

A STUDY OF THE MECHANISM OF DECAY OF ALLYL MACRORADICALS IN CROSSLINKED POLYETHYLENE

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Free radicals were generated in peroxide-crosslinked polyethylene with different gel fraction contents by exposition to a gamma dose of 20 kGy at 293 K. The decay of allyl macroradicals was examined by the ESR method in dependence on the crosslinking concentration. The rate constants of the allyl radical decay decreased with increasing gel content of the samples, and the activation energies, determined from the temperature dependences of the rate constants, increased with increasing extent of crosslinking. The results are discussed from the energy aspect of the conformational motions dominating in the temperature region used and controlling the allyl radical decay in crosslinked polyethylene.

The application potential of linear and branched polyethylenes can be increased significantly by their crosslinking. The additional chemical bonds formed induce changes in the macroscopic properties of the polymeric molecules. The rate of decay of free radicals is closely related with the physico-chemical properties of the solid polymeric matrix. The crosslinking is assumed to have an effect on the local mobility of the polymeric chain. Little attention has been paid to the effect of the crosslinking concentration on the free radical decay. Pioneering work has been done by Kuzminskii, Fedoseeva and coworkers on gamma-irradiated vulcanizates¹ and on thermally cured butadiene rubber². The effect of crosslinking on the free radical decay rate was studied³ on crosslinked poly(2-hydroxyethylmethacrylate); crosslinking characterized by 20% bifunctional monomer brings about slowdown of the internal mobility to a sufficient extent and additional increase in the crosslinking agent concentration has practically no effect on the decay rate. In chemically crosslinked isotactic polypropylene the decay rate has been found⁴ independent of the crosslinking over the temperature region of -30°C to 20°C . The results have been interpreted in terms of the degradation processes taking place simultaneously with the crosslinking in the isotactic polypropylene.

The reactivity of allyl macroradicals at elevated temperatures (above 330 K) has been studied on a series of morphological forms of polyethylene exposed to relatively high doses (10^2 kGy). The rates of free radical decay decrease with increasing dose owing to the increased number of radiation-produced crosslinkings which lower the mobility of chains in the amorphous zones⁵.

The aim of the present work was to investigate the role of the chemical crosslinking in the process of the allyl radical decay. Primarily crosslinked polyethylene was

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chosen for this purpose because this readily crosslinked polymer forms a well-developed network, its crosslinking is accompanied by side reactions to a low extent, and the material finds wide use in the practice.

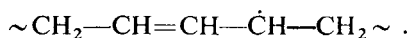
EXPERIMENTAL

Low density polyethylene Bralen RB 03-23, $M_v = 1.3 \cdot 10^5$, $\rho_{20} = 0.923 \text{ g cm}^{-3}$, nonstabilized powder (Slovnaft, Bratislava) was modified by heating with bis(α,α -dimethylbenzyl) peroxide (0.05–2.0% (*m/m*)) in sealed ampules in an inert atmosphere at 428 K for 5 h; the low molecular weight fractions were removed by extraction with chloroform. The primarily crosslinked samples were evacuated and exposed to gamma radiation from a ^{60}Co source at 293 K (radiation rate 0.50 kGy h^{-1} , total dose 20 kGy). The total crosslinking was characterized by weight per cent of the gel fraction with respect to the initial weight, after 20 h extraction with boiling benzene.

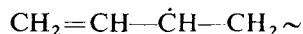
The concentration of free radicals in the gamma-irradiated samples was measured by the ESR method on a Varian E-4 spectrometer at 303 K. The total concentration of free radicals was obtained by double integration of the first derivative of the ESR spectrum and comparison with a Strong Pitch standard (Varian). The elimination of the alkyl radicals with a spectral width of 16.5 mT was evidenced by the vanishing of the outermost wing peak. The kinetic measurements of the allyl radical decay for a series of temperatures were accomplished with a Varian E-257 temperature equipment using nitrogen as carrier gas.

