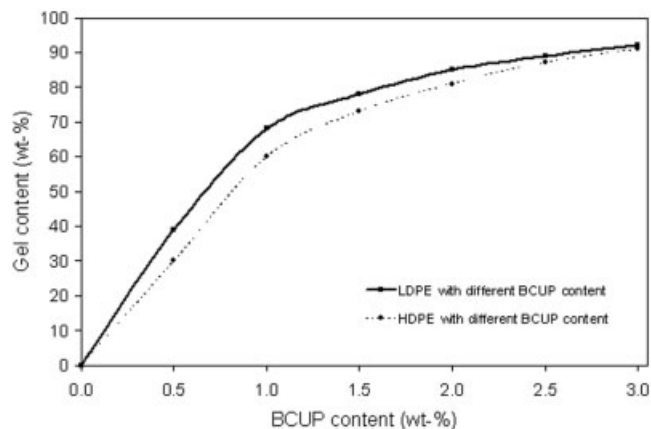


Figure 1 Effect of peroxide (BCUP) content on the gel content of crosslinked LDPE and HDPE.

= 10... 45° and integration of the 2-dimensional primary data over an azimuthal range $2\varphi = \pm 22.5^\circ$ using eq. (2):

$$\alpha_x = I_{cr} / (I_{cr} + I_{am}) \quad (2)$$

The strongest (hk0) reflections, that is (110) and (200), in the applied 2θ -range were used as indicators for the determination of crystallite size, D_{hkl} , by applying the Scherrer equation [eq. (3)], with $FWHM_{hkl}$ as the full width at half maximum of the (hkl) reflection:

$$D_{hkl} = \lambda / (FWHM_{hkl} \cos \theta_{hkl}) \quad (3)$$

In this simple kind of manner, the influence of any crystal distortion on FWHM has been neglected. Therefore, the derived data D_{hkl} are of minimum sizes.

RESULTS AND DISCUSSION

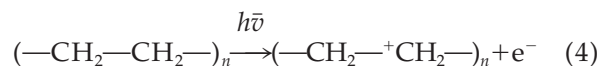
Gel fraction

Peroxide crosslinking takes place randomly at elevated temperatures in the molten state, where the polymer has only amorphous structure. Determination of gel content, which is an indication of the extent of crosslinking, is reported elsewhere.^{30,31} Figure 1 shows the variation of gel content against BCUP content for the crosslinked LDPE and HDPE. As the curve indicates, there is a continuous increase of the gel content with peroxide content up to about 2.5 wt %, and thereafter the curve gradually levels off. A comparison between the gel content of LDPE and HDPE shows that LDPE with its long-chain branched structure and tertiary carbon atom is more prone to crosslinking, and hence it has higher gel content when compared with HDPE at the same peroxide content.

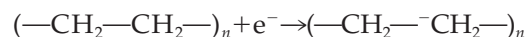
The use of radiation for PE crosslinking, which has been known for several decades, belongs to the economically most successful products of radiation chemistry research. The main advantage of radiation initiation consists of the possibility of generating active intermediates in the solid polymer within a large temperature interval. The sources of radiation for the crosslinking of PE used industrially are the betatrons that allow one to obtain high radiation doses within a short time lag. The mechanism of crosslinking in PE under interaction of high-energy electrons can be visualized by the following scheme [eqs. (4) and (5)]²¹⁻²³:

The primary step of interaction of radiation and polymer involves the formation of macroions:

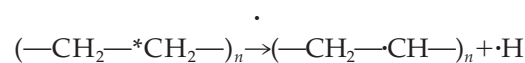
Initiation:



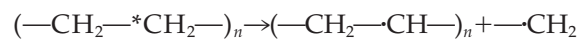
The electron released has so much energy that it may induce further ionization and excitation of other macromolecules. The electron thus gradually transmits an excess of its kinetic energy to the environment, and is finally captured by some cavity in the electroneutral polymer matrix,



or recombines with a positive ion. Recombination of particles of opposite charges leads to the formation of excited electroneutral macromolecules that are capable of cleaving to free radicals. The dissociation may either involve an elimination of hydrogen atom,



or cleavage of the carbon-carbon bond:



Part of the excitation energy may be transformed to the kinetic energy of dissociation products (where * represents the molecule-excited state). This is a route by which hot hydrogen atoms of high reactivity are formed.

