Effect of radiation on the crystallinity of low-density polyethylene

V. M. Aslanian, V. I. Vardanian, M. H. Avetisian, S. S. Felekian and S. R. Ayvasian
Department of Molecular Physics and Biophysics, Yerevan State University, Mravian str. 1, Yerevan, Armenian SSR, USSR
(Received 19 July 1985; revised 10 July 1986)

By methods of X-ray analysis and microcalorimetry it has been shown that the crystallinity and melting enthalpy of low-density polyethylene samples under γ-irradiation increase with increasing radiation dose. It is established that, with increasing radiation dose, the degree of crystallinity and melting enthalpy of irradiated and recrystallized samples do not change at first and then begin to decrease. It is shown that, with increasing radiation dose in crystalline regions, crosslinks are formed. The emergence of low-temperature endothermal peaks on the calorimetric melting curves is due to an increase in crystallinity and in crosslink formation.

(Keywords: polyethylene; radiation; dose; crystallinity; melting enthalpy; recrystallization)

INTRODUCTION

The numerous experimental results obtained by different authors testify that the main radiochemical effects in polyethylene (PE) caused by radiation are macromolecular chain destruction, crosslinking and the emergence of double bonds[1,2]. In fact, crosslinking and decrease in the degree of crystallinity of PE upon irradiation are described in many works[3-6]. It must also be mentioned that, upon heating samples treated with high doses of γ-radiation (up to 3 Grad) in vacuum, a transition from orthorhombic to hexagonal lattice is realized[5]. However, recently a number of papers were published in which the authors discussed the fact that, with increasing radiation dose (at relatively small doses) in the open air, the degree of crystallinity of PE increases[7,8].

The present series of papers reports important results in support of this concept. This first paper considers radiographical and calorimetric investigations of γ-irradiated low-density polyethylene (LDPE).

EXPERIMENTAL

LDPE 100 μm thick films were studied. The specifications of the studied LDPE are: $[\eta] = 1.33$ dl g^{-1}, $\bar{M}_v = 75\,000$, $\bar{M}_w = 181\,000$; the average number of branches per macromolecule is 26.

Irradiation was carried out on the device RCM-20 in the open air in a ^{60}Co source. The irradiation dose rate was 0.4 Mrad h^{-1}. The temperature on the film surface was 40°C. Radiation doses up to 300 Mrad were used. The degree of crystallinity was defined from diffraction curves, obtained on the X-ray diffractometer DRON-3, according to the procedure described elsewhere[9]. The interplanar distances were calculated by the Wolf–Bragg equation. The definition error of interplanar distances was ±0.001 Å.

The melting curves were obtained on a differential scanning calorimeter. All specimens, approximately 10 mg in weight, were scanned at the rate of 10°C min^{-1}. The enthalpy of fusion was determined by comparison of areas under the melting curves of the studied sample and of indium. The maximum error in determination of the enthalpy of fusion was ±1.5 cal g^{-1}.

RESULTS AND DISCUSSION

As is seen from the thermogram given in *Figure 1*, irradiation is accompanied by the emergence of a low-temperature endothermal peak, the temperature of localization and intensity of which grow with increasing irradiation dose. At considerable irradiation doses (175 Mrad and more), an additional high-temperature endothermal peak emerges on the thermograms, the localization of which in fact does not change (82°C at 175 Mrad and 85°C at 300 Mrad). The low-temperature peak on the thermograms disappears upon remelting of the samples, while the high-temperature peak remains and its localization temperature increases a little. The increase of irradiation dose is accompanied by a localization temperature shift of the main melting peak to the left.

The X-ray investigations testify (*Table 1*) that, firstly, the degree of crystallinity of the samples increases with increasing radiation dose and, secondly, though not great, some increase in interplanar distances d_{110} and d_{200} is observed. The increase in the degree of crystallinity is due to recrystallization of the macromolecular assemblage under the influence of irradiation. The authors of other papers[7,8] are of the same point of view.

The melting of these small and imperfect new crystalline forms favours the appearance of the low-temperature endothermal peak. The change in

0032-3861/87/050755-03$03.00

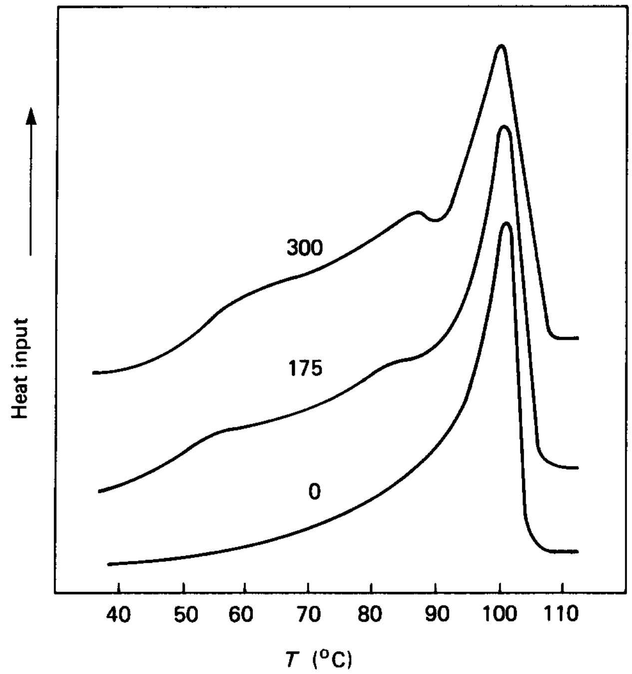

Figure 1 Thermograms of irradiated LDPE samples. Dose (in Mrad) is marked on each curve

