ESR and DSC Study of the Radiation Crosslinking Effect on Macroradical Decay in Poly(vinylidene Fluoride)

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Synopsis

The decay of polyenyl macroradicals in irradiated poly(vinylidene flouride) and its dependence on radiation crosslinking was studied by the ESR method. The decay rate constants were found to decrease in the lower temperatures region but they show some anomaly at higher temperatures with respect to radiation dose. Temperature dependences of kinetic constants are correlated with thermodynamic parameters from DSC measurements and are interpreted as a result of the steric hindrances changes on molecular mobility due to structural changes caused by radiation crosslinkings and phase transition in a semicrystalline matrix.

INTRODUCTION

A study of complex mechanisms leading to the decay of macroradicals in solid polymers is one of the actual problems in the field of the reactivity in the solid phase. It provides information about physical and chemical processes which ensure migration of free valences. The information is important for the processes of aging, stabilization, and modification of polymers.

Arrangement and dynamics of macromolecules belong to the most important factors affecting the course of decay process of free radicals. These may be changed by the presence of crosslinking from radiation[1] or chemical[2-5] sources.

Poly(vinylidene flouride) (PVDF) belongs to a group of polymers modified in a commercial scale by radiation crosslinking.[6] The complex examination of radiation-chemical effects in PVDF showed that the crosslinking proceeds mainly through alkyl macroradicals.[7] Allyl and polyenyl macroradicals formed simultaneously under irradiation are relatively stable at room temperature.[8-10]

The aim of this paper is to find the influence of radiation-induced crosslinking on the reactivity of macroradicals, especially of polyenyl type in PVDF during the decay.

EXPERIMENTAL

Poly(vinylidene fluoride), Solef 1010, homopolymer with $M_w = 1.46 \times 10^5$, 4.5% head-to-head defects, $T_g = 228$ K, $T_c = 423$ K was used. A foil 0.55 ± 0.15

mm thick prepared from this polymer on the apparatus Brabender at 463 K was cooled in room temperature in air.

The irradiation of the foils was performed at an electron accelerator with electron energy of 4 MeV, always with 50 kGy dose per one passage in air at 298 K. The gel content in mass percent was determined by extraction in dimethyl sulfoxide at 348 K.

The thermal characteristics of crosslinked PVDF samples were obtained on a Perkin-Elmer DSC-1B. Relatively high rate of heating $\phi_h = 32°C/min$ was used for suppressing reorganization and recrystallization processes during the dynamic-temperature regime.

ESR spectra were recorded on a Varian E-4 spectrometer. Kinetic measurements of free radical decay were done over the temperature interval between 353 and 423 K using the temperature equipment E-257. Concentrations of macroradicals were obtained on a Varian computer.

RESULTS

The PVDF samples were irradiated at 298 K in air, radiation doses ranging between 0.10 and 0.98 MGy. Gel and thermal characteristics of these irradiated samples are in Table I. Figure 1 shows the ESR spectra of macroradicals in the samples of irradiated PVDF registered at 298 K after irradiation. At lower doses (to 0.3 MGy) the spectra have the shape similar to the type in Figure 1(a). After irradiation at 0.309 MGy the spectrum is composed by superposition of allyl and polyenyl macroradicals in comparable ratios. In the region of higher doses (from 0.4 MGy) the ESR spectra are similar to the types Figure 1(b), resp. 1(c), where the singlet spectrum of polyenyl macroradicals dominates. The comparison of these spectra with the results from the paper[10] dealing with the identification of the kinds of macroradicals in radiolyzed PVDF shows that the allyls not only grow with radiation dose at a slower rate than polyenyls but are less stable and disappear during short heating at 343 K as well.[9] Figure 2 shows the ESR spectra of the dominating polyenyls in irradiated PVDF at radiation dose 0.610 MGy and as is evident they persist at the higher temperatures. The spectra show that although both irradiation and ESR measurement of PVDF samples were carried out in air,

TABLE I
Gel Fraction and Temperatures of the Endotherms
of Melting as Function of the Irradiation

D (MGy)	Gel fraction (wt %)	$T_{m,i}$[a] (K)	$T_{m,p}$[a] (K)
0	0	389	445
0.101	0	388	444
0.309	35.0	388	442
0.406	57.5	385	441
0.610	69.9	382	439
0.819	76.0	380	437
0.982	77.3	379	435

