EPR and DSC Study of the Decay of Allyl Macroradicals in Chemically Crosslinked Polyethylene

[a]M. KLIMOVÁ, [b]J. BARTOŠ, and [a]F. SZÖCS

[a]Polymer Institute, Slovak Academy of Sciences, CS-842 36 Bratislava

[b]Research Institute of Rubber and Plastic Technology, CS-764 22 Zlín

The decay of allyl macroradicals in chemically crosslinked polyethylenes was studied as a function of the chemical crosslinking and temperature by the EPR method. The decay rate constant was found to decrease in the temperature range between 293 and 323 K with the increasing gel fraction until the reaching of stable value at higher crosslinkings. On the other hand, the rate constant for decay increases monotonously with temperature in the region of lower gel fractions but within the region of higher gel contents its increase is stepwise. Dependences of the rate constant on the gel content are closely associated with the structural-chemical changes of the amorphous phase caused by the crosslinking of macromolecules. Temperature dependences of the rate constant are influenced by the course of phase change indicated by compensation effect and proved by DSC technique.

The importance of classical polymers which are modified in various physical or, more often, in physicochemical ways is at present increasing [1]. One of the best known polymers is polyethylene (PE) crosslinkable by radiation or by chemical initiators. It is widely used especially in electrotechnical industry, where not only mechanical and electric properties but also its lifetime are significant. Generally speaking, the presence of radical centres and physicochemical conditions of the reactions plays a substantial role in chemical ageing of polymers [2].

The aim of this paper is to investigate in detail the decay of relatively stable allyl macroradicals in crosslinked low-density polyethylene in dependence on the crosslinking extent and temperature. Some results from this study have been published in a preliminary paper [3].

EXPERIMENTAL

Low-density polyethylene PE, Bralen 03-23, ρ_{20} = 0.923 g cm^{-3}, M_w = 1.3 x 10^5, was used. A series of samples modified by chemical crosslinking was prepared from this polymer using dicumyl peroxide (DCP) in amount between 0 and 2.0 mass % in inert N$_2$ atmosphere at 428 K during 5 h. After taking the samples from the annealing bath, they were cooled at laboratory temperature. All samples were evacuated and gamma-irradiated from ^{60}Co source at 293 K with a total radiation dose of 20 kGy.

The contents of gel fractions were determined by weighing insoluble portions in nonirradiated and irradiated samples after their extraction in boiling benzene for 20 h.

Thermal characteristics were recorded on a DSC-1B Perkin—Elmer apparatus equipped with an additional cooling circuit. The calibration of the temperature scale of the calorimeter was done by using indium. The measurements were done in an inert atmosphere of gaseous N$_2$ at the heating rate of 16 °C min^{-1}

A Varian E-4 spectrometer was used for ESR measurements. The kinetic measurements of the decay of macroradicals were done using an E-257 temperature equipment. The concentrations of free radicals were obtained by comparing with a Varian Strong Pitch standard and processed on a Varian computer.

Table 1. Gel and Temperature Characteristics for the Series of the Chemically Crosslinked and Gamma-Irradiated PE

w(initiator)/%	w(gel)/%	$T_{m,i}$/K	$T_{m,p}$/K
0	0	310	384
0.05	21.8	309	383
0.2	57.4	307	383
0.4	68.9	306	382
0.8	79.3	306	381
1.5	84.5	305	380
2.0	89.4	304	377

RESULTS AND DISCUSSION

Table 1 contains gel and temperature characteristics of polyethylene as a function of the content of crosslinking initiator. Gel fractions of irradiated samples were taken as a measure of the crosslinking of the amorphous phase of PE matrix.

The EPR spectra of all samples give septet signal [3] belonging to allyl macroradicals of vinylene type [4]. Kinetic measurements of the decay of these free-radical centres were carried out over the temperature range between 293 and 323 K. The time dependences of the total concentrations of free radicals were found to obey the second-order kinetic equation [3]. On this basis we can use a model of the diffusion-controlled reactions in a condensed phase for the interpretation of the decay mechanism

$$R^{\bullet} + R^{\bullet} \underset{k_{-m}}{\overset{k_m}{\rightleftharpoons}} (R^{\bullet}R^{\bullet}) \xrightarrow{k_r} P \qquad (A)$$
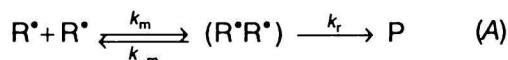
Here k_m, k_{-m}, and k_r are the rate constants for migration of the reactants into and out of the cage complex and final reaction.

