

Graft polymerization of acrylamide onto linear low-density polyethylene film by electron beam pre-irradiation in air or argon: 3. Morphology

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The crystallinity of linear low-density polyethylene (LLDPE) after electron beam irradiation and subsequent grafting with acrylamide in aqueous solution was investigated by differential scanning calorimetry and X-ray diffraction. The LLDPE was pre-irradiated in air or argon in the dose range up to 20 Mrad. The pre-irradiation atmosphere influences the grafting kinetics due to differences in the resulting morphology in the LLDPE. The cross-sections of the LLDPE film samples are grafted completely through before the final degree of grafting is reached, as analysed by scanning electron microscopy and scanning electron microprobe quantometry. The progression of grafting is related to a decrease in the degree of crystallinity and at higher graft yields also in the average crystallite size of the LLDPE trunk polymer. The difference in grafting behaviour of the LLDPE pre-irradiated in air or argon was investigated by comparing the decline in crystallinity in the material during grafting after the two types of pre-irradiation.

(Keywords: polyethylene; acrylamide; grafting)

INTRODUCTION

The present investigation was preceded by kinetic studies on heterogeneous grafting of linear low-density polyethylene (LLDPE) film in aqueous acrylamide (AAM) solution. These studies have been submitted for publication^{1,2}.

Polyethylenes contain three continuously transient phases differing in degree of order: amorphous, crystalline and an intermediate transitive phase^{3–5}. When LLDPE is homogeneously exposed to high-energy radiation, commonly from a gamma-ray or electron beam (EB) source, alkyl radicals are primarily generated throughout the material. Above 77 K, the alkyl radicals start to decay by recombination or generation of allyl and polyenyl radicals^{6–8}. Recombination leads to crosslinking primarily in the amorphous and transitive phases^{9,10}. However, even at room temperature, alkyl radicals remain trapped in the crystalline phase, although with a limited lifetime^{8,11}. Several investigations have found that alkyl radicals in the crystalline phase migrate to the lamellar surfaces^{7–9,11}. When a radical scavenger such as oxygen is present during the irradiation of polyethylenes, crosslinking is significantly reduced^{1,12}. Since the diffusion of oxygen is much slower in the crystalline phase, oxygen will react with free radicals as they are formed in the amorphous phase or as they appear on the crystallite surfaces. Initially, oxygen reacts readily with alkyl, allyl and polyenyl radicals to

form peroxy radicals^{13–15}. These are converted to peroxides, which may further transform into carbonyl and hydroxyl compounds partly in combination with chain scission. An increase in crystallinity has been reported in polyethylene after γ irradiation in the presence of oxygen due to reorganization and crystallization facilitated by chain scission^{16,17}. When irradiation is carried out under inert conditions, crosslinking increases rapidly with dose and crystallization is suppressed¹⁶. The different morphologies obtained when pre-irradiating in air or under inert conditions have a great influence on the grafting kinetics^{1,12}.

In this study, LLDPE was pre-irradiated by EB in air or argon at about 20°C below room temperature¹. Seguchi and Tamura⁸ detected mainly alkyl radicals trapped in the crystalline phase immediately after EB irradiation of polyethylene at room temperature in air. In a later article¹⁸, they concluded that graft polymerization of vinyl monomers diffusing into EB-irradiated LLDPE is initiated at the surface of the crystallites by alkyl or allyl radicals, depending on monomer supply. Uezu *et al.*¹⁹ analysed radicals formed in polyethylene EB-irradiated at ambient temperature in nitrogen atmosphere. After exposing irradiated samples to air, they found alkyl, allyl and a small amount of peroxy radicals. Also in this case, it was suggested that graft polymerization of vinyl monomers would be initiated mainly by alkyl radicals at the surface of the crystalline phase. Interpretations concluding that the crystalline phase is a source of free radicals were also made when AAM was grafted onto nylon-6 pre-irradiated in air at ambient temperature^{20,21}.

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Owing to the high dose rates used in the EB pre-irradiation, it is generally considered that the subsequent graft polymerization is initiated at or near the crystallite surfaces and proceeds into the amorphous phase regardless of the pre-irradiation atmosphere. During the grafting process, the degree of crystallinity within the semicrystalline trunk polymer decreases, but some crystallinity may still remain up to very high graft yields^{21,22}.

The aim of the present investigation is to study the morphology of LLDPE after EB irradiation and after subsequent grafting with AAm. Pre-irradiations in air or argon are compared since the presence or exclusion of oxygen during irradiation gives different degrees of crosslinking in the LLDPE matrix.

EXPERIMENTAL

Materials

LLDPE 8568 was provided by Neste, Stenungsund, Sweden, as biaxially blown film with a thickness of 40 μm . The average branch content was given as 18 ethyl branches per 1000 main-chain carbons. The molecular-weight averages $\langle M_n \rangle = 21\,900\text{ g mol}^{-1}$ and $\langle M_w \rangle = 93\,300\text{ g mol}^{-1}$ were measured by g.p.c.¹. The degree of crystallinity was determined by differential scanning calorimetry and X-ray diffraction to be 41% and 47% respectively. Acrylamide (AAm), electrophoresis-grade (Pharmacia LKB 80-1128-10), and Mohr's salt (Merck 3792) were used as received.

Irradiation and grafting

Details concerning the EB irradiation and grafting are given elsewhere¹.

In short, the EB irradiation was performed with a 6.5 MeV pulsed electron accelerator (Microtron, Acceleratorteknik, The Royal Institute of Technology, Stockholm). The LLDPE film samples were irradiated to a dose of 15 Mrad on a cooling plate kept at 2.5°C in air or argon atmosphere at an average dose rate of 0.83 Mrad min^{-1} . After intermittent storage in liquid nitrogen the pre-irradiated samples were grafted under argon in deaerated solutions containing 20 wt% AAm and 0.05 wt% Mohr's salt. For the samples in the present investigation the grafting temperature was kept at 70°C. The degree of grafting or graft yield (*GY*) is the percentage increase in weight relative to the weight of the ungrafted film.

X-ray diffraction

Measurements of film samples were performed by the normal beam transmission technique under vacuum using a Philips generator PW 1830 with nickel-filtered Cu K_α radiation ($\lambda = 1.542\text{ \AA}$). Since the ungrafted LLDPE films are biaxially oriented, randomized measurements were obtained by stacking the film strips at 0 and $\pm 45^\circ$ of orientation. Photographic films were obtained and evaluated using a Warhus camera and an image analysis system: Northern Light model B90 light table, Dage MTI 70 series camera, DTK 486-33 MHz PC, Optimas software by Bioscan Inc. and UN-Scorpion Framegrabber. The intensities from the photographic film were determined according to the procedure proposed by Baltá-Calleja and Vonk²³ and averaged by measuring over six to ten radial directions. The

diffractograms obtained in the image analysis system were converted from light to intensity and analysed, assuming a linear Lorenz-Gaussian relation²⁴, using the Kaleidagraph 3.0.2 software with a Macintosh computer.

