DIFFERENTIAL SCANNING CALORIMETRY OF IRRADIATED POLYMERS

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DSC was used to study the influence of fast electron irradiation on the molecular mobility and melting of semicrystalline polymers and copolymers of ethylene and of fluorocopolymer. The heat capacity-temperature dependences obtained in the range from 100 K to 500 K revealed the specific features of the irradiation effect on four relaxational transitions associated with the appearance of segmental motion in different molecular elements of the disordered regions in the polymer. The pronounced dependence of the radiation stability of crystallites on the thermal prehistory of the object under study was found. The results were interpreted on the basis of the decisive role of the molecular mobility and free volume for the predominance of the radiation cross-linking of the molecules. Correlations were established between the characteristics of the thermal transitions and the mechanical properties of the irradiated polymers.

Keywords: DSC, irradiated polymers

Introduction

The radiation of polymers brings about various changes in their structure and properties, which result from the chemical cross-linking and destruction of macromolecules. Both processes usually occur simultaneously, but with different rates. Their study is of great importance for both the evaluation of the radiation stability of materials and the choice of optimal conditions for radiation modification of their properties [1, 2].

DSC turned out to be the most informative method for evaluation of the conversions in irradiated polymers on the basis of determination of the phase and relaxational transitions parameters [3]; the body of information obtained naturally increases when DSC is combined with X-ray analysis, infrared spectroscopy, solubility measurements, etc. DSC was used in a number of papers relating to irradiated polymers [3–16], but only isolated detailed studies are known on the effects of irradiation on the melting characteristics and crystallinity of polymers

[4–6]. The influence of irradiation not only on crystallites, but also on relaxations in intercrystalline regions, appears to have been studied by DSC only in [7, 8].

In our research, the DSC data on the effects of fast electrons irradiation on the different elements of the molecular structure in semicrystalline polymers are considered.

Experimental

High-density PE ($\overline{M}_w \approx 1 \cdot 10^6$), low-density PE ($\overline{M}_w \approx 6 \cdot 10^4$), ultrahigh molecular PE ($\overline{M}_w \approx 3 \cdot 10^6$) and copolymers of ethylene with 10% vinyl acetate (CEV) or 1% hexene (CEH), as well as their filled compositions, and a copolymer of vinylidene fluoride with tetrafluoroethylene (94:6) were used for the experiments.

10–30 mg samples were cut from 1 mm thick plates pressed at 430 K or 450 K (in the case of the fluorocopolymer) and at 0.4 MPa. Fast electron irradiation was carried out in argon or air atmosphere at 8 Mrad/min and 1.6 MeV. The irradiation dose varied from 5 to 800 Mrad. In some cases, irradiated samples were subjected to heat aging for 300–600 h at 448 K.

Measurements were carried out with a DSC-2 Perkin-Elmer calorimeter calibrated via the melting points of acetone (178 K), water (273.1 K) and indium (429.8 K), and the heat capacity of sapphire. The reference material was poly(dimethacrylate ethylene glycol). The temperature dependence of the heat capacity was measured in the range 100 K to 500 K, mainly at a heating rate $V=20$ deg/min, but also at 5, 10 and 40 deg/min. All transition temperatures, ΔC_p steps, activation energies of relaxational transitions $Q= -R \ \mathrm{d}\ln V/\mathrm{d}(1/T)$ and degrees of crystallinity $\chi = \Delta H_m / \Delta H_m^o \cdot 100\%$ (where for PE crystal $\Delta H_m^o = 294$ J/g and ΔH_m is the enthalpy of melting) were determined.

Results and discussion

Effect of irradiation on relaxational transitions

For melt-crystallized polymers with higher degrees of crystallinity ($\chi > 50\%$), the complex morphology results in more complicated features for the relaxational behaviour. The intercrystalline regions in such polymers have a peculiar conformational structure (Fig. 1). Three groups of molecular elements are formed in these regions:

1) long loops (1), folded tie molecules (2) and long ends of molecules (3) protruding from crystallites;

2) slightly folded tie chains (4) and folds (5), the segmental mobility in which is limited by crystallites;

3) fully extended tie chains (6) with the ends fixed by crystallites.

The combined (DSC, NMR and X-ray analysis) investigation of PE samples varying in molecular weight and thermal prehistory [17–19] allowed the separate characterization of the melting of crystallites and four temperature ranges involving segmental motion in the intercrystalline regions. Various degrees of chain folding appeared to determine the gradual increase in mobility with temperature increase, especially in the temperature ranges of relaxations. In these cases, the ΔC_p steps in the DSC curves were related [18]: at 150–200 K (relaxation I): to the segmental motion in the molecular elements of the first group; at 240–290 K (relaxation II): to the co-operative motion of some neighbouring segments of the same group; at 300–360 K (relaxation III): to the segmental motion of the second group of molecular elements; and at temperatures 20–30 deg below the melting point (relaxation IV): to the beginning of this motion in wholly extended tie chains. In accordance with the new, experimentally proved interpretation of major (α, β) relaxational transitions in polymers [3, 20–22], relaxation I and II must be related, respectively, to quasi-independent (β-transition) or co-operative (α-transition at T_g) rotations in parts of the chains close in magnitude to the Kuhn segment.
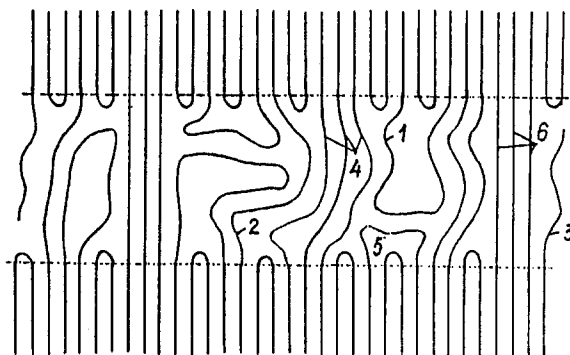