Table 1 Values of interplanar distances and of the degree of crystallinity (ν) under γ-irradiation (ν^* – recrystallized samples)

Dose (Mrad)	d_{110} (Å)	d_{200} (Å)	ν (%)	ν^* (%)
0	4.089	3.704	38	38
10	4.090	3.704	43	40
70	4.090	3.705	43	40
100	4.092	3.705	46	37
150	4.093	3.708	50	35
200	4.095	3.715	57	32
250	4.095	3.715	57	28
275	4.096	3.716	59	22
300	4.095	3.716	57	16

interplanar distance is due to the emergence of defects in crystalline regions included in spherulite composition and their destabilization, which results in a decrease in localization temperature of the main peak on the thermograms.

Figure 2 illustrates the temperature dependence of interplanar distances d_{110} and d_{200} for a sample irradiated with a dose of 225 Mrad, and in *Table 2* values of the degree of crystallinity determined from radiograms obtained at different temperatures are given. In temperature intervals where the high-temperature endothermal peak is observed on the thermogram, the temperature dependence of d_{200} levels off over an interval of approximately 10°C, then increases. As follows from *Table 2*, an analogous picture is also observed with the values of the degree of crystallinity in the range 80–90°C. We think that this is due to crosslinking in LDPE crystalline regions. Really, in the process of γ-radiation not only amorphous but also crystalline regions are attacked. Scissions of the chains may be formed in the latter[5], which under certain conditions may be accompanied by crosslinking. The number of defects in crystallites must grow and their destabilization must take place. The considerable shift of the main peak to the left, towards the low-temperature region, is apparently due to this. At the same time, chain scissions are also observed in amorphous regions, which promote recrystallization processes. On account of straightened regions, crystalline structures are formed. The size of these crystallites must increase with irradiation dose and correspondingly with irradiation time. Simultaneously the possibility of crosslink formation in the crystallites, which in this case play the role of clips, increases. The increase in size and the emergence of random clips in these defective crystallites firstly must be accompanied by an increase in their melting temperature and, secondly, must promote the restoration of these crystalline regions after melting. We think that the emergence of the high-temperature peak reproduced at remelting is due to formation of such crystalline regions during the recrystallization process. Also the appearance of a plateau in the temperature dependence of the interplanar distance d_{200} is due to this fact.

Evidence for the above suggestion comes from the fact that high-temperature endothermal peak localization temperatures on thermograms of samples, the γ-radiation doses of which are 175–300 Mrad, in fact coincide at first and second melting. In another paper[5] it is established (and this seems interesting to us) that, for samples irradiated with high γ-radiation doses (up to 3 Grad) in vacuum, the calorimetric melting curves behave analogously, with the only difference being that under these conditions of treatment the high-temperature endothermal peak is due to the transition from an orthorhombic lattice to a hexagonal one. The results presented in *Figure 2* testify to the absence of such a

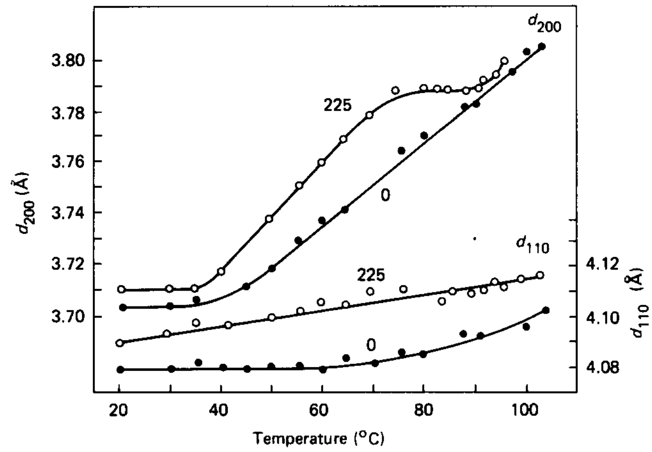

Figure 2 The dependence of interplanar distances d_{110} and d_{200} on temperature for unirradiated and irradiated (225 Mrad) samples

Table 2 Values of the degree of crystallinity at different temperatures (radiation dose 225 Mrad)

T (°C)	ν (%)	T (°C)	ν (%)
25	57.0	80	29.6
30	56.5	82	29.3
40	53.6	84	28.6
50	49.9	86	27.9
55	47.4	88	27.4
60	46.5	90	27.2
65	43.5	92	23.8
70	38.9	94	22.1
75	34.2	96	20.3
78	30.7	100	14.9