In addition, the virgin LLDPE was investigated by a counting method: focusing Guinier-Hägg camera with transmission geometry, at the University of Stockholm. The crystallinity values obtained by the film method were similar to those evaluated by the counting method, as has been reported earlier²⁵.

Corrections were made according to the procedures proposed by Kakudo and Kasai²⁶. The absorption correction for the thin-film samples measured (0.2 to 0.3 mm) is small in normal beam transmission²⁷ with negligible dependence on diffraction angle in the range investigated, $0 < 2\theta < 35^\circ$.

As a measure of the degree of crystallinity of the ungrafted LLDPE samples, we used the expression²⁸:

$$w_c = \frac{I_c^{110} + I_c^{200}}{I_a + I_c^{110} + I_c^{200}} \quad (1)$$

where I_a and I_c^{hkl} are the areas under the amorphous halo and the hkl reflections, respectively.

In order to obtain w_c for the LLDPE backbone in grafted samples, a polyacrylamide correction was made for the contribution of PAAm to the amorphous halo. This was obtained from diffractograms of randomly oriented film samples made by stacking ungrafted LLDPE films with varying amounts of PAAm films, thus simulating different graft yields. Since w_c , which only refers to LLDPE, is kept unchanged, an internal correction for the contribution of PAAm is obtained as a function of graft yield.

From the X.r.d. reflections the crystallite dimensions were determined according to the Scherrer equation²⁹:

$$l_{hkl} = \frac{0.9\lambda}{b \cos \theta_{hkl}} \quad (2)$$

where $2\theta_{hkl}$ is the Bragg angle and b is the corrected half-width of the respective reflection.

Differential scanning calorimetry

Melting endotherms were measured on a Perkin-Elmer DSC-7 calorimeter with sample weights of $6 \pm 2\text{ mg}$ and a heating rate of $20^\circ\text{C min}^{-1}$. The instrument was calibrated with indium ($T_m = 429.8\text{ K}$, $\Delta H_f = 28.46\text{ J g}^{-1}$). The crystallinity values obtained by d.s.c. are the averages of two measurements, unless otherwise indicated. Samples were preheated to 140°C and cooled at $20^\circ\text{C min}^{-1}$ to -20°C and kept at that temperature for 5 min prior to the d.s.c. measurements. Ungrafted LLDPE samples were also measured in the first d.s.c. run, i.e. prior to recrystallization.

In evaluating the crystallinity it is assumed that the only contribution when grafting with polyacrylamide originates from the remaining trunk polymer. According to separate measurements by d.s.c. and X.r.d., PAAm is essentially amorphous, having a T_g well above the melting endotherm for LLDPE. The degree of crystallinity was evaluated according to the baseline method proposed by Gray³⁰, either in a modified version:

$$w'_c = \Delta H_f / \Delta H_{T_m}^0 \quad (3)$$

or in its original form:

$$w'_c = \Delta H_f / \left[\Delta H_{T_m^0} - \int_{T_1}^{T_m^0} (c_{pa} - c_{pc}) dT \right] \quad (4)$$

where ΔH_f is the value of the measured heat of fusion, $\Delta H_{T_m^0}$ is the heat of fusion for 100% crystalline polyethylene, c_{pa} and c_{pc} are the specific heats of amorphous and 100% crystalline phases of polyethylene, respectively, T_m^0 is the equilibrium melting temperature and T_1 is an arbitrary temperature below the melting range.

Values of T_m^0 (=414.6 K), $\Delta H_{T_m^0}$ (=291.3 J g⁻¹), c_{pa} and c_{pc} for polyethylene were obtained from Wunderlich and Baur³¹; $(c_{pa} - c_{pc})$ over the temperature interval in equation (4) is approximated with a nine-degree polynomial.

For ungrafted LLDPE samples exposed only to irradiation, the crystallinity was determined using both equation (3) as well as equation (4). For grafted samples only equation (3) was used.

The degree of crystallinity of the LLDPE backbone in the grafted samples is obtained by correcting for graft yield (GY) according to:

$$w_c = w'_c [1 + GY(\%)/100] \quad (5)$$

where w'_c is obtained from equation (3).

Scanning electron microscopy

The specimen was prepared in liquid nitrogen (LN₂) and the sputtering material was applied from an Au/Pd cathode to a thickness of approximately 10 nm. Microscopy investigation was performed on a JEOL SEM-5400 with an acceleration voltage of 20 kV and a working distance of 20 ± 5 mm.

Scanning electron microprobe quantometry

The distribution of grafted material over a cross-section of the sample was obtained implicitly by determination of the nitrogen profile by a scanning electron microprobe quantometer (Applied Research Laboratories) using a PbSD crystal. The scanning was made in steps of approximately 2 μm over the entire cross-sectional area.

RESULTS AND DISCUSSION

Ungrafted LLDPE

The degree of crystallinity (w_c) as defined in the 'Experimental' section was determined for EB-irradiated ungrafted samples by d.s.c. and X.r.d. The d.s.c. traces in Figure 1 show the endotherms from the first and second d.s.c. runs. For unirradiated LLDPE (Figure 1A) the native sample (upper curve) shows two peaks at 118°C and 123°C and a broad shoulder culminating at 105 and 110°C. Upon irradiation to 20 Mrad in air or argon (upper curves in Figures 1B and 1C, respectively) one narrow peak is observed at 116°C for both pre-irradiation atmospheres. This agrees in principle with the observations reported in the survey by Wunderlich³², according to which the merged peak sharpens and moves towards lower temperatures with increasing irradiation dose. However, there is only a minor decrease in melting enthalpy. From the upper curves in Figures 1A–1C, the heat of fusion (ΔH_f) is obtained as 127 kJ g⁻¹ for