It is obvious that the more the radicals formed move away from the initial radical pair, the lower is the probability of their back self-recombination at the site of their generation and thus of regeneration of an original molecule:

Crosslinking:

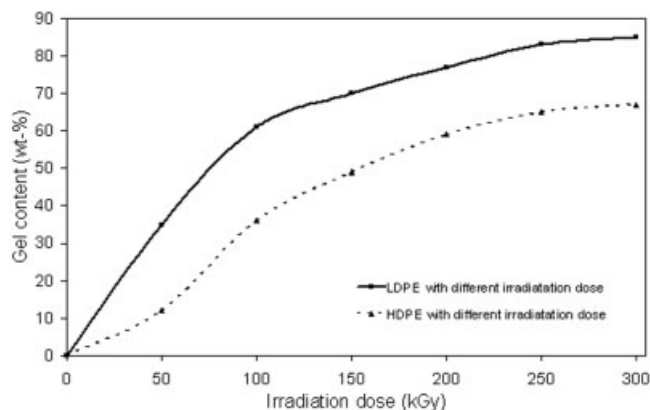
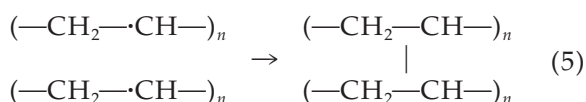


Figure 2 Variation of gel content of the irradiated LDPE and HDPE versus irradiation dose.



PE is a semicrystalline thermoplastic consisting of a continuous amorphous phase, in which the crystalline domains are distributed. On irradiation with high-energy beams, it predominantly undergoes crosslinking in the amorphous regions.^{1,2} The probability of free radicals that are being generated at the adjacent sites is higher in the amorphous regions. The amorphous region includes the interlamellar volume and the defect sites in the lamellae. The HDPEs are more crystalline when compared with the low-density ones. The higher crystallinity leads to a greater proximity of the crystal lamellae, which decreases the extent of crosslinking in the high density samples.

Radicals in both crystalline and amorphous regions can be identified. Radicals formed in the crystalline regions have much lower mobility and longer lifetimes because macromolecular diffusion movement is strongly restricted; such radicals can migrate slowly to the amorphous region; where they subsequently react.

Figure 2 shows the gel content of the irradiated LDPE and HDPE versus irradiation dose. The extent of gel formation in the exposed samples is strongly dependent on the dose values. The higher gel content corresponds with a higher portion of the network structure in the amorphous region of the polymer, which is insoluble in the solvent. The sol content corresponds with the linear portion of the polymer in both amorphous and crystalline regions. It should be noted, by way of reminder, that the crystalline portion of the polymer is soluble in xylene at 140°C, which is inferred from the zero gel content of noncrosslinked PE. Further, from melting point and enthalpy of fusion measurements of crosslinked PE (see DSC results), it is concluded that the crystalline regions remain effectively intact, that is, noncrosslinked. Thus, the higher

the gel content the higher the degree of crosslink density in amorphous regions. The gel content increases rapidly up to a dose of 100 kGy, and then the extent of gel formation slows down with further increase in dose rates. This can be attributed to the restricted movement of radical species at a tighter network, which makes the rate of crosslinking slower at higher dose values. The LDPE with higher amorphous content has a higher gel content when compared with HDPE, since the crosslinking takes place in solid state, and therefore, HDPE with a higher crystalline content undergoes less crosslinking when compared with LDPE. For HDPE, a part of the radiation does not participate in crosslinking, since it is being wasted in the crystalline region which is resistant to crosslinking.

Thermal properties

The degree of crystallinity of semicrystalline polymers has considerable effect on their mechanical and thermal properties.