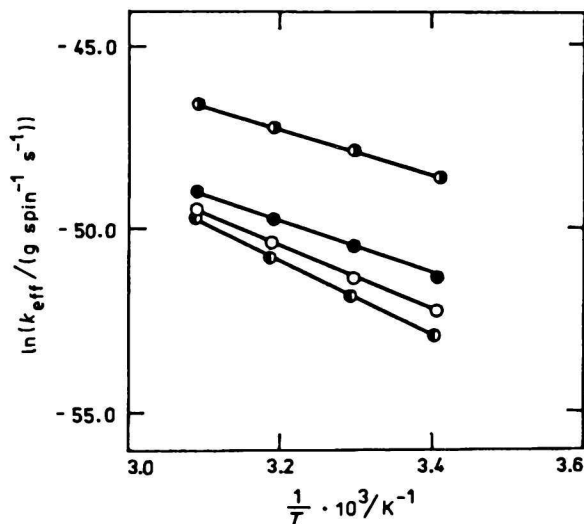The effective second-order rate constant k_{eff} is here given by the relation

$$k_{eff} = \frac{k_m k_r}{k_m + k_r}$$

which, within the limit $k_r \gg k_m$, k_{-m} changes to $k_{eff} \approx k_m$. In the case of allyl macroradicals, because of their thermodynamic stability, $k_m = k_{phm}$, where k_{phm} is the rate constant for physical migration, i.e. for some molecular motion that leads to an approaching of reactants. Table 2 shows the values of the effective rate constants for the decay of allyls and gel fraction at four temperatures from the mentioned temperature interval. The rate constants for allyl decay decrease at all temperatures with increasing crosslinking and saturate at the highest gel contents for each temperature.

A treatment of temperature variations of the rate constants of the series of polyethylenes studied is based on the application of Arrhenius equa-

Fig. 1. Arrhenius plot for allyl decay rate constants in uncrosslinked PE (◐), and in chemically crosslinked PE with gel content in mass %: ● 21.8, ○ 57.4, ◑ 89.4.

tion (Fig. 1). Table 3 summarizes values of the effective pre-exponential factors $k_{o,eff}$ and effective activation energies E_{eff}. Both parameters increase with the increasing gel content. In addition, they are connected in the so-called compensation dependence. Fig. 2 gives the test of the compensation effect, i.e. linearity between ln $k_{o,eff}$ and E_{eff}. These properties of both parameters may be interpreted in two ways.

Let us assume that the effective values of kinetic parameters characterize the real physicochemical process of the decay of allyls in a series of samples examined and that they have a physical significance. Then it is possible to apply a model of transient state in connection with the concept of the cooperation of elementary reactions in the condensed phase [5, 6]

$$k_m = \frac{kT}{h} e^{\frac{n \Delta S}{R}} e^{\frac{-E_{chem} + nV}{RT}} \qquad (1)$$

where k is the Boltzmann constant, h the Planck constant, T the absolute temperature, n the number of segments in molecular motion, ΔS the acti-

Table 2. The Values of the Effective Rate Constants for the Allyl Decay in Chemically Crosslinked PE

w(gel)/%	$k_{eff} \cdot 10^{22}/(\text{g spin}^{-1} \text{ s}^{-1})$			
	$T = 293$ K	$T = 303$ K	$T = 313$ K	$T = 323$ K
0	7.81	16.0	31.0	57.9
21.8	0.49	1.45	2.5	5.1
57.4	0.21	0.49	1.38	3.1
68.9	0.17	0.39	1.17	2.65
79.3	0.13	0.37	0.97	2.4
84.5	0.11	0.37	0.89	2.4
89.4	0.11	0.32	0.88	2.3

Table 3. The Kinetic Parameters of the Allyl Decay and the Estimated Quantities from Lebedev's Model in Chemically Crosslinked PE