RESULTS AND DISCUSSION

The gel fraction content of the polyethylene samples after their heating with the peroxide initiator and exposition to a gamma dose of 20 kGy at 293 K depends considerably on the initiator concentration; for concentrations of 0.05, 0.2, 0.4, 0.8, 1.5, and 2.0% (*m/m*) the gel fractions made 21.8, 57.4, 68.9, 79.3, 84.5, and 89.4% (*m/m*), respectively. The basic form of the spectra of the free radicals in the crosslinked polyethylene samples with different gel fraction contents at 303 K (Fig. 1) is a septet which remains preserved throughout the whole sample series. This signal is generally attributed to vinylene allyl macroradicals⁶



In principle it is not impossible that a terminal vinyl



is also present. The preference of inner allyls, however, is suggested by the known facts of the radiation chemistry of polyethylene⁷, namely, the decrease in the concentration of vinyl groups, presumably due to their reaction with the radical centres giving rise to Y-branches⁸, and the increase in the concentration of vinylene groups during the radiolysis⁷. This concept is also supported by the result of analysis of the conformation dynamics of the motion of the terminal segments which is given later.

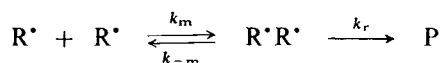
The kinetic study of the allyl centre decay process was performed at 293–323 K. The results were tested by a kinetic model of two simultaneous 2nd order reactions⁹ and by a model with a time dependent rate constant¹⁰ expressed as $k(t) = Br^{t-1}$, which reduces to the particular case of the ordinary 2nd order kinetics for $\alpha = 1$. This particular case fits well the time dependence of concentration of the allyl centres over the entire temperature and gel content regions, as documented by Fig. 2 for a chosen temperature.

Fig. 3 shows the rate constants of the allyl macroradical decay at various temperatures in dependence on the gel fraction content. The rate constants drop first rapidly with the gel fraction content to attain saturation at approximately 70% gel content. The reactivity changes only slightly with additional increase in the concentration of the nodal points (H-bridges and Y-branches).

The activation energies, determined from the Arrhenius temperature dependence of the rate constants, show a similar course (Fig. 4). For the minimally crosslinked system the activation energy attains a value of 60.3 kJ mol^{-1} , for the maximum gel content the value is 80.3 kJ mol^{-1} ; a slight increase in the activation energy is observed at higher gel contents.

Consider now the problem of localization of the decay process. After radiolysis, allyl radicals occur both in the amorphous and in the crystalline polyethylene regions¹¹. From the reactivity point of view, centres in the disordered regions (amorphous phase, crystallite defects) vanish preferentially at relatively lower temperatures whereas at higher temperatures in the region of α_c -molecular motions, macroradicals vanish also from the crystalline regions¹¹. Fig. 3 shows that the rate constant of the allyl radical decay is highly sensitive to the gel fraction content particularly at lower crosslinking concentrations. This indicates that the decay of the allyl centres takes place within the crosslinked amorphous zones. If the decay occurred in the crystallite defects or even in the crystallites themselves, the sensitivity to the gel fraction should be very weak. Moreover, the temperature region for the kinetic measurements is below the limit for the α_c -molecular motions¹². This conclusion is also supported by the established fact that at low radiation doses the crosslinking reaction in semi-crystalline polyethylene takes place in the amorphous zones only¹³.

The above experimental results can be interpreted in a semiquantitative way at least, within the scope of the concept of diffusion-limited reactions using the activation-energy approach¹⁴. Here the effective activation energy of decay of the radical centres for the reaction pathway



is regarded as approximately equal to the activation energy of the migration stage of the decay process ($E_{\text{eff}} \approx E_m$). Allyl macroradicals are known to vanish by a com-

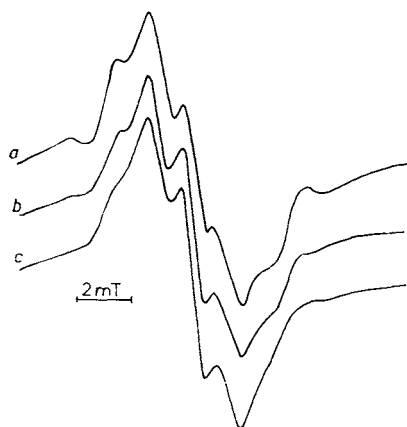


FIG. 1

ESR spectra of free radicals in crosslinked polyethylene at 303 K after its exposition to a gamma dose of 20 kGy at 293 K. Initial gel fraction content (% (m/m)): a 21.8, b 68.9, c 89.4