Figure 3 shows the DSC diagram of samples with 0–2.5% BCUP content. It is seen that with increasing peroxide content the melting point, crystallization temperature, and crystallinity of the crosslinked HDPE decreases. The results of DSC measurements of chemically crosslinked LDPE and HDPE are shown in Table I. Figure 4 shows the DSC diagram of HDPE with 0–250 kGy irradiation doses. It is seen that with increasing irradiation dose, the melting point and crystallinity of the irradiation-crosslinked HDPE and LDPE are not changed significantly, but rather show very small tendency of increase of melting temperature on first heating only. On the other hand, during the cooling cycle, crystallization temperature (T_c) shows a decrease with increasing irradiation dose. The

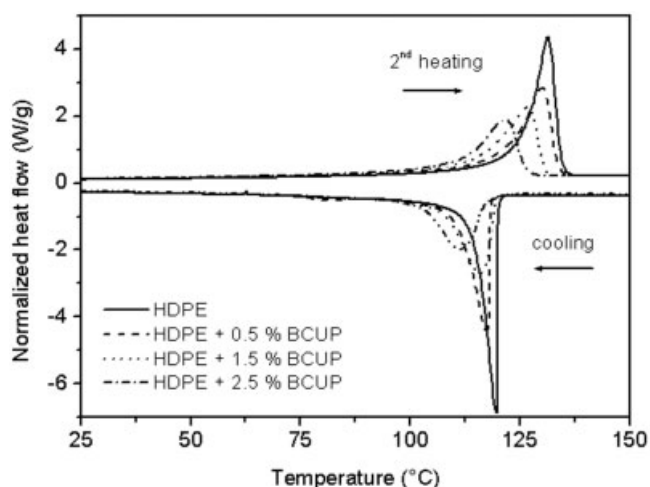


Figure 3 DSC diagram of noncrosslinked HDPE and crosslinked HDPE containing 0.5 to 2.5 wt % BCUP.

TABLE I
Melting Temperature, T_m , Heat of Fusion, ΔH_m , Degree of Crystallinity, X_c , and Crystallization Temperature, T_c , of LDPE and HDPE Crosslinked with Different Peroxide (BCUP) Content

Peroxide content (wt %)	LDPE				HDPE			
	ΔH_m (J/g)	X_c (%)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	X_c (%)	T_m (°C)	T_c (°C)
0.0	141.4	49.1	108.8	96.0	220.5	76.5	131.4	119.7
0.5	135.9	47.2	107.0	95.2	195.5	67.8	129.9	117.3
1.0	130.5	45.3	106.1	93.3	192.8	66.9	128.5	116.7
1.5	127.6	44.3	103.9	91.7	182.2	63.3	126.8	115.6
2.0	126.8	44.0	103.1	91.0	178.9	62.1	125.9	114.7
2.5	126.3	43.8	101.4	90.4	164.8	57.2	121.6	111.4
3.0	124.8	43.3	99.5	88.8	158.3	54.9	121.0	111.2

results of DSC measurements of irradiated LDPE and HDPE are shown in Table II. The melting temperature and total crystallinity are related to the crystal size and the amount of crystals revealed, as the endothermic peak temperature and area under the peak in DSC curves, respectively. Formation of crosslink junctions while the polymer is at melt state (amorphous phase) disturbs the reorganization and chain folding during crystallization process, and this results in formation of an imperfect crystallite with smaller size and lesser content. Hence, the melting point, crystallization temperature, and total crystallinity decrease with increase of crosslink density. In case of radiation-crosslinked method, the crosslinking takes place while the polymers are in solid state. Therefore, the radiation mainly affects the amorphous phase while the crystalline phase remains intact. Hence, no change in melting temperature is observed for the radiation-crosslinked samples.

As a matter of fact, normally, during the second heating run in DSC the previous thermal history of a sample is completely erased. Here, the main aim of

this work is to study and compare the two methods of crosslinking namely, by way of irradiation and peroxides, on the thermal properties of PE. Since the irradiation of the PE samples in solid state does not make any changes in the crystalline region, but rather only on the amorphous phase, it can be assumed that the melting temperature of the irradiated samples should not be changed. To verify this hypothesis, one has to look into the first heating run which is a representation of actual state (real thermal history) of the sample without undergoing subsequent changes during further heating and cooling cycles of DSC. Otherwise, this effect cannot be seen properly during the second run, which erases the previous thermal history. During the second heating run, when the samples are completely melted and forms an isotropic amorphous phase, subsequent cooling to an ambient temperature leads to reformation of the crystalline regions. But the presence of crosslink junctions inhibits this process (crystal growth) to some extent, and hence decreases the degree of crystallinity and size of crystals. On the other hand, the situation is quite different for the PE samples crosslinked by chemical method. In this case, the crosslink junctions already formed during the processing stage (and not only during the DSC runs) hinder the crystallization process. Hence for this set of samples, both the first and second heating runs remain the same. Therefore, the first heating run for the irradiated samples and the second heating run for the chemically crosslinked samples were used to show and explain differences between these two methods of crosslinking.