Fig. 1 The schematic picture of conformational molecular structure of the intercrystalline regions in polymer (see text)

The following was taken into account in the analysis of the experimental data.

In the initial stage of the radiation process, the changes in the polymer take place according to the law of chance, i.e. with equal probability for crystallites and intercrystalline regions. However, the future of the free macroradicals formed depends on the chain structure, its mobility and the presence of free volume close

to them. Thus, in a close-packed crystalline lattice, for example, orthorhombic in PE, the suppressed mobility means that ~CH₂–ĊH type macroradicals mainly recombine, resulting in recovery of the initial system of interatomic bonds: radiation cross-linking is practically non-existent [23].

A low mobility of extended tie chain results in a higher rate of their destruction as compared with that of cross-linking ($V_d \gg V_c$) [1, 24, 25]; the disjoining dangling ends of degraded chains prevents their recombination. The destruction process may also predominate in tightly cross-linked structures which have lost their segmental mobility.

For the prevailing of cross-linking over destruction, specific conditions are necessary for the secondary (diffusive) stage of the radiation chemical process, namely the sufficient segmental mobility for the rotational-translational displacement of chain segments up to contact with the nearest macroradicals.

Figures 2-5 show the specific features of the irradiation effect on relaxational transitions I–IV in PE and ethylene copolymers.

At the lowest dose of 5 Mrad, only step ΔC_p^I decreases, i.e. the intensity of relaxation I at 150–170 K. After 15–70 Mrad doses, this step disappears, but when the dose exceeds 100 Mrad, it appears again and grows. The transition temperature at the half-height of step ΔC_p^I increased from 160 to 180 K (Fig. 2).
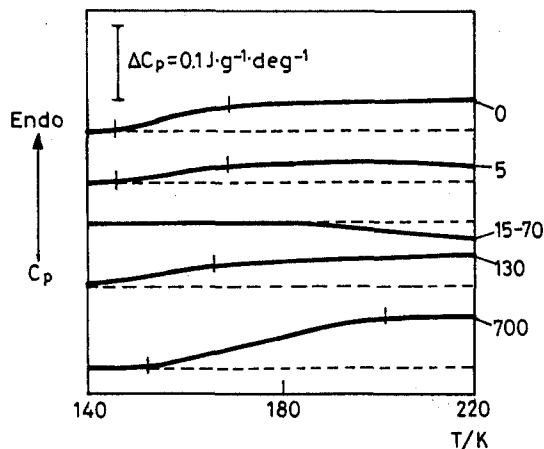

Fig. 2 The effect of irradiation by fast electrons in argon atmosphere on DSC curve for high-density PE in the region of relaxation I. Doses are indicated. Heating rate equals 20 deg/min

According to the NMR data [17], the small step $\Delta C_p^I \approx 0.04$ J/g·deg in the DSC curve for the initial high-density PE may be related to the appearance of the segmental mobility in approximately half of the volume of the disordered phase.

The low value of ΔC_p^I is explained by the fact that the motion in the mentioned temperature range occurs at sites with sufficient free volume and does not require