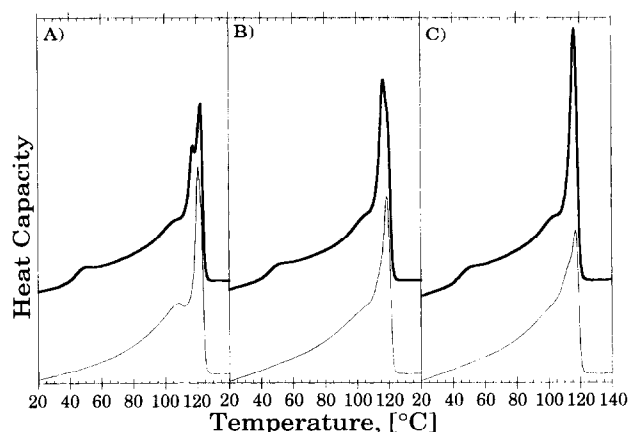


Figure 1 D.s.c. endotherms of virgin and pre-irradiated, ungrafted LLDPE. Upper curves: prior to recrystallization (first d.s.c. run). Lower curves: recrystallized samples (second d.s.c. run). (A) Virgin LLDPE; (B) irradiated in air to 20 Mrad; (C) irradiated in argon to 20 Mrad

unirradiated LLDPE and 126 kJ g⁻¹ and 123 kJ g⁻¹ after irradiation to 20 Mrad in air and argon respectively. Nikolova *et al.*³³ found a decrease in the heat of fusion for LLDPE irradiated in air by EB irradiation up to 40 Mrad. This was interpreted thermodynamically as being the result of an increase in surface energy due to crosslinking in the surface regions of the lamella rather than to a decrease in crystallinity.

The main influence on crystallinity of high-energy irradiation at the relatively low doses used in the present study is the influence on reorganization and crystallization imposed by crosslinking and chain scission.

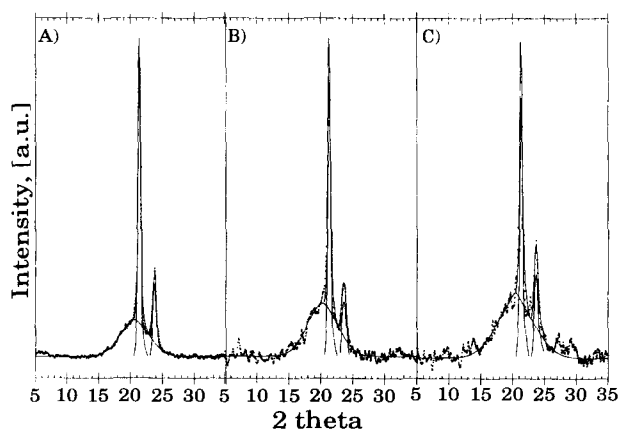
The second d.s.c. runs give the endotherms of the recrystallized samples as shown by the lower curves in Figure 1. As seen in Figure 1A, recrystallization of unirradiated LLDPE gives a merged peak at 121°C, which is interpreted as being the melting endotherm for the fraction containing the largest crystallites formed under the specific heating cycle of the d.s.c. analysis. After irradiation to 20 Mrad in air, where crosslinking in the LLDPE is low¹ (5 to 10% gel content), the endotherms in Figure 1B show only minor differences upon recrystallization. The lower curve displays a slightly higher peak temperature, 119°C versus 117°C for the first d.s.c. run (upper curve), indicating a slight annealing process³⁴. After irradiation to 20 Mrad in argon, a high degree of crosslinking is obtained, as evidenced by a gel content of about 60%¹. In Figure 1C, recrystallization diminishes the high-melting fraction but increases the amount of lower-melting crystallites, as judged from the shape of the melting endotherms for the first (upper curve) and second (lower curve) d.s.c. runs. In this case re-formation of the larger crystallite sizes is restrained by the crosslinking.

In spite of the differences in the d.s.c. traces, particularly in Figure 1C, the heat of fusion is still not significantly changed by the recrystallization in the d.s.c. analysis. When the arbitrary temperature T_1 (see 'Experimental' section) is chosen to be the same as when determining ΔH_f for the first d.s.c. runs, similar data are obtained: 128, 123 and 123 kJ g⁻¹ for unirradiated LLDPE and irradiated LLDPE in air and argon, respectively.

The w_c (d.s.c.) data calculated from the second d.s.c.

Table 1 Crystallinities obtained by means of d.s.c. and X.r.d., and lamellar dimensions of virgin and pre-irradiated, ungrafted LLDPE samples in the dose range 0 to 20 Mrad

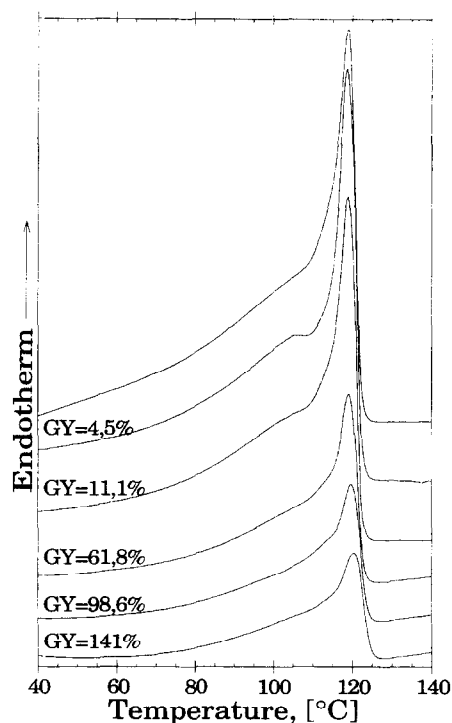
Dose (Mrad)	Crystallinity (%)			Lamellar dimensions (Å)	
	w_c (d.s.c.) (eq. (3))	w_c (d.s.c.) (eq. (4))	w_c (X.r.d.)	$\langle l_{110} \rangle$	$\langle l_{200} \rangle$
0	41.1 ^a	40.9 ^a	47.4	148	97
Irradiation performed in air					
2.5	43.1	42.8	43.1	147	102
5	41.6	41.4	42.9	140	96
10	41.6	41.3	43.0	139	97
15	41.7	41.4	41.3	146	108
20	41.2	41.0	38.3	141	92
Irradiation performed in argon					
2.5	43.9	43.6	42.3	147	102
5	41.2	41.0	42.3	141	103
10	41.4	41.2	42.5	149	105
15	40.7	40.5	42.3	142	101
20	40.2	40.0	38.9	131	95

^a An average of 13 measurements**Figure 2** X-ray diffractograms of virgin and pre-irradiated, ungrafted LLDPE. (A) Virgin LLDPE; (B) irradiated in air to 20 Mrad; (C) irradiated in argon to 20 Mrad

runs are listed in *Table 1*. Within experimental error there is no significant decline in w_c (d.s.c.) in the dose range studied regardless of irradiation atmosphere. In *Table 1*, it is also evident that w_c (d.s.c.) data as calculated from equations (3) and (4) are in good agreement.