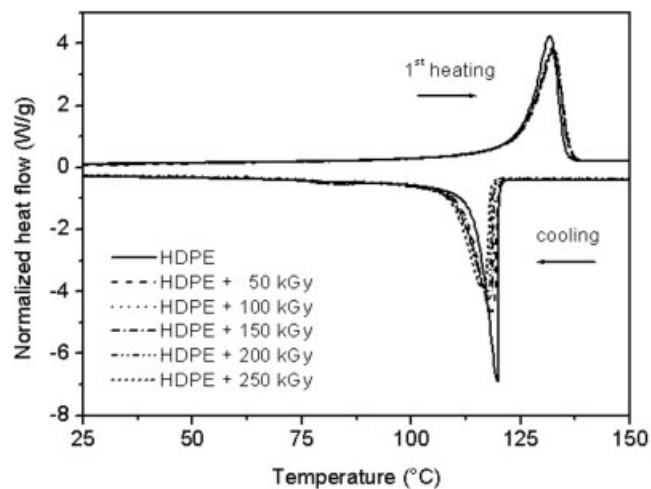


Figure 4 DSC diagram of noncrosslinked HDPE and crosslinked HDPE irradiated with 50 to 250 kGy.

WAXS studies

X-ray scattering experiments were done to get information about crystallinity and crystallite size in selected crystallographic directions. For the basic scattering behavior of the PE samples under investigation, two 2-dimensional scattering pictures were shown in Figure 5. The differences in crystallinity of the LDPE and HDPE are clearly visible from their scattering

TABLE II
Melting Temperature, T_m , Heat of Fusion, ΔH_m , Degree of Crystallinity, X_c of First Heating of Samples, and Crystallization Temperature, T_c , of Irradiated LDPE and HDPE with Different Irradiation Dose

Irradiation dose (kGy)	LDPE				HDPE			
	ΔH_m (J/g)	X_c (%)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	X_c (%)	T_m (°C)	T_c (°C)
0	146.3	50.8	109.2	96.0	230.2	79.9	131.6	119.7
50	149.1	51.7	108.3	95.4	220.0	76.4	132.2	118.4
100	144.7	50.2	107.6	95.1	214.7	74.5	132.4	117.8
150	145.2	50.4	107.5	93.9	227.3	78.9	132.4	117.6
200	140.9	48.9	107.5	93.5	217.3	75.4	132.6	117.1
250	137.9	47.9	107.6	92.7	223.2	77.5	132.7	116.2
300	137.8	47.8	105.2	92.1	223.1	77.5	132.7	115.8

patterns. As it is known, the crystallinity is dependent on the molecular structure of the polymer chains. LDPE has higher content of branched chain segments that hinder the crystallization in their neighborhood. Consequently, the crystallinity of LDPE is obviously smaller than that of HDPE.

Crystalline behavior of a polymer can be altered through chemical modification. Crosslinking of polymer chains results in reduction in T_m , crystallization rates, and the observed degree of crystallinity.³² Special investigations were directed to show the dependency of the peroxide content on the crystalline structure. The Figures 6 and 7 illustrate the decreasing tendency of the crystallinity with increasing crosslinking initiated by the peroxide. The calculated data corresponding to the scattering curves are summarized in Table III. The crystallite sizes are calculated for the possible two crystallographic directions (perpendicular to the (110) and (200) net planes). As it is seen, there is a decrease in the crystallite size and degree of crystallinity with increasing peroxide content. However, LDPE shows relatively smaller reduction when compared with HDPE. This can be explained by higher crystallinity content of HDPE.

As compared to the DSC results (see Table I), correlation between specific parameters are suggested. The melting temperature, T_m , depends on the crystallite size, D_{hkl} , whereas the crystallinity, α_x , corresponds to the area of the heat of fusion, ΔH_m . The same trend was found in both the analytical methods.