energy expenditure for the formation of new holes [18]. Therefore, the most favourable conditions for the radiation cross-linking of the chains are provided in these most mobile elements of intercrystalline regions (long loops, macro-molecule ends, folded tie chains).
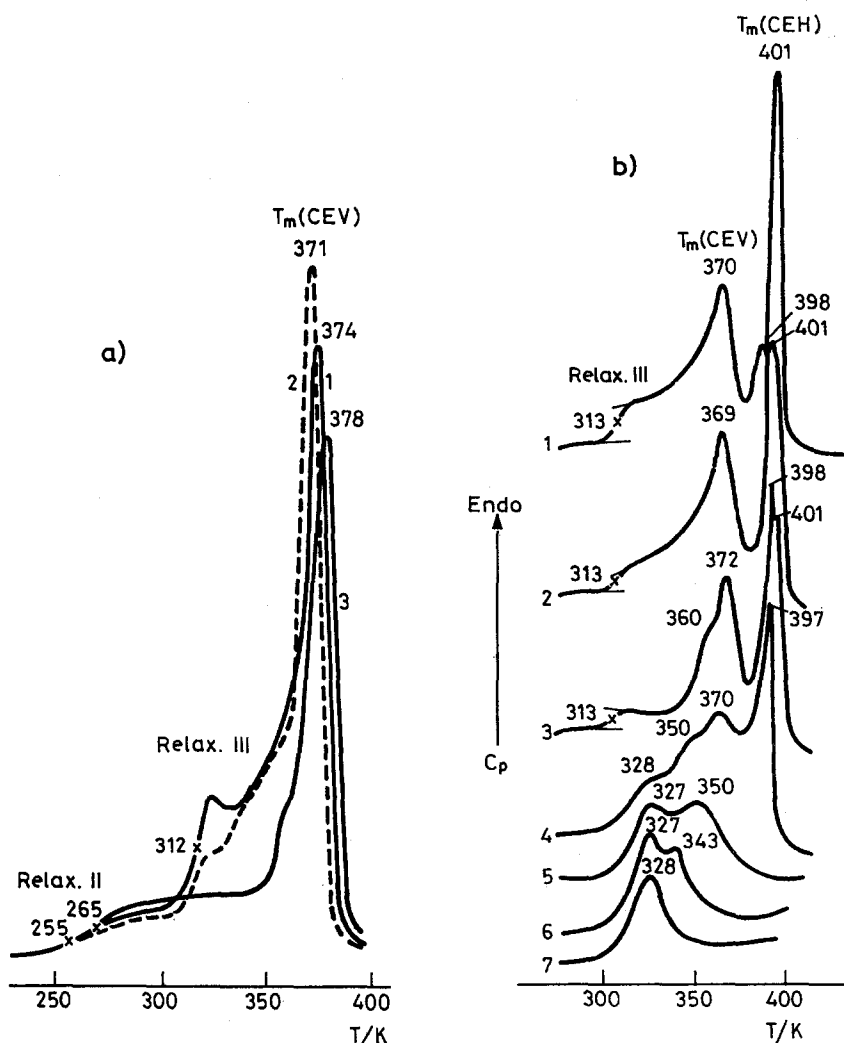
Fig. 3 DSC curves for CEV samples containing flame retardants (a:) and for CEV/CEH mixture filled with aluminium hydroxide; (b): before irradiation (1), after irradiation in air to 25 (2), 225 Mrad (3), 25 Mrad+300 hrs heat ageing (4), 25 Mrad+600 hrs heat ageing (5), 100 Mrad+600 hrs heat ageing (6) and 225 Mrad+600 hrs heat ageing at 448 K (7). Heating rate equals 20 deg/min

Step ΔC_p^I disappears when the average distance between cross-links M_c becomes comparable with the Kuhn segment magnitude S and the segmental motion is suppressed (in PE, $S \approx 16$ CH$_2$ groups). Indeed, on irradiation of PE in the melt, the segmental mobility was suppressed when the value of M_c in the homogeneous molecular lattice formed dropped to 20 CH$_2$ groups [4].

The crosslinking of mobile molecular elements in intercrystalline regions of PE ($V_c \gg V_d$) established by DSC is confirmed by the increase in the modulus of elasticity for these regions (see below). The rise in ΔC_p^I at high irradiation doses occurs for two reasons: the decrease in the crystallinity degree, and the destruction of the low-mobile lattice (where $V_d > V_c$). In the range 300–700 Mrad, a dynamic equilibrium between chain destruction and cross-linking is established: $\Delta C_p^I \approx$ const (Fig. 4).
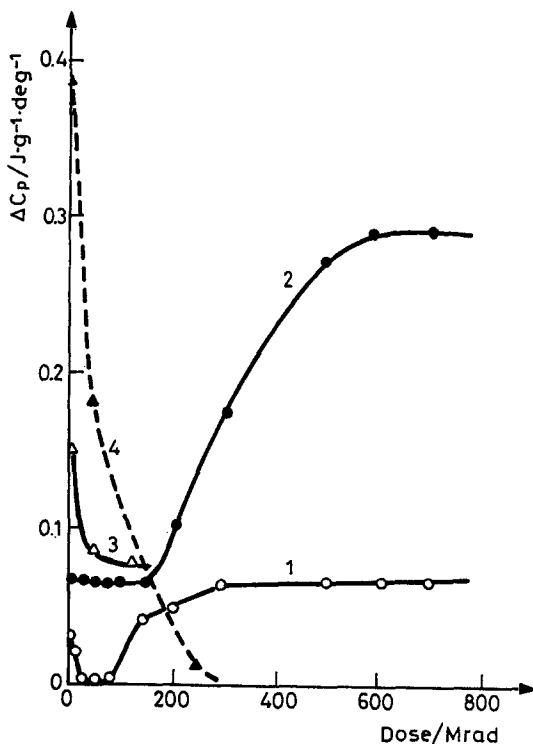

Fig. 4 Dependences of ΔC_p step values in temperature ranges of relaxations I (1), II (2) and III (3, 4) on the irradiation dose for high-density PE (1, 2), ultrahigh molecular PE (3) and CEV (4)

In the temperature region of the co-operative glass transition (relaxation II at 240–290 K), the step $\Delta C_p^{II} \approx 0.2$–0.6 J/g.deg (the highest for CEV) was observed for the ethylene polymers and copolymers under study. At 5–130 Mrad doses, the

irradiation caused practically no change in ΔC_p^{II}. Increase of the dose from 200 to 500–700 Mrad resulted in ΔC_p^{II} increasing fourfold (Fig. 4), mainly as a consequence of sample amorphization. T_g was determined at the half-height of step ΔC_p^{II}; and on irradiation, it changed from 255±5 K to 265±5 K. In this case, the significant effect of cross-linking is not available, which may be explained by the insufficient free volume in microvolumes where the co-operative segmental motion occurs.