The X.r.d. diffractograms for the same samples are shown in *Figure 2*. The peaks of the Bragg reflections appear at $2\theta_{110} \approx 21.4^\circ$, $2\theta_{200} \approx 23.8^\circ$ for the crystalline phase and there is a broad amorphous peak culminating at $2\theta \approx 19.8^\circ$. As seen in *Figure 2*, the X.r.d. diffractograms are not appreciably affected by irradiation to 20 Mrad in either atmosphere.

The crystallinity data obtained by X.r.d. are compiled in *Table 1*. There is no significant difference for pre-irradiation in air or argon. According to the X.r.d. analysis, there was a decrease in w_c (X.r.d.) from about 47% to 38% over the dose range from 0 to 20 Mrad. However, the initial decrease from about 47% to 42–43% after irradiation to 2.5 Mrad seems somewhat erroneous in comparison with the crystallinity data in this range obtained by d.s.c. In the dose range from 2.5 to 15 Mrad, the X.r.d. and d.s.c. results are in fair

**Figure 3** D.s.c. endotherms. Top curve: ungrafted LLDPE irradiated to 15 Mrad in air. Lower curves: grafted samples as indicated by graft yield (GY). Grafting conditions: AAm = 20 wt%, Mohr's salt = 0.05 wt%, grafting temperature = 70°C

agreement, the X.r.d. data exhibiting a hardly measurable decline in crystallinity.

From the X.r.d. analysis, the lamellar dimensions $\langle l_{110} \rangle$ and $\langle l_{200} \rangle$ were obtained from the Scherrer equation²⁸. The small decrease in w_c is accompanied by a small decrease in $\langle l_{110} \rangle$. There is no decline in $\langle l_{200} \rangle$ until the highest dose of 20 Mrad regardless of irradiation atmosphere. As mentioned in the 'Introduction', γ irradiation in oxygen or air may generate increased crystallinity due to chain scission and reorganization^{16,17}. Crosslinking, which occurs during γ irradiation in the absence of oxygen, prevents reorganization^{16,34}. In the investigation on fast electron irradiation of LDPE in air at ambient temperature to 40 Mrad³³, it was found that the crystallinity showed a slight decrease. In that case crosslinking was extensive, 72% gel content, at 20 Mrad as compared to 10% in our study¹. Only when irradiating in argon did we observe appreciable crosslinking, about 40% gel content at 15 Mrad. However, in our study no recrystallization was observed at ambient temperature even for the LLDPE irradiated in air.

Progression of grafting into LLDPE

In *Figures 3* to *5*, d.s.c. curves and X.r.d. diffractograms are shown as the grafting proceeds into the LLDPE film pre-irradiated to 15 Mrad when exposed to the grafting solution from both sides at 70°C.

As defined in the 'Experimental' section, w_c is related exclusively to the amount of LLDPE also in the grafted material. For samples not completely grafted throughout the cross-section of the LLDPE film, the d.s.c. and X.r.d. analyses will give crystallinity data averaged over the grafted and ungrafted parts of the film in proportion to the graft yield.

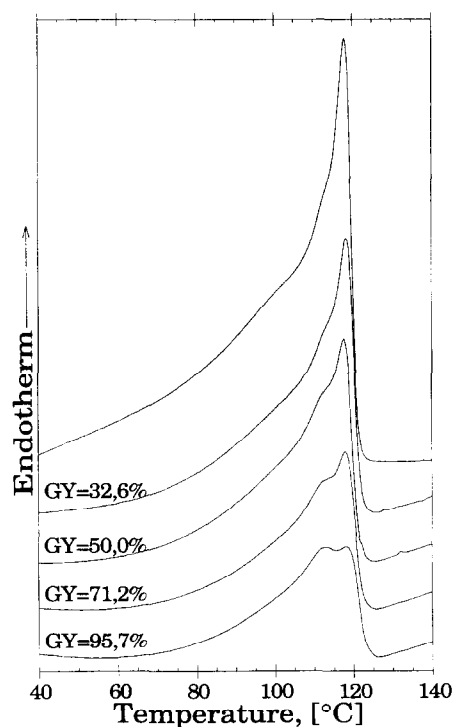


Figure 4 D.s.c. endotherms. Top curve: ungrafted LLDPE irradiated to 15 Mrad in argon. Lower curves: grafted samples as indicated by graft yield (*GY*). Grafting conditions as in *Figure 3*

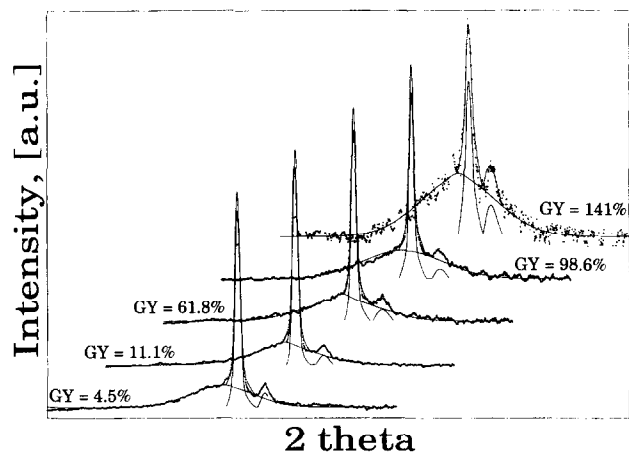


Figure 5 X.r.d. diffractograms for $5^\circ < 2\theta < 35^\circ$ for samples irradiated to 15 Mrad in air and subsequently grafted. From bottom left to top right: *GY* = 4.5%, *GY* = 11.1%, *GY* = 61.8%, *GY* = 98.6%, *GY* = 141%. Grafting conditions as in *Figure 3*

The data in *Table 2* show graft yields ranging from zero to the final degree of grafting (G_f) representing the ultimate yield obtained under a given set of grafting conditions¹. The G_f values in *Table 2* are 399% and 105% for pre-irradiation in air and argon, respectively¹. According to the SEMQ and SEM analyses the samples are grafted through long before G_f is reached. Already at a *GY* of about 30% grafting has penetrated the entire cross-sections of the film samples. SEM images and the nitrogen distribution over the cross-sectional areas are shown in *Figures 6* and *7*.

After the film is grafted through, the grafting continues in the entire volume of the film until initiation and propagation are exhausted and G_f is reached.