For understanding the behavior of the irradiated samples, an annotation to the radiation treatment is necessary. Since the radiation-induced crosslinking procedure was performed in the solid state of PE, as expected, the parameters α_x and D_{hkl} remain constant, which confirm the results of DSC (compare Table II). The scattering curves are not distinguishable depending on the irradiation-induced crosslinking. For the illustration, only the scattering curves of HDPE were shown in Figure 8, because the same results were found for LDPE (but on another level of crystallinity).

CONCLUSIONS

Measurement of the gel content indicated an increase in the degree of crosslinking by addition of peroxide content. Also, this trend was found for the irradiated PEs with increasing irradiation doses.

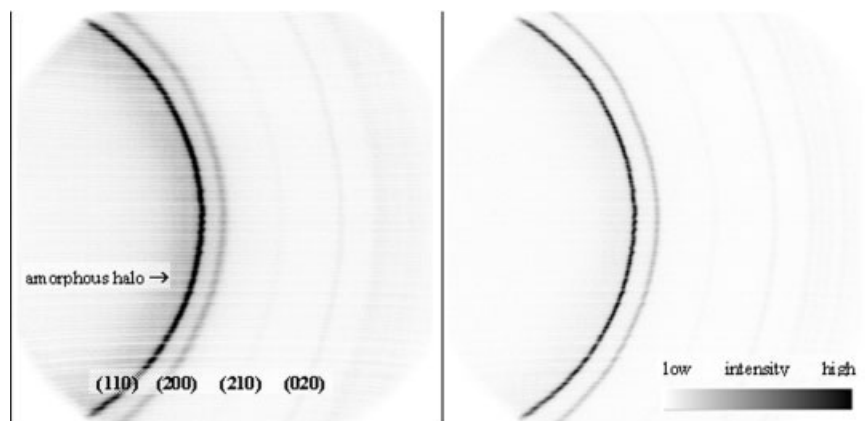


Figure 5 Two-dimensional-WAXS pattern of LDPE (left, with assigned (hkl) reflections) and HDPE (right), respectively. The pictures show the nontreated samples. Moreover, independence on irradiation dose pattern without significant changes were measured.

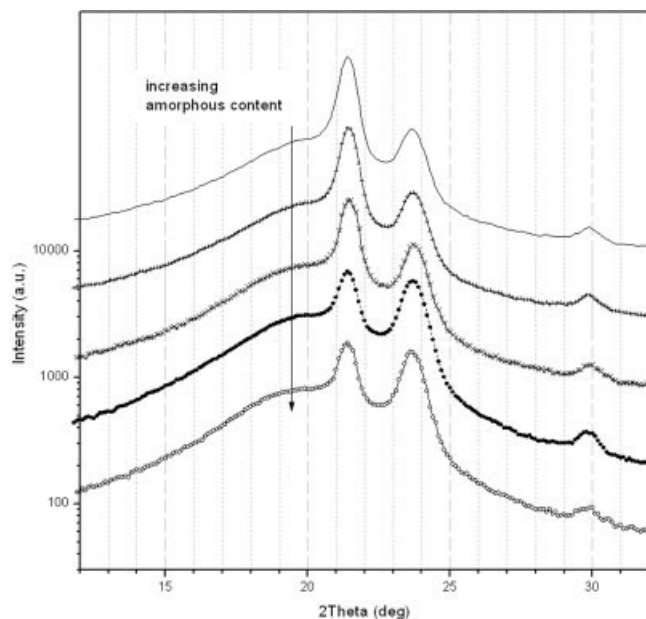


Figure 6 Comparison of WAXS curves for LDPE with different amount of BCUP (content in wt %: —0.0; +- 0.5; -×- 1.0; -●- 1.5; -○- 2.0).

When compared with HDPE, LDPE was more prone to crosslinking (more gel content) owing to the presence of tertiary carbon atoms and long-chain branching as well as owing to its being more amorphous in nature. HDPE with its higher crystalline content showed lesser tendency toward crosslinking especially by way of irradiation at solid state. Investi-