Relaxation III, related to the segmental motion in low-folded tie chains and folds, is appreciably pronounced in the DSC curves for PE, and especially for ethylene copolymers when ΔC_p^{III} amounts to 0.5–1.0 J/g·deg (Figs 3 and 5).
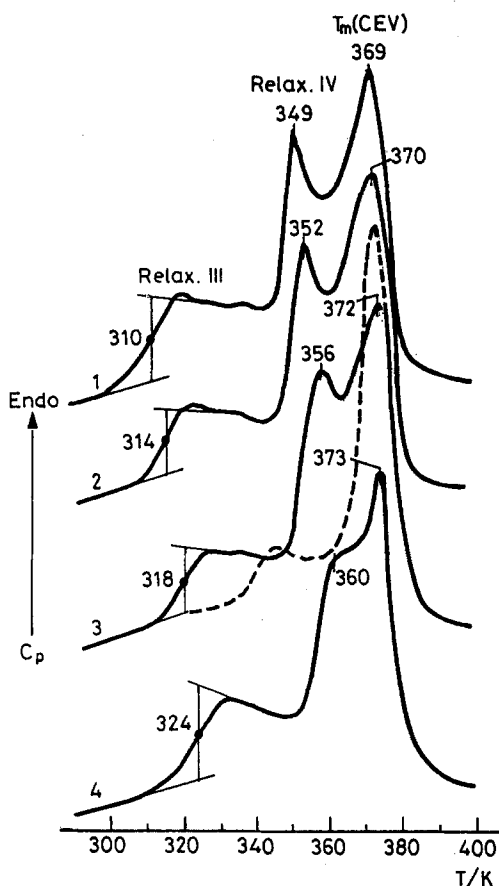

Fig. 5 DSC curves for CEV samples containing flame retardants. Previous annealing at 353 K. Dashed line: after the irradiation in air to 225 Mrad dose. Heating rate equals 5 (1), 10 (2), 20 (3) and 40 deg/min (4)

The irradiation of low-density PE in argon atmosphere with 15–30 Mrad doses appreciably decreases step ΔC_p^{III}. However, the irradiation of CEV in the air was most effective for relaxation III: step ΔC_p^{III} became half as much after 25 Mrad, and with further increase of the dose it disappeared completely (Figs 3–5). This step sometimes shifts by 15–30 deg to higher temperatures or transforms into two steps, namely a decreased initial one and a new one at higher temperature. The suppression of relaxation III depends here on the cross-linking of the molecular elements mentioned above.

The appearance of segmental mobility in the extended tie chains of semicrystalline polymers (relaxation IV) takes place at temperatures 15–20 deg below the melting point when the last crystallites begin to melt. As a result of annealing at temperatures close to the melting point, the proportion of extended chains in the intercrystalline regions of PE increases [17]. As indicated above, the destruction of these chains prevails over cross-linking on irradiation ($V_d \gg V_c$), and it brings about the observed decrease in C_p for high-density PE at 380–400 K (circles in Fig. 7) or even the disappearance of step ΔC_p^{IV} observed for CEV samples at 350–360 K (Fig. 5).

The preliminary annealing or irradiation of the samples under study may bring about the appearance of endotherms in the DSC curves, resembling a double peak of melting (Fig. 5). These cases are of methodological interest for the DSC of semicrystalline polymers. In general, there are many reasons for the appearance of similar double peaks associated with the phase transitions in polymers [3], but these do not hold in this case.
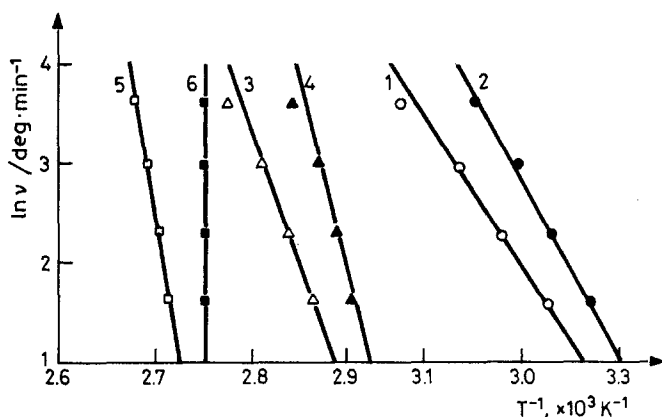
Fig. 6 Dependences of transition temperatures in Fig. 5 on heating rate for relaxation III (1, 2), relaxation IV (3, 4) and melting (5, 6). 1, 3, 5: experiment, 2, 4, 6: ditto but the results were corrected with due account of the thermal lagging

The nature of this double peak was revealed by measuring DSC curves at various heating rates V (Fig. 5). the melting peak at 369 K was shifted by only

4 deg, because of the usual thermal lag, but the heat capacity anomaly at 349 K (step plus peak) was shifted similar to step ΔC_p^{III} at 310–320 K, when the transition temperatures changed by 11 and 14 deg, respectively; this indicates the relaxational nature of both transitions.