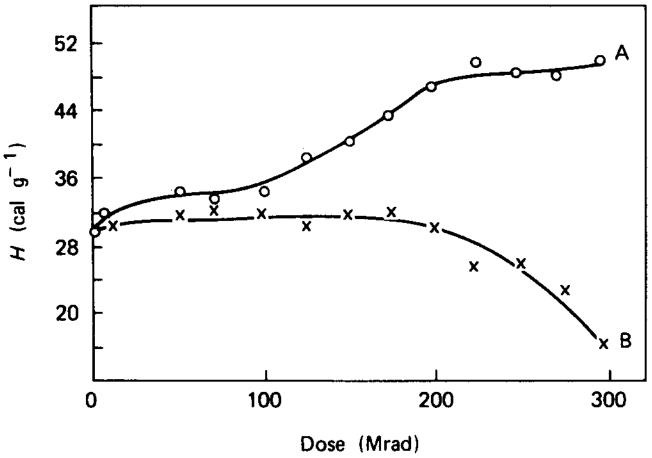

Figure 3 The dependence of melting enthalpy on irradiation dose for irradiated (curve A) and recrystallized (curve B) LDPE samples

transition (the presence of reflexes 110 and 200) in the γ-radiation intervals investigated.

A note of another interesting observation will conclude this paper. For samples irradiated with different doses and subsequently recrystallized, the degree of crystallinity determined at room temperature in fact remains unchanged up to 175 Mrad and then decreases.

We have established that the melting enthalpy of the irradiated samples does not change with increase in the irradiation dose in the interval concerned and later it begins to increase (*Figure 3*, curve A). The melting enthalpy of irradiated samples with subsequent recrystallization also does not experience any change over rather a large dose interval (*Figure 3*, curve B). Investigations of the scattering of polarized light under small angles testify that the supermolecular structure of recrystallized samples in fact does not change either. The comparison of values of melting enthalpy determined calorimetrically and radiographically (in the latter case on the basis of the degree of crystallinity calculated by this method) shows remarkable differences: the melting enthalpy is considerably greater in the first case. For example, for the sample irradiated with a dose of 300 Mrad the melting enthalpy is ~48 cal g^{-1} (see *Figure 3*) and the X-ray melting enthalpy (determined according to the degree of crystallinity, presented in *Table 1*) is approximately 40 cal g^{-1}. This is explained by the fact that, for calorimetric melting enthalpy, the surface effects make a great contribution (the free energy of the boundary surface of amorphous and crystalline regions).

In a first approximation we tried to represent the calorimetric melting enthalpy as a sum of energies of crystalline regions and boundary surfaces[10]:

$$\Delta H_{\mathrm{cal}} = \Delta H_{\mathrm{cryst}} + nf_{\mathrm{s}}$$

Here f_s is the boundary free energy, n the number of joints. Taking into account that new crystalline regions and hence new boundary surfaces are formed upon irradiation, it is clear that the growth of ΔH_{cal} makes a considerable contribution in the increase of f_s.

It is apparent that during repeated crystallization, the new crystalline forms disappear (up to 175 Mrad doses), and so the degree of crystallinity and the calorimetric melting enthalpy of recrystallized samples remain unchanged. According to the above data, in a certain interval of irradiation dose, though remarkable changes take place in the initial molecular assembly defining the polymer's supermolecular structure, no significant changes are observed in molecular chain localization (especially in crystalline regions). However, beyond 175 Mrad irradiation dose, the changes in molecular assembly are accompanied by changes in polymer supermolecular structure. In consequence of this a decrease in the degree of crystallinity as well as in the melting enthalpy of recrystallized samples is observed.

CONCLUSIONS

The crystallinity increases with irradiation dose in γ-irradiated LDPE samples. At the same time it must be noted that with increasing irradiation dose the degree of crystallinity and the melting enthalpy of recrystallized samples at first do not change and then decrease. In the present paper cogent arguments are obtained in favour of the emergence of changes under high doses of irradiation in LDPE crystalline regions and of chemical crosslink formation in them.

REFERENCES

1 Dole, M. (Ed.), 'The Radiation Chemistry of Macromolecules', Academic Press, New York, 1972

2 Charlesby, A., 'Atomic Radiations and Polymers', Pergamon, London, 1960

3 Patel, G. N. and Keller, A. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 323

4 Nielsen, L. E. *J. Macromol. Sci., Macromol. Chem.* 1969, **C3**, 69

5 Ungar, G. and Keller, A. *Polymer* 1980, **21**, 1273

6 Ahmad, S. R. and Charlesby, A. *Int. Radiat. Phys. Chem.* 1976, **8**, 585

7 Bhateja, S. K. *Polymer* 1982, **23**, 654

8 Pabiot, J. and Verdu, J. *Polym. Eng. Sci.* 1981, **21**, 32

9 Chung, F. H. and Scott, R. W. *J. Appl. Crystallogr.* 1973, **6**(3), 225

10 Aslanian, V. M., Morosov, V. F. and Vardanian, V. I. *Uch. Zapisky YGU* 1980, **2**, 152