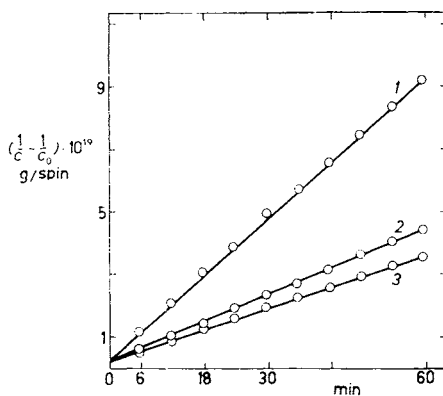


FIG. 2

Testing the 2nd order kinetics for the allyl macroradical decay in crosslinked polyethylene at 313 K. Gel content (% (m/m)): 1 21.8, 2 68.9, 3 84.9

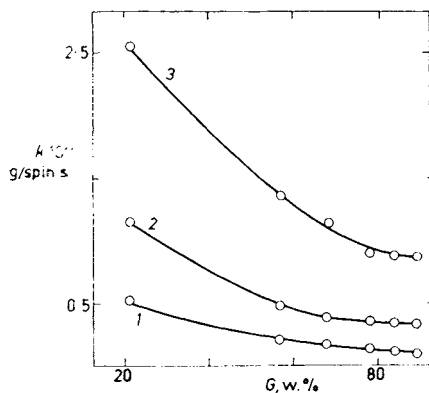


FIG. 3

Dependence of the rate constants of allyl macroradical decay in crosslinked polyethylene on the gel fraction content. Temperature (K): 1 293, 2 303, 3 313

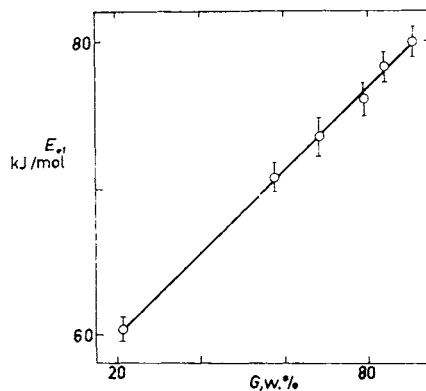


FIG. 4

Dependence of the activation energy of allyl macroradical decay in crosslinked polyethylene on the gel fraction content at 293–323 K

bination reaction¹⁵ which is a fast reaction. Moreover, the participation of the chemical nearing of the radical centres can be ruled out for allyls because of their higher thermodynamic stability^{5,15} in comparison with alkyl macroradicals. Therefore, only transport mechanisms involving molecular motions of the chains are to be considered. Assuming that the motions have the character of segmental conformation transition¹⁴, E_m can be put approximately equal to \bar{E}_{fm} , the statistically averaged energy barrier of the molecular motions in the amorphous phase, given by the relation

$$\bar{E}_{fm} = \sum_a c_a E_{fm}(a),$$

where

$$E_{fm}(a) = E_{intra} + E_{inter} = \sum_n E_n(s, s') + \sum_m r_m \epsilon_m.$$

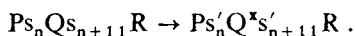
Here $E_n(s, s')$ is the energy barrier of transition of the n -th bond from the s -th initial state to the s' -th final state and r_m is the number of structure groups of the m -th kind with an average cohesion energy of ϵ_m . The data for polyethylene are given in refs^{16,17}.

This concept can be used for supporting the hypothesis of the preferential participation of vinylene allyl radicals in the decay process. Vinyl type allyl centres have been shown⁵ to form by free valency migration towards the vinyl unsaturations at the ends of the chains which are 90–99% localized in the amorphous polyethylene zones¹⁸. The appropriate kind of motion of the terminal segments with vinyl centres can be found by applying a set of criteria: the radical criterion stating that the mobile part of the segment includes the macroradical, the mobility criterion demanding a minimal motion of the chain tail, and the energy criterion claiming a minimal conformation energy content of the segment. Taking these criteria into account it is suggested that the motions sought can be crank type motions of the terminal segments. The mechanism of these motions for a minimal three-bond segment can be written as $Ps_nQ \rightarrow Ps'_nQ^*$ with $n = 4$, *i.e.* the rotational state is altered ($s \rightarrow s'$) for the fourth bond from the chain end and the mobile part of the segment Q with the radical centre shifts to the final position Q^* . The kinetic energetics estimate for these motions leads to very low values of the energy barriers, *viz.* 22.1 kJ mol⁻¹ for $g^+ \rightarrow t$ transition and 24.5 kJ mol⁻¹ for $t \rightarrow g^+$ motion. So low barriers imply rapid motions of the chain ends and consequently, decay of the vinyl allyls during the radiolysis at room temperature. This conclusion is consistent with the data indicating a rapid vanishing of the vinyl groups during the radiolysis, largely due to their high mobility in conjunction with the migration of alkyl centres⁸.