Figure 6 shows curves for all three transition temperatures of ln $V(1/T)$ type; these curves were drawn with due account to the thermal lag and without it. On the basis of this information, activation energies $Q=-R$ dln$V$/d$(1/T)$ were determined; these relate to relaxations III and IV at 310–320 and 349–360 K, which equal ~200 and 350 kJ/mole.

2. Radiation stability of polymeric crystallites

Experiments with PE single crystals [23], the dependence of radiation cross-linking on the degree of crystallinity [1] and other data show that cross-linking occurs mainly in the intercrystalline regions with higher mobility and free volume. However, irradiation was found to affect PE crystallites in different ways: for example, it can result in a completely disordered state of the sample [1], or slightly decrease its degree of crystallinity χ after 1000 Mrad [13], while sometimes it has no effect on χ after a 400–600 Mrad dose [23, 26].

The experimental data described below also show considerable differences in the radiation stability of polymeric crystallites and permit their explanation from the common point of view, based on the important role of molecular mobility and free volume for the development of radiation processes.

Figures 7–9 show the effects of irradiation with electrons in an argon atmosphere on the DSC curves and melting parameters for high-density PE. The radiation stability of crystallites is strongly dependent not only on the irradiation dose, but also on the thermal prehistory of the polymer.

Three stages of the effects of irradiation are characteristic for unannealed samples (Fig. 7a). In the first stage (30–70 Mrad), the shape of the melting peak and χ value are practically not changed, while the melting point becomes even 1–2 deg higher. Beginning from a 100 Mrad dose, the melting peak splits into the initial one at 410 ± 2 K and a new one at 398–399 K. After a 200 Mrad dose, the initial peak is completely converted to the second one. After a 300–800 Mrad dose, χ drops from 50 to 10% and the melting point of the residual crystalline phase decreases to 315 K (Figs 8 and 9).

As a result of previous annealing of high-density PE for 20 h at 400 K, the radiation resistance of the crystallites sharply increases. The DSC curves, T_m and χ show that the crystallites were hardly damaged, even after an irradiation dose of 500 Mrad (Figs 7b, 8 and 9). It may also be seen that after moderate annealing for 5 h at 383 K PE crystallites demonstrated intermediate characteristics of radiation stability.

Figure 3 shows the dependence of the radiation stability of polymeric crystallites on the composition of the sample containing a filler. The irradiation of CEV
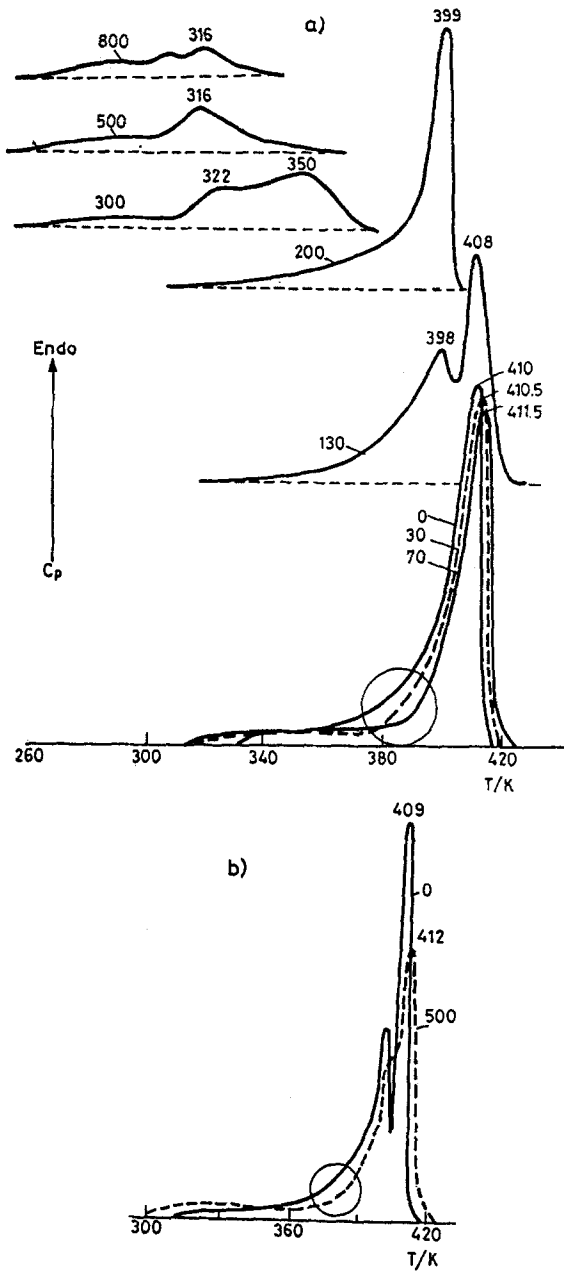
Fig. 7 DSC curves for high-density PE at temperatures above glass transition temperature. Unannealed at 400 K, 20 h (b). Irradiation in argon (the doses are indicated). Heating rate equals 20 deg/min

sample containing flame retardants up to 225 Mrad is seen not to damage the crystallites; the melting point even increases slightly.
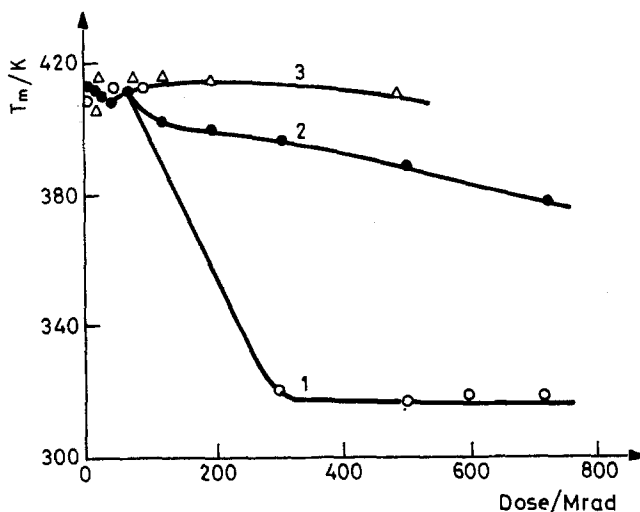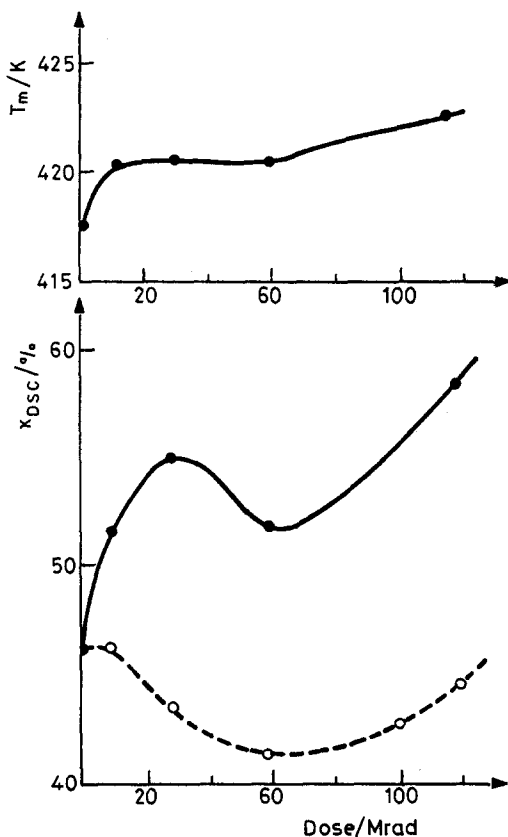

Fig. 8 Dependences of melting temperature on the irradiation dose for high-density PE in unnealed state (1) and after annealing at 383 K, 5 h (2) or 400 K, 20 h (3). Heating rate equals 20 deg/min
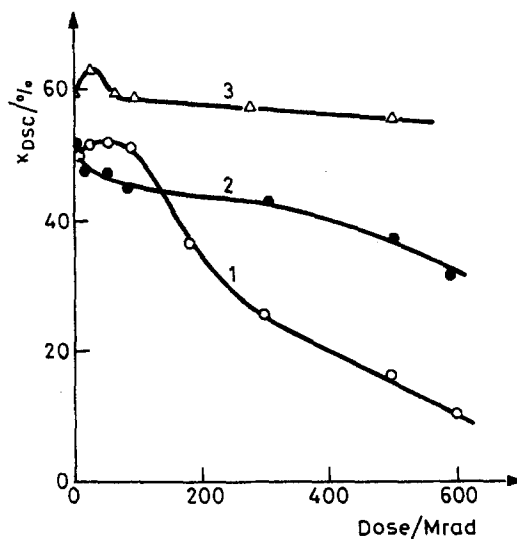
Fig. 9 The crystallinity degree as a function of irradiation dose for high-density PE. The sample prehistory corresponds to Fig. 8

Another picture is observed for compositions including mixtures of CEV, CEH and aluminium hydroxide. In this case the copolymers were crystallized separately (T_m=370 K for CEV and 401 K for CEH). In the course of irradiation, the double melting peak again appeared (397 K and 401 K, 360 K and 370 K) and the initial peaks were gradually transformed to the newly-formed ones. The thermal ageing of irradiated samples at 448 K sharply affected the melting parameters, especially with increase of the irradiation dose. As a result, T_m decreased to ~330 K and the degree of crystallinity χ decreased 3–4-fold (Fig. 3).

Unusual behaviour was displayed by ultrahigh molecular PE. After irradiation, its T_m was appreciably increased and the degree of crystallinity rose from 46 to 59%. For this polymer, the role of molecular entanglements is particularly high, and therefore the chain destruction by irradiation facilitates additional crystallization. However, the radiation cross-linking of chains also occurs in this case

Fig. 10 Dependences of melting temperature and crystallinity degree on the irradiation dose for ultrahigh molecular PE (dashed line is scan II). Heating rate equals 20 deg/min
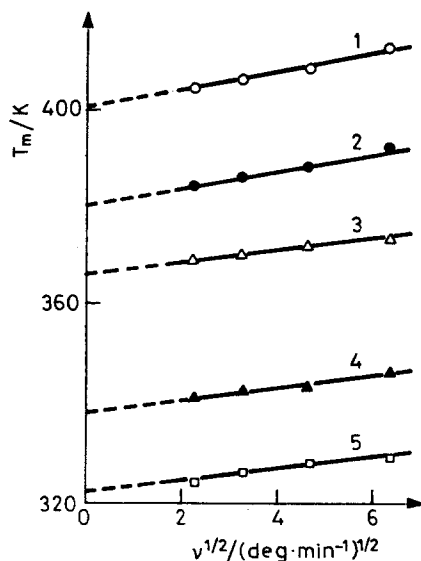
Fig. 11 Typical dependences of the melting temperatures on heating rate for polyolefines and their filled compositions irradiated to 225 Mrad dose (1–3) or irradiated and heat aged for a long time at 448 K (4, 5)

because the value of χ proved to be much lower on scan II (Fig. 10). For nonirradiated samples, T_m and χ were approximately identical on scans I and II.

The small change induced in T_m by polymer irradiation need not be explained by variation in the crystallite size or the degree of its perfection. Thus, the T_m increase may be due to the cross-linking of chains in the intercrystalline regions; this results in more local order in the melt of the radiation cross-linked sample, and decreases its conformational entropy. For this reason, the melting entropy ΔS_m decreases, but $T_m = \Delta H_m / \Delta S_m$ rises.

On the other hand, the Thomson–Gibbs equation [27] $T_m^t = T_m^o (1 - \dfrac{2\,\gamma_i}{\Delta H_m^o \, \rho_c \, l_c})$ shows that a slight decrease in T_m can be induced by the rise in the free surface energy γ_i of crystallites on irradiation. Here, ρ_c and l_c are the density and thickness of the crystallite, T_m^o is the equilibrium melting point of an infinite crystal (for PE 416±1 K [27]) and T_m^t is the true melting point of the crystallites. The latter is determined [3] by measuring T_m for identical samples at different heating rates and by extrapolating the linear dependences $T_m(V^{1/2})$ to $V=0$ (Fig. 11).

Transformations undoubtedly occur in crystallites in response to considerable irradiation doses. The differences observed in the radiation stability of polymeric crystallites can also be explained from the standpoint of different molecular mobilities. Thus, the decrease in the chain density packing and the high con-

centration of defects result in an increased mobility, which contributes to irradiation damage to the crystalline structures.
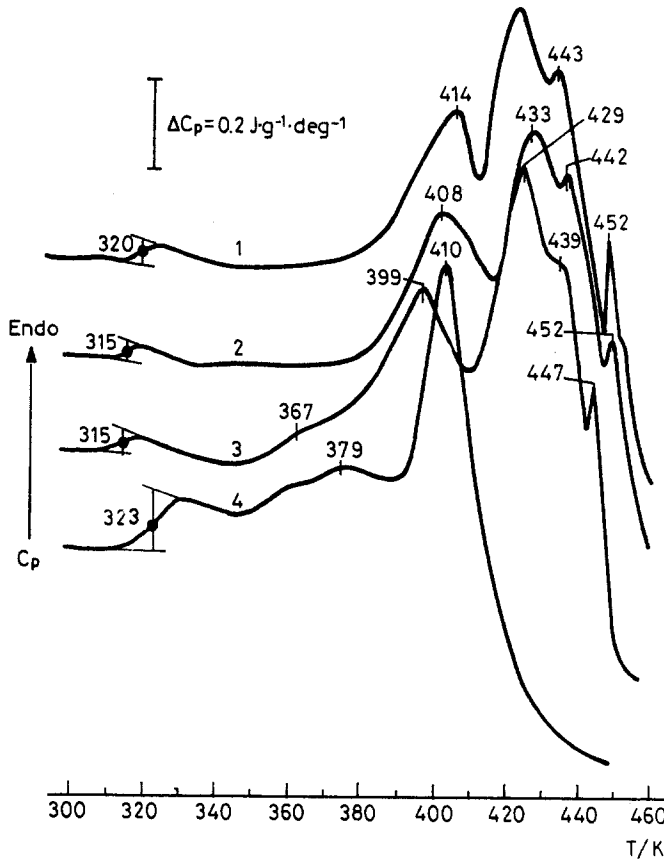
Fig. 12 DSC curves for vinylidene fluoride/tetrafluoroethylene copolymer (94:6) in the initial state (1) and after irradiation to 25 (2) 60 (3) and 230 Mrad (4). Heating rate equals 20 deg/min

The crystallites of unannealed PE are damaged by electrons comparative easily because they contain a considerable extent of loosely-packed and mobile pseudohexagonal structures peculiar to the melt and to the state of PE at temperatures close to T_m. X-ray and DSC data [11–13] show that radiation damage to well-annealed orthorhombic PE lattices converts them to pseudohexagonal lattices with azimuthal disorder, their degradation being realized by the gradual development of the process from the surface into the crystallite.

The influence of any filler on the radiation stability of crystallites consists in the changes produced in the supermolecular structure of the polymer, its packing density and the molecular mobility by the presence of the filler.

To conclude this section, we shall consider the effects of irradiation on the DSC curve of vinylidene fluoride/tetrafluoroethylene copolymer. The four endothermic peaks observed (Fig. 12) can be regarded as a result of the gradual conversion to conformationally disordered (condis [28]) crystallites as the temperature is increased or as the different crystalline modifications melting. In the latter case, T_m=414 K should be related to the most loosely packed structure with highest mobility. Therefore, it is natural that a 25 Mrad dose does not influence the 434, 443 and 452 K peaks, but decreases the 414 K peak by 6 deg; after irradiation with a 60 Mrad dose, this peak is shifted by as much as three times the shifts for the other peaks. Long-term irradiation (230 Mrad) results in the disappearance of the three more perfect crystalline modifications and the copolymer finally melts at 410 K (Fig. 12).

3. Relations between DSC parameters and mechanical properties of irradiated polymers

Ionizing irradiation can change the mechanical properties of polymers considerably. Cases of radical radiation embrittlement are known, for example, even at low irradiation doses because of intensive chain destruction (polyethylene terephthalate, polycaprolactone, etc.) [10, 16].

We have established the direct correlations between the thermal transition characteristics obtained by using DSC and the changes in the mechanical properties of the ethylene polymers and copolymers under study [3, 7, 9, 24].

Paper [24] shows that the dependences of the modulus of elasticity of amorphous regions E_a and the tensile strength σ_F for isotropic PE on the irradiation dose exhibit a maximum at 15–30 Mrad. The latter corresponds to the maximum number of loaded tie chains. This result is in accordance with the disappearance of step ΔC_p in the relaxation I region, caused by crosslinking of the more mobile elements in the intercrystalline regions (Fig. 2). For oriented PE containing a high concentration of extended tie chains destroyed by irradiation ($V_d \gg V_c$), the modulus of elasticity and tensile strength were sharply decreased after irradiation, including low doses [24].

Paper [7] reveals a correlation between the value of the heat capacity step ΔC_p^{III} at 310–320 K and the elongation to fracture ε_f at 293 K for the large number of initial and irradiated (25–225 Mrad) materials investigated in this work. Figure 13 shows that the radiation suppression of this anomaly in the DSC curve is accompanied by an ε_f value decrease from 600–800 to 30–50%. The sense of the correlation is that realization of high plastic deformation of irradiated polymers is limited by cross-links of slightly folded tie chains and folds.
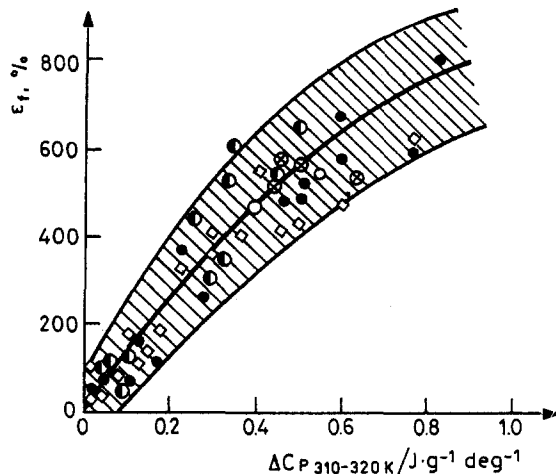
Fig. 13 Relation between ΔC_P^{III} value and breaking tensile deformation for polyolefins under study and their filled compositions including those irradiated to 25–225 Mrad dose

Finally, the third relation, between the yield point σ_y and the crystallite thickness l_c, is of considerable interest [9]. Irradiation (25–225 Mrad) with subsequent heat ageing of polyolefins and their filled compositions led to variation of T_m^t in a wide range (Fig. 11) and thus to change in the crystallite thickness by one order of magnitude (see the Thomson-Gibbs equation above).

The linear relation that the yield point σ (MPa) at room temperature is numerically equal to 15–20 l_c (nm) proved to be valid for the whole group of substances under study. This correlation indicates the important role of an intracrystalline shift for the beginning of unelastic deformation of polymers at temperatures above the glass transition temperature.

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Zusammenfassung — DSC wurde zur Untersuchung des Einflusses von Bestrahlung mit schnellen Elektronen auf die molekulare Mobilität und den Schmelzvorgang von semikristallinen Polymeren und Kopolymeren von Ethylen und von Fluorkopolymer angewendet. Die Temperaturabhängigkeit der Wärmekapazität im Bereich 100 bis 500 K zeigte die besonderen Wesenszüge des Bestrahlungseffektes auf vier Relaxationsumwandlungen in Verbindung mit dem Auftreten von Segmentbewegungen in verschiedenen Molekülteilen der gestörten Regionen des Polymers. Man fand, daß die Bestrahlungsbeständigkeit der Kristallite eindeutig von der Vorgeschichte des untersuchten Objektes abhängt. Die Ergebnisse wurden ausgehend von der bestimmenden Rolle von Molekülbeweglichkeit und freiem Volumen für das Überwiegen der Strahlungsvernetzung der Moleküle gedeutet. Es wurden Zusammenhänge zwischen den Wesenszügen der thermischen Umwandlungen und den mechanischen Eigenschaften der bestrahlten Polymere festgestellt.