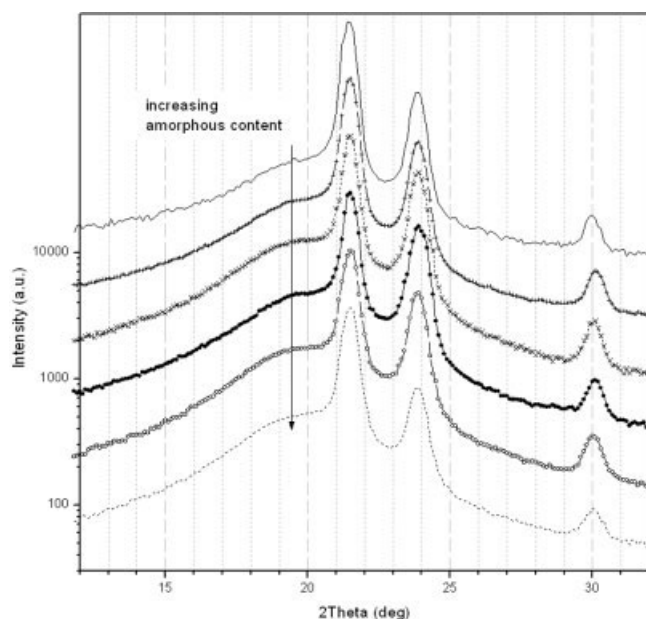


Figure 7 Comparison of WAXS curves for HDPE with different amount of BCUP (content in wt %: —0.0; +- 0.5; -×- 1.0; -●- 1.5; -○- 2.0; 2.5).

TABLE III
Crystallinity, α_X , and Crystallite Size, D_{hkl} , As Calculated from the Scattering Curves for the PE Samples Under Investigation

Peroxide content (wt %)	Crystallinity ($\Delta\alpha_X \approx \pm 0.02$)	Crystallite size ($\Delta D \approx \pm 0.2$ nm)	
		In (110) direction	In (200) direction
LDPE			
0.0 ^a	0.38 ^a	>14.4 ^a	>10.6 ^a
0.5	0.35	>14.1	>10.6
1.0	0.32	>13.8	>11.0
1.5	0.30	>13.9	>10.0
2.0	0.28	>13.9	>10.5
HDPE			
0.0 ^a	0.64 ^a	>17.1 ^a	>15.1 ^a
0.5	0.56	>16.8	>14.8
1.0	0.51	>17.0	>14.6
1.5	0.49	>16.8	>14.4
2.0	0.45	>16.1	>14.4
2.5	0.46	>15.7	>13.8

^a The results are given for the nontreated samples. Moreover, they are valid also for all irradiated samples divided in HDPE and LDPE types.

gation of the thermal properties of the chemically crosslinked PE showed that the melting temperature, T_m , heat of fusion, ΔH_m , crystallinity, X_c , and crystallization temperature, T_c , are reduced by increasing the peroxide content. Thermal properties of irradiation-crosslinked PEs showed that T_m , ΔH_m , and X_c were not changed significantly by increasing the irradiation doses, but the T_c is reduced. WAXS analysis showed that the crystallinity, α_X , and crystallite size, D_{hkl} , of chemically crosslinked PE reduced by increasing the peroxide content. But, α_X and D_{hkl} of irradiation-crosslinked PE were not changed by increasing the irradiation doses. These changes in crystalline struc-

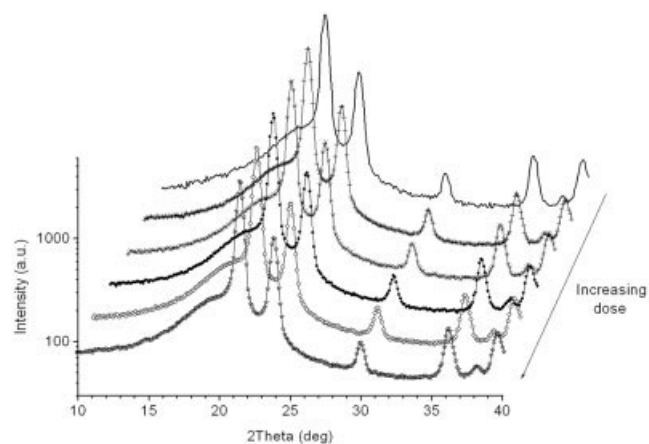


Figure 8 WAXS curves (shifted three-dimensional plot) for HDPE irradiated with different dose rates (dose in kGy: —0; +- 50; -×- 100; -●- 150; -○- 200; -☆- 250).

ture in chemically crosslinked samples could be attributed to the reduction in mobility of chains because of the formation of crosslink junctions between the macromolecular chains, and hence it decreased the crystallinity. These effects were more pronounced for HDPE when compared with LDPE because of its higher crystalline content.