If the vinylene macroradicals are situated at the chain ends, the above analysis leads to the participation of crank motions of five-bond terminal segments. The

kinetic energetics calculations give energy barrier values of 37.9 kJ mol^{-1} for $t \rightarrow g^\pm$ transitions and 35.4 kJ mol^{-1} for the reverse conformation motions. The barrier estimates are again substantially lower than the determined activation energies of decay of the allyl free radicals in the crosslinked samples, and it is not reasonable to assume that the increased concentration of crosslinking would increase the barrier as much as two times.

Thus it is appropriate to consider the motion modes associated with the motion of the inner segments. The mobility, radical and energy criteria imply that the smallest inner segment that can carry a free valency includes eleven bonds and the motion species is of crankshaft type,



The possibility of motions of segments of this size even in high-crystallinity polyethylene within the temperature region of our kinetic measurements has been shown in a recent paper¹⁹. However, decisive for assessing the possibility of these motions in crosslinked polyethylene samples is a comparison of the segment suggested with the average number of bonds between the nodal points. It follows from the determination in ref.²⁰ that the average molecular weight between nodes is $M_r = 1140$ for polyethylene with 18.1% (*m/m*) gel fraction and $M_r = 810$ for sample with 89.2% (*m/m*) gel fraction. This corresponds to 41 and 29 bonds between the nodes in polyethylene with the minimum and maximum degrees of crosslinking, respectively. Despite these rather approximate values it can be admitted that the crankshaft motions of the size mentioned can occur throughout the entire series of crosslinked samples and contribute to the transport of the radical centres with the decay process. A kinetic energy analysis of these motions in the amorphous phase of non-crosslinked polyethylene for $\bar{T} = (T_{\min} + T_{\max})/2 = 308 \text{ K}$ gives the averaged energy barrier $E_{\text{fm}} = 66.2 \text{ kJ mol}^{-1}$. This value is close to the activation energy of 60.3 kJ mol^{-1} for the allyl decay in samples with the minimum gel fraction content, where the distance between the nodes is rather long.

The slight increase in the effective activation energy with increasing gel fraction content can be explained qualitatively as follows. It follows from a study of the effect of crosslinking on the local dynamics of the crosslinked chain²¹ that the restricted mobility can be due either to the occurrence of kinematic and dynamic hindrance along the chain or to changes in the local environment of the kinetic motion units. Moreover, the nature of the restriction depends on the structure, length, and flexibility of the crosslinking and on the thermodynamic and kinetic flexibility of the chains. In connection with our suggestion of the motion mechanism, the extent of the effect of the crosslinking element (H-bridge, Y-branch) on the rotation mobility of the bonds between the nodes is of importance; clearly, the energetics of the motion will depend on the position of the crankshaft segments with respect

to the nodal points. For H-bridges this aspect has been investigated by the molecular dynamics method on a condensed system formed by a set of bonded identical particles with a density of the amorphous polyethylene phase²¹. The rotation mobility has been found affected only in a close vicinity to the H-type node. For Y-type nodes a smaller or at most a similar effect can be expected. And since the probability of location of an eleven-bond segment in chain regions between the nodes in a sample with maximum crosslinking is approximately 7 times higher than that of localization of the crankshaft segment in a close vicinity to the nodes, the intramolecular contribution to $E_{fm}(a)$ can be expected to be basically constant. The observed increase in the effective activation energy with increasing gel fraction content then can be ascribed to increased intermolecular contribution to $E_{fm}(a)$. It is clear that if the number of crosslinkings between the chains is increased, an increased average cohesion energy of the structure units in the crosslinked polyethylene will result.

It can be concluded that the experimental data point to a significant effect of the primarily present crosslinkings on the decay of allyl macroradicals in polyethylene, manifesting itself by a lowering of the rate constant and increase in the activation energy with increasing degree of crosslinking. An activation-energy correlation has been observed between the averaged energy barrier of crankshaft motions of the inner segments in the amorphous phase and the effective activation energy of allyl decay in the polyethylene sample with minimum crosslinking, indicating a potential role of the conformation-segmental mobility in the reaction process.

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