Table 2 Progression of grafting front. Crystallinities as obtained by means of d.s.c. and X.r.d., and lamellar dimensions for samples pre-irradiated to 15 Mrad in either air or argon

Graft yield (%)	Crystallinity (%)		$\langle l_{110} \rangle$ (Å)
	w_c (d.s.c.)	w_c (X.r.d.)	
Irradiation performed in air			
0	41.7	41.3	146
4.5	41.8	48.1	152
11.1	39.6	49.0	146
31.6	—	46.5	147
55.8	—	45.6	141
61.8	32.5	46.1	144
98.6	32.4	41.0	133
112	29.3	36.4	107
136	22.8	37.0	104
141	25.1	—	—
159	19.9	37.3	109
240	—	32.8	90
262	23.1	36.1	94
314	—	32.1	90
399	17.2	28.0	80
Irradiation performed in argon			
0	39.6	42.3	142
32.6	34.3	43.7	130
32.6	28.3	39.5	131
50.0	27.2	42.8	144
54.9	31.8	44.0	146
71.2	24.8	37.5	138
95.7	23.1	39.0	135
97.3	—	36.0	120
105	24.0	31.0	100

The calculated w_c and $\langle l_{110} \rangle$ values for the LLDPE backbone are given in *Table 2*. The main trend is a decrease in the crystalline fraction and in the crystallite dimension with increasing graft yield. The corresponding d.s.c. endotherms and X.r.d. intensities in *Figures 3* to *5* show the combined effects of a decrease in the dilution of the crystalline phase. All the d.s.c. analyses were performed on recrystallized samples due to the high stresses in the grafted samples. Thus, the results obtained by d.s.c. depend on the ability of the material to recrystallize. For the grafting systems studied here, the pre-irradiation dose was 15 Mrad, which creates significantly higher crosslinking in argon: about 40% gel content as compared to 5–10% in air¹. As seen in *Figure 1* the d.s.c. curves in *Figures 3* and *4* show a lower regain in the larger crystallite sizes for the crosslinked system. However, in the grafting systems there is a simultaneous decrease in the smaller crystallites owing to their preferential reaction in the grafting process, as is further discussed below.

Crystallinity dependence on graft yield

The crystallinity data for the LLDPE in the grafted samples in *Table 2* are plotted versus *GY* in *Figures 8* to *10*. The time scales in these figures are derived from the time conversion curves and refer only to the *GY* scales.

By comparison of the crystallinity data in *Table 1* with *Table 2* and *Figures 8* to *10*, it is concluded that the decrease in crystallinity during grafting is related to the grafting process. Unlike the d.s.c. analysis, X.r.d. measures the original unperturbed crystalline status of the sample. The different shapes of the curves in *Figures 8* and *9* may be attributed to the recrystallization by the first d.s.c. run preceding the d.s.c. analysis in *Figure 8*.

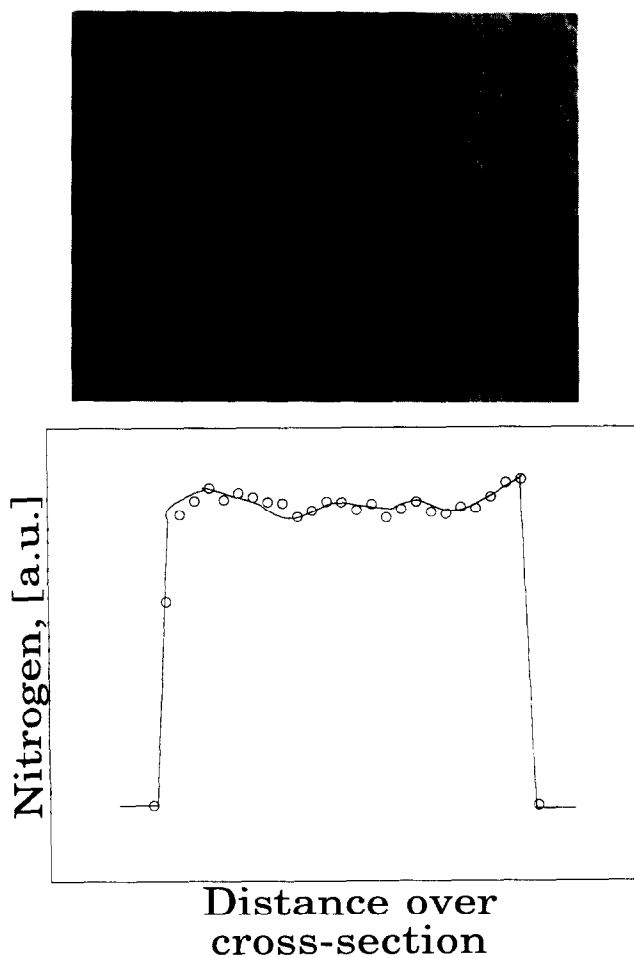
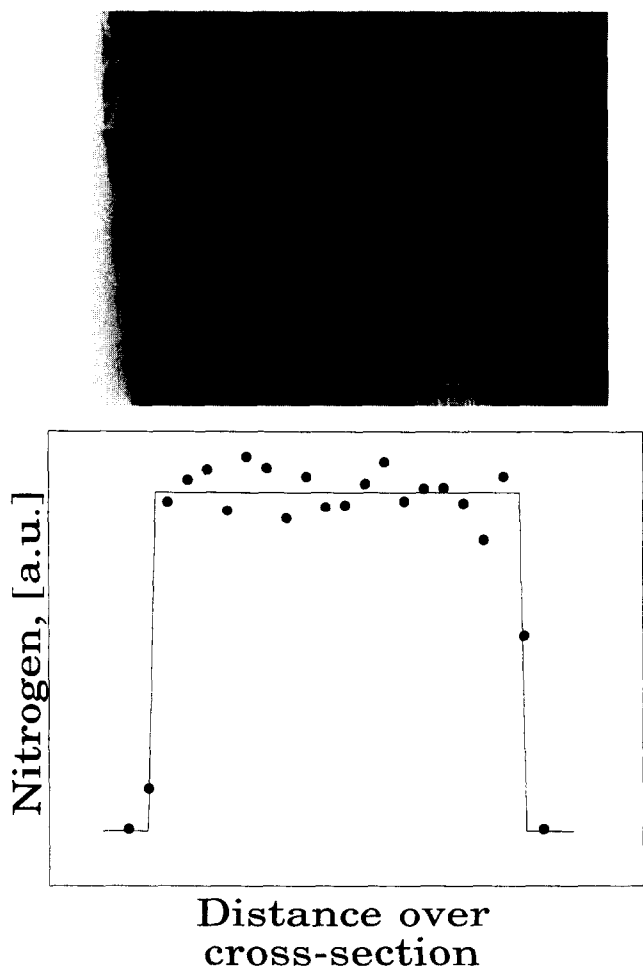