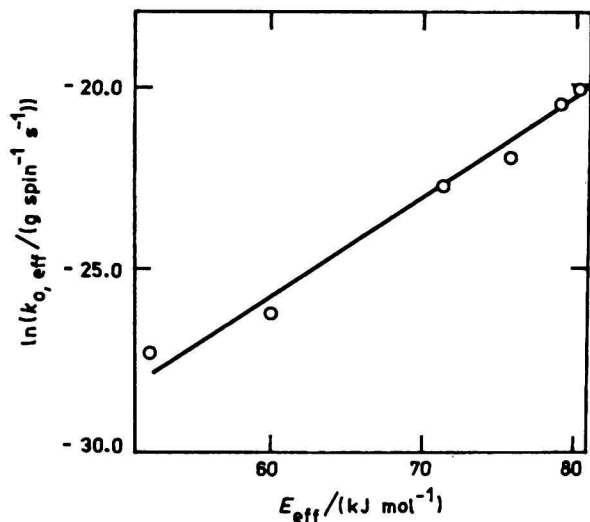| w(gel)	$k_{o,eff}$	E_{eff}	$\partial E/\partial T$	k_o
%	g spin^{-1} s^{-1}	kJ mol^{-1}	kJ mol^{-1} K^{-1}	g spin^{-1} s^{-1}
0	1.65×10^{-12}	52.3	0	1.65×10^{-12}
21.8	2.82×10^{-12}	60.3	-0.026	1.24×10^{-13}
57.4	1.24×10^{-10}	71.7	-0.063	6.35×10^{-14}
68.9	2.00×10^{-10}	73.5	-0.069	5.08×10^{-14}
79.3	5.01×10^{-9}	76.2	-0.078	4.43×10^{-14}
84.5	1.53×10^{-9}	79.2	-0.087	4.17×10^{-14}
89.4	1.28×10^{-9}	80.4	-0.091	3.91×10^{-14}

Fig. 2. Compensation dependence between the effective pre-exponential factor $k_{o,eff}$ and the effective activation energy E_{eff} for the allyl decay in chemically crosslinked PE.

vation entropy of segmental rearrangement, nV the activation enthalpy contribution of segmental rearrangement, and E_{chem} the activation enthalpy contribution from chemical migration (in our case it equals zero). Then the increasing pre-exponents and activation energies should reflect the increasing extent of the cooperation of various degrees of freedom in amorphous regions of the matrix and the corresponding increasing energetic demands for the formation of the transient state for the decay reaction. The probable reason for this cooperation may be associated with the presence of the chemical crosslinkings that increase the size of the rearrangement regions in the amorphous domains of the sample.

Another explanation is based on the assumption that the experimental effective values of both parameters are apparent and follow from the application of Arrhenius equation in the temperature region of structural change in a polymer. In this case we can use Lebedev's model of the temperature dependence of the true activation energy as a consequence of phase transformation [7]. Relations between apparent and true kinetic parameters are

$$E_{eff}(gel) = E(gel) - T\frac{\partial E}{\partial T} \qquad (2)$$

$$k_{o,eff}(gel) = k_o(gel)\ e^{-\frac{1}{R}\frac{\partial E}{\partial T}} \qquad (3)$$

For applying these relations it is necessary to know the dependence of the true activation energy for decay on gel content $E(gel)$ which is, however, unknown. To verify the validity of the concept of the temperature dependence of the true
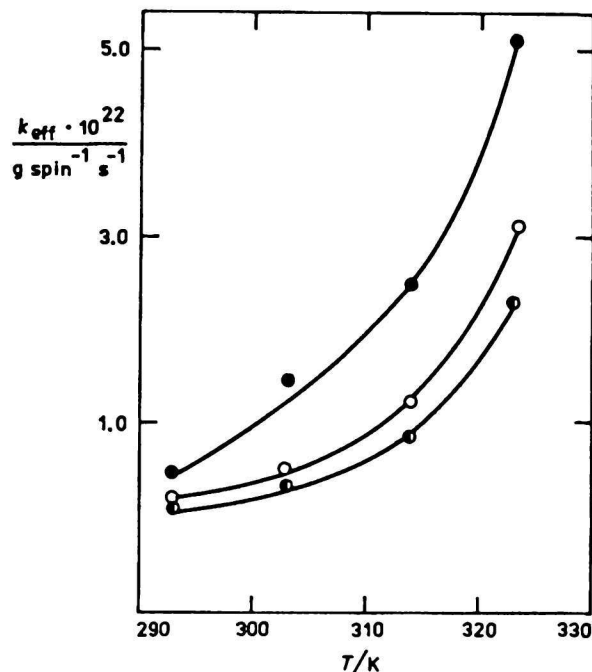

Fig. 3. Temperature variation of the rate constant for allyl decay in chemically crosslinked PE with gel content in mass %: ● 21.8, O 57.4, ◐ 89.4.

activation energy, it is reasonable to assume for the series of samples: $E(gel) \approx E_{eff}\ (w(gel) = 0)$. This assumption has been motivated by the fact that $k_{o,eff}$ and E_{eff} have acceptable values in the reference sample. Application of eqns (2) and (3) for mean temperature $\overline{T} = 308$ K leads to a decrease of k_o with increasing crosslinking. It evidently reflects the effect of increasing steric hindrances on the transport of allyl centres (Table 3). Results from this approximative analysis of Arrhenius parameters E_{eff}, $k_{o,eff}$ point to the validity of the hypothesis on the decrease of true activation energy with temperature and to the influence of the structural transformation on the decay of allyls in chemically crosslinked PE.

DSC analysis helps elucidate many features of temperature dependences of the effective rate constants for the decay of allyl macroradicals. Table 1 summarizes the temperatures of melting: the initial $T_{m,i}$ and the peak $T_{m,p}$, respectively. The values of both quantities evidently decrease with the increasing gel content. A comparison of Fig. 3 with Table 1 may lead to the following results. In the case of reference and low-crosslinked sample, the temperature interval of kinetic measurements covers the region of temperatures below and near $T_{m,i}$. On the other hand, for high-crosslinked samples, as follows from a comparison of the temperature intervals, the acceleration of the decay of allyls correlates with the onset of the melting of the crystalline regions in semicrystalline matrix. It is thus the transformation of

the crystalline phase to the amorphous one that speeds up the transport of allyl centres during their decay. This DSC evidence supports conclusions following from both interpretations of Arrhenius parameters. From a microscopic point of view it means that at temperatures 313 K and 323 K the phase transformation, *i.e.* the decay of crystallites increases the molecular mobility in the matrix. Consequently, the rate of migration of allyl macroradicals is in their decay reaction enhanced.

On the basis of the present results from the study of the decay of allyls in chemically cross-linked PE, we can state that this reaction próceeds dominantly in amorphous regions and is affected by crosslinking and by the course of phase transition.

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Determination of Arsenic in Soils by Cathodic Stripping Voltammetry

D. RÚRIKOVÁ and A. BEŇO

Department of Analytical Chemistry, Faculty of Natural Sciences, Comenius University, CS-842 15 Bratislava

An analytical procedure has been developed for determination of low contents of As in soils by the cathodic stripping voltammetry method using HMDE. Arsenic was determined after $AsBr_3$ extraction from the medium of 11.5 M-H_2SO_4, 0.05 M-NaBr, and 0.002 M-$NH_2NH_2 \cdot H_2SO_4$ into toluene and back-extraction into the solution of 1.5 M-HCl and 0.03 M-$NH_2NH_2 \cdot H_2SO_4$. Optimum procedure for decomposition of the soil sample and for separation of As from the interfering components as well as optimum conditions for electrochemical determination itself were investigated. Deposition of As on HMDE was achieved in the presence of Cu(II) by electroreduction in the form of intermetallic compounds from the medium of 1 M-HCl, 0.02 M-NH_2NH_2 H_2SO_4, and 0.0002 M-$CuCl_2$. Concentration of As was evaluated by the method of standard additions on the basis of the signal arising on reduction of As to AsH_3. The developed procedure is simple as to the number of operations preceding the determination itself and reliable, as evidenced by low values of relative standard deviations (1.1 to 3.2 %) and by the results of analyses of standard materials.

For determination of trace amounts of inorganic components in real samples of various origin, beside atomic spectrometry also differential pulse polarography and stripping voltammetry are used, the latter enabling *in situ* preconcentration of the component to be determined. In polarographic and voltammetric determinations in common base electrolytes only As(III) provides a signal. Therefore, when determining total amount of As in samples, it is necessary to reduce the inactive As(V) to electroactive As(III). This may be achieved by using various reductants ($NaHSO_3$, Na_2SO_3, $NH_2NH_2 \cdot H_2SO_4$, Cu(I) in concentrated HCl, *etc.*) and procedures. The reductant should be chosen so that its excess or the by-products of the reduction reaction might not interfere with the determination of As.

In voltammetric determinations As(III) is deposited by electroreduction mostly on solid electrodes, *e.g.* Au [1], Au film [2—4], graphite [5—7], and Pt [1, 8, 9], and the anodic polarization curves are evaluated. Insolubility of As in Hg means a limited use of the hanging mercury drop electrode (HMDE). The presence of Cu(II) [10—12] or Se(IV) [13] in the base electrolyte brings about a noticeable increase of the preconcentrating factor as a