[a] $T_{m,i}$ = initial temperature of the endotherm of melting; $T_{m,p}$ = temperature of the melting peak endotherm.
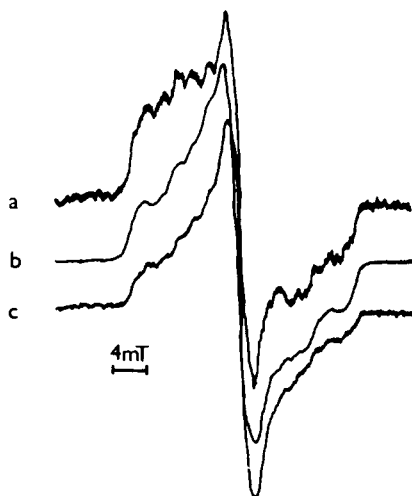
Fig. 1. ESR spectra of macroradicals in irradiated PVDF recorded at 298 K for radiation doses (MGy): (a) 0.309; (b) 0.610; (c) 0.982.
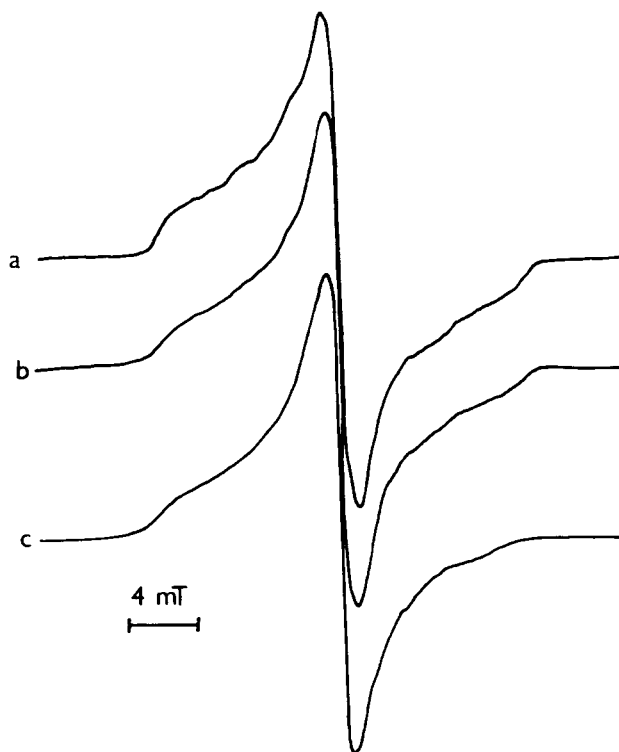

Fig. 2. ESR spectra of macroradicals in irradiated PVDF with radiation dose 0.610 MGy recorded at temperatures (K): (a) 343; (b) 353; (c) 363.
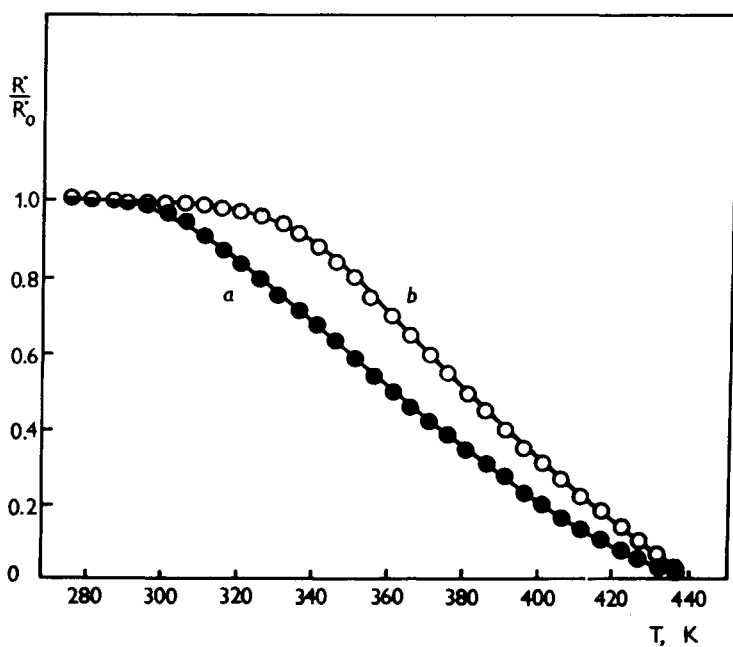