Figure 6 Verification of grafted-through state. SEM and SEMQ profile over the cross-section of a sample pre-irradiated to 15 Mrad in argon and subsequently grafted to 32.6%. The nitrogen concentration is arbitrary and the length scale is indicated in the SEM image

Figure 7 Verification of grafted-through state. SEM image and SEMQ profile over the cross-section of a sample pre-irradiated to 15 Mrad in air and subsequently grafted to 61.8%. The nitrogen concentration is arbitrary and the length scale is indicated in the SEM image

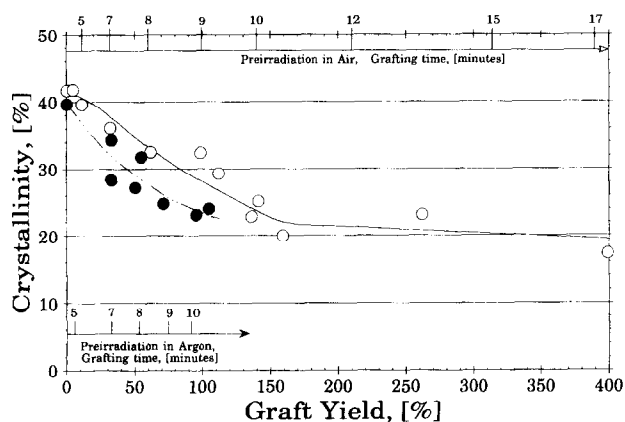


Figure 8 Crystallinity of LLDPE in grafted samples after correction for PAAm content as a function of graft yield by means of d.s.c.; samples pre-irradiated in either air (open symbols) or argon (closed symbols) and subsequently grafted. Grafting conditions as in Figure 3

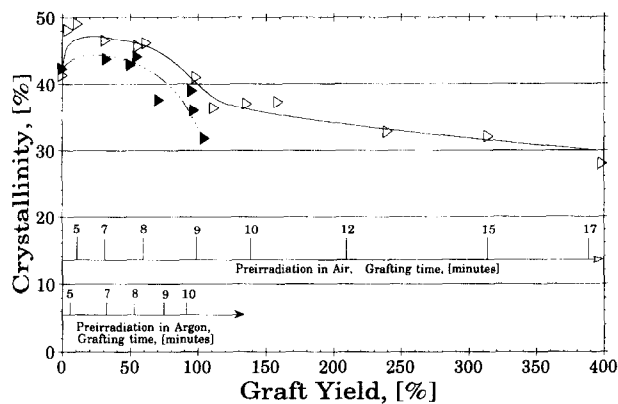


Figure 9 Crystallinity of LLDPE in grafted samples after correction for PAAm content as a function of graft yield by means of X.r.d.; samples pre-irradiated in either air (open symbols) or argon (closed symbols) and subsequently grafted. Grafting conditions as in Figure 3

The w_c (X.r.d.) and $\langle l_{110} \rangle$ curves in Figures 9 and 10 show similar dependences on graft yield up to a GY of about 100%. Although the w_c (X.r.d.) is slightly higher for pre-irradiation in air, there is no obvious difference in the average crystallite size between the two grafting systems. Thus annealing in terms of lamellar growth at the grafting temperature of 70°C is not prominent for the

LLDPE whether pre-irradiated in air or argon in spite of the differences in crosslink density. In the former case this may indicate crosslinking localized to the transient phase^{9,33} since the bulk data for pre-irradiation in air show a low degree of crosslinking, only 5 to 10% gel content.

The w_c (X.r.d.) data in Figure 9 show persistence in

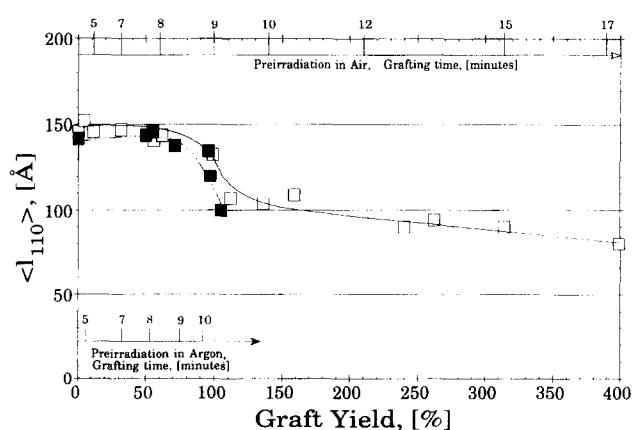


Figure 10 Lamellar dimensions $\langle l_{110} \rangle$ as a function of graft yield by means of X.r.d.; samples pre-irradiated in either air (open symbols) or argon (closed symbols) and subsequently grafted. Grafting conditions as in Figure 3

crystallinity at low graft yields as the grafting is building up in the LLDPE film. This observation is further emphasized by the influence of the progression of grafting on the average crystallite size as expressed by the plot of $\langle l_{110} \rangle$ when plotted versus G_Y in Figure 10. The higher persistence in $\langle l_{110} \rangle$, in comparison with w_c (X.r.d.), will result from the faster consumption of the smaller crystallites. This is not only a matter of higher surface-to-mass ratio but is also due to the smaller migration distance of the trapped radicals. As shown by Seguchi and Tamura^{8,18}, the momentary graft initiation will increase with decreasing crystallite size. As grafting proceeds, deterioration of the crystalline phase predominates as seen in Figures 8 to 10.

In Figure 9 it is seen that the decline in crystallinity, expressed as w_c (X.r.d.), becomes larger in relation to G_Y when grafting is well established over the entire cross-section of the film sample. After pre-irradiation in air, w_c (X.r.d.) decreases from about 46% to 36% while the graft yield increases from 60% to 150%. For pre-irradiation in argon, there is a similar decline from about 44% to 31% while the graft yield increases from 60% to merely 105%. Moreover, in contrast to pre-irradiation in air, the large decline in w_c (X.r.d.) stops at G_f , which in this case amounts to 105%. A large decline in $\langle l_{110} \rangle$, from about 150 to 100 Å, is also observed in this G_Y range for both systems (see Figure 10).

After the major decline in w_c and $\langle l_{110} \rangle$ for both pre-irradiation systems, as seen in Figures 8 to 10, the difference in grafting behaviour when approaching G_f becomes prominent.

For pre-irradiation in air, the curves in Figures 8 to 10 level off markedly towards G_f . Above a graft yield of about 150%, a further increase to a G_f value close to 400% requires a relatively small decrease in w_c from about 36% to 28%, as seen in Figure 9. Also the average crystallite size, as expressed by $\langle l_{110} \rangle$ in Figure 10, shows a markedly smaller decrease in this region from about 110 to 80 Å.

In the case of pre-irradiation in air, a contribution from peroxide initiation should be considered. As a first interpretation this would explain the high increase in G_Y relative to the crystallite consumption in the G_Y range of 150% to 400% as shown in Figure 9. However, in the lower G_Y range, below 100%, the w_c and $\langle l_{110} \rangle$ curves in

Figures 9 and 10 are quite congruent. From the time scales in Figures 9 and 10 it is seen that the time lag between the two systems does not increase significantly until a G_Y of about 60% is reached and the grafting is well established over the cross-section of the LLDPE film. This is where the need for volume expansion becomes increasingly important. Up to this point the grafting rates are comparable for both systems. The rather slowly increasing time lag above this G_Y is due to differences in crosslinking, i.e. different restrictions for expansion. A significant contribution from peroxide initiation in the least crosslinked system should give an earlier differentiation between the two grafting systems in terms of grafting rate. Moreover, w_c (X.r.d.) in Figure 9 decreases continuously until G_f is reached. It is unlikely that initiation by peroxides and trapped radicals should stop simultaneously at a point where the decrease in w_c (X.r.d.) is terminated.

A more probable reason for the increase in G_Y above 100% for pre-irradiation in air is an increase in propagation by the expansion of the grafting system. In the earlier investigations^{1,2} it was found that chain termination is essentially monomolecular in chain radicals for the present grafting systems. No change in termination mode was seen even for the swellable system at a grafting temperature of 70°C. Since the mobility of the grafted chain radicals may increase without significant bimolecular chain termination, propagation is favoured by volume expansion.

The ability to expand is dependent on degree of crosslinking. The high degree of crosslinking in the LLDPE pre-irradiated in argon prevails in the grafted part. This will restrain expansion, and continued grafting will generate a considerable pressure, which will restrict the system mobility. Eventually graft polymerization stops at a lower G_f value as compared to a non-crosslinked system.

In the absence of significant crosslinking the grafting system pre-irradiated in air may expand, and above a certain G_Y it may increase considerably in size until G_f is reached. Actually, when grafting LLDPE pre-irradiated in air, enlargement of the sample generally becomes observable at a G_Y of about 150%.

As discussed previously in connection with Figures 9 and 10 the large increase in G_Y from about 150% to 400% corresponds to a relatively small decrease in w_c (X.r.d.) and $\langle l_{110} \rangle$. Assuming initiation by trapped radicals at the crystallite surfaces, this may indicate a lower amount of chain initiations in this G_Y region. However, the interpretation needs consideration of several factors. The number of chain initiations for a given pre-irradiation dose will depend on the amount and surface area of the crystalline phase, lifetime and migration of radicals and diffusion of monomer.

Crystallite surface area

Although the crystallites in polyethylenes have irregular shapes, they have been approximated as spheres using the lamellar thickness as linear dimension. This model was successfully used in studies of the decay of radicals in EB-irradiated polyethylenes upon exposure to air⁸. The results were also considered applicable to the initiation of monomer at the crystallite surfaces^{8,18,19}.

In this work $\langle l_{110} \rangle$ is used as a comparative measure when studying the variation in crystallite size. For a unit

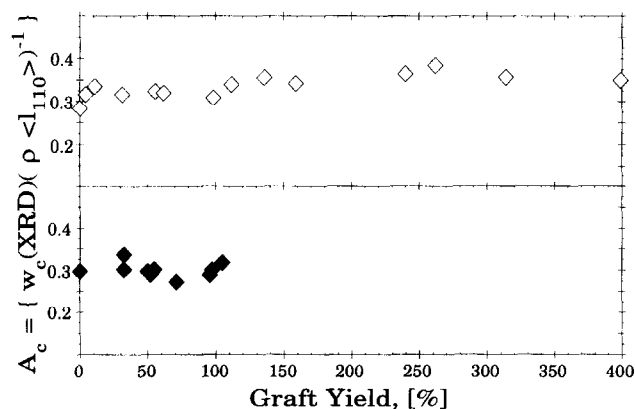


Figure 11 Relative variation of the surface area (A_c) of the LLDPE crystallites as a function of graft yield. Pre-irradiation in air and subsequently grafted (open symbols); pre-irradiation in argon and subsequently grafted (closed symbols). Grafting conditions as in Figure 3

mass of the LLDPE contained in the grafted sample and having a weight percentage, w_c , of crystalline material, a measure of the crystalline surface area, A_c , is given by:

$$A_c \sim w_c(\rho \langle l_{110} \rangle)^{-1} \quad (6)$$

where ρ is the density of the crystalline phase.

The entity A_c , calculated from the data in Table 2 while setting $\rho = 1$, is shown in Figure 11 as a function of GY. For GY levels up to 105%, i.e. where the two systems can be compared, A_c remains unchanged. This GY interval contains the region where w_c and $\langle l_{110} \rangle$ undergo the largest decreases in relation to GY for both systems. From the data in Figures 8, 9 and 10 a massive attack on the crystallites is evident as the grafting penetrates the LLDPE film disintegrating its original structure. Thus the relative constancy of A_c does not correspond to the trivial case where the crystallites remain unaffected.

Above the GY level of 100% to 150%, where the system pre-irradiated in air expands, and up to G_f at about 40%, A_c remains largely unchanged although shifted to a slightly higher level (see Figure 11). In this region an increase in the crystallite surface area might be expected by mechanical distortion of crystallites due to the large macroscopic expansion. Such an effect should accelerate with the swelling, which is not observed in the present system. In the microscopic perspective the mechanical distortion of crystallites is obviously more prominent during the disintegration of the LLDPE film in the lower GY region, between 60% to 100%, as shown in Figures 8 to 10.

In expression (6) for A_c , deterioration of crystallites by surface degradation will decrease w_c and $\langle l_{110} \rangle$. As mentioned above the smaller crystallites are primarily consumed. Depending on the size distribution of crystallites, a small decrease in w_c may give a large decrease in A_c . This will also delay the decrease in the average value of $\langle l_{110} \rangle$. Thus a geometrical calculation based on $\langle l_{110} \rangle$ as well as the decline in w_c (X.r.d.) will initially underestimate the decrease in A_c in surface degradation. On the other hand, disruption of the crystallites by local stresses will increase A_c .

In the long run a constancy in X_c over a large range of GY indicates that the two processes in surface degradation and mechanical disruption of crystallites

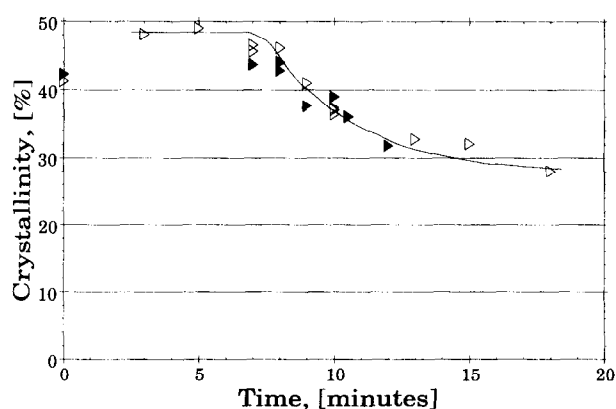


Figure 12 Crystallinity of LLDPE in grafted samples after correction for PAAm content as a function of grafting time by means of X.r.d.; samples pre-irradiated in air (open symbols) or argon (closed symbols). Grafting conditions as in Figure 3

compensate for each other with regard to the crystalline surface area.

According to the A_c data in Figure 11 the crystalline surface area is comparable for the two grafting systems. Furthermore it remains unchanged up to G_f within a standard deviation of $\pm 10\%$ for each grafting system.

Crystallinity dependence on grafting time

In Figure 12 w_c (X.r.d.) is plotted versus grafting time. It is seen that the decline in w_c (X.r.d.) has the same time dependence for both systems. This is in agreement with initiation from the crystalline phase since all crystallites have received the same dose regardless of pre-irradiation atmosphere. Furthermore it was found previously¹ that at a temperature of 70°C the dependence of grafting rate on pre-irradiation dose is of the same order for the two grafting systems. At this temperature they will have a similar dependence on the diffusion of reactants with regard to chain initiation.

According to Seguchi and Tamura^{8,18} the alkyl radicals in the crystalline phase migrate to the crystallite surfaces. Here they will react directly, or via transformation to allyl radicals, with reagents in the amorphous phase. As the grafting proceeds, the grafted chain segments at the crystallite surfaces become solubilized. This will gradually expose the underlying crystalline phase to further reaction with monomer. The surface degradation is seen as a decline in the amount of crystalline phase expressed as w_c in Figures 8, 9 and 12.

As indicated by the SEMQ analyses there is a fast penetration of AAm monomer through the LLDPE film. Assuming that monomer is excluded from the crystalline phase, the initiation is determined by the migration of radicals to the crystallite surfaces. The decrease in w_c (X.r.d.) with time in Figure 12 will then correspond to the decay of initiating radicals.

The decrease in $\langle l_{110} \rangle$ is plotted versus time in Figure 13. Also in this case both systems show similar time dependences with some delay for the more crosslinked system. The curves in Figure 13 have a steep decline during a limited time period from about 8 to 12 min. In contrast to the decline in w_c (X.r.d.) in Figure 12, the decline in $\langle l_{110} \rangle$ is to a large extent caused by disruption of crystallites. The maximum rate of disruption coincides

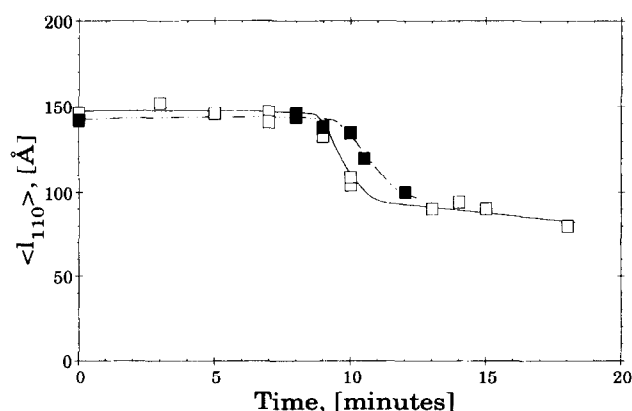


Figure 13 Crystallite dimension ($\langle l_{110} \rangle$) as a function of grafting time by means of X.r.d.; samples pre-irradiated in air (open symbols) or argon (closed symbols). Grafting conditions as in Figure 3

with the disintegration of the LLDPE film as the cross-section is grafted through.

Interpretation of crystallinity and graft yields

According to this investigation, the decline in crystallinity follows the initiation for both grafting systems. Then the large decrease in crystallinity in the GY range of 50% to 105% as shown in Figures 9 and 10 is again explained by the differences in crosslinking. For the system pre-irradiated in argon crosslinking will restrain propagation much more than initiation and w_c (X.r.d.) will decrease with a very low increase in GY until G_f is reached at 105%. For the system pre-irradiated in air, which has a low degree of crosslinking, this stage is overcome since the system may expand.

A comparative measure of the total yield of grafted chains in the two systems has to consider the longer duration for the grafting of the LLDPE pre-irradiated in air. Since A_c remains largely unchanged the initiation for the latter system continues at a low and decaying rate as indicated by the decline in w_c (X.r.d.) in Figure 12. When comparing w_c (X.r.d.) at the respective G_f values for the two systems, the difference is only a few per cent: 28% at $G_f = 399\%$ and 31% at $G_f = 105\%$ for pre-irradiation in air and argon, respectively (see Figures 9 and 12).

Thus the large difference in G_f is not explained by the amounts of chain initiation. As suggested earlier, this implies a major increase in the kinetic chain length, i.e. propagation, for the system pre-irradiated in air as the system expands above a GY of about 100% (see Figure 9).

Then it is concluded that the difference in G_f data for the two grafting systems is mainly related to the average molecular weight of the grafted chains and to a lesser degree to a difference in the number of grafted PAAM chains.

CONCLUSIONS

Under the grafting conditions studied, the grafting of LLDPE pre-irradiated in air or argon is in agreement with the postulated model of initiation from the crystalline phase.

The alteration in crystallinity when grafting EB-irradiated LLDP in aqueous acrylamide solution is related to the initiation and progress of the grafting process.

The main difference in grafting performance as a result of pre-irradiation atmosphere is due to differences in the amount of crosslinking, which restricts expansion of the graft polymerizing system.

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