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References

1. Chodak, I. J. *Prog Polym Sci* 1995, 20, 1165.
2. Lyons, B. J. *Radiat Phys Chem* 1983, 22, 135.
3. Rado, R. *Int Polym Sci Technol* 1993, 20, 78.
4. Ota, S. *Radiat Phys Chem* 1981, 18, 81.
5. Rado, R.; Zelenak, P. *Int Polym Sci Technol* 1992, 19, 33.
6. Kampouris, E. M.; Andreopoulos, A. G. *J Appl Polym Sci* 1987, 34, 1209.
7. Morton-Jones, D. H.; Ellis, J. W. *Polymer Products*; Chapman & Hall: London, 1986.
8. Hoffman, J. W. *IEEE Electr Insul Mag* 1991, 7, 33.
9. Khonakdar, H. A.; Morshedian, J.; Mehrabzadeh, M.; Wagenknecht, U.; Jafari, S. H. *Eur Polym J* 2003, 39, 1729.
10. Rado, R.; Zelenak, P. *Int Polym Sci Technol* 1992, 19, 72.
11. Hamley, I. W.; Fairclough, P. A.; Bates, F. S.; Ryan, A. J. *Polymer* 1998, 39, 1429.
12. Androsch, R.; Blackwell, J.; Chvalun, S. N.; Wunderlich, B. *Macromolecules* 1999, 32, 3735.
13. Androsch, A.; Stribeck, N.; Lüpke, T.; Funari, S. S. *J Polym Sci Part B: Polym Phys* 2002, 40, 1919.
14. Kolb, R.; Wutz, C.; Stribeck, N.; von Krosigk, G.; Riekkel, C. *Polymer* 2001, 42, 5257.
15. Wasiak, A. *Polymer* 2001, 42, 9025.
16. Murakami, S.; Senoo, K.; Toki, S.; Kohjiya, S. *Polymer* 2002, 43, 2117.
17. Murthy, N. S.; Wang, Z. G.; Akkapeddi, M. K.; Hsiao, B. S. *Polymer* 2002, 43, 4005.
18. Cho, J.; Baratian, S.; Kim, J.; Yeh, F. *Polymer* 2003, 44, 711.
19. Kawana, S.; Durrell, M.; Lu, J.; Macdonald, J. E.; Grell, M.; Bradley, D. D. C.; Jukes, P. C.; Jones, R. A. L.; Bennett, S. L. *Polymer* 2002, 43, 1907.
20. Bhateja, S. K. *J Macromol Sci Phys* 1983, 22, 159.
21. Lazar, M.; Rado, R.; Rychly, J. *Adv Polym Sci* 1990, 95, 149.
22. Bhateja, S. K.; Andrews, E. H.; Young, R. J. *J Polym Sci Polym Phys Ed* 1983, 21, 523.
23. Patel, G. N.; Kellar, A. *J Polym Sci Polym Phys Ed* 1975, 13, 303.
24. Khonakdar, H. A.; Jafari, S. H.; Wagenknecht, U.; Jehnichen, D. *Radiat Phys Chem* 2006, 75, 78.
25. Kitamaru, R. *Die Makromol Chem* 1974, 175, 255.
26. Klein, P. G.; Ladizesky, H.; Ward, I. M. *J Polym Sci Part B: Polym Phys* 1986, 24, 1093.
27. Ungar, G.; Keller, A. *Polymer* 1980, 21, 1273.
28. Krupa, I.; Luyt, A. S. *J Appl Polym Sci* 2001, 81, 973.
29. Wunderlich, B. *Macromolecular Physics*, Vol. 2; Academic Press: New York, 1973.
30. Khonakdar, H. A.; Morshedian, J.; Mehrabzadeh, M.; Eslami, H. *Adv Polym Tech* 2003, 22, 112.
31. Khonakdar, H. A.; Morshedian, J.; Wagenknecht, U.; Jafari, S. H. *Polymer* 2003, 44, 4301.
32. Weimann, P. A.; Hajduk, D. A.; Chu, C.; Chaffin, K. A.; Brodil, J. C.; Bates, F. S. *J Polym Sci Part B: Polym Phys* 1999, 37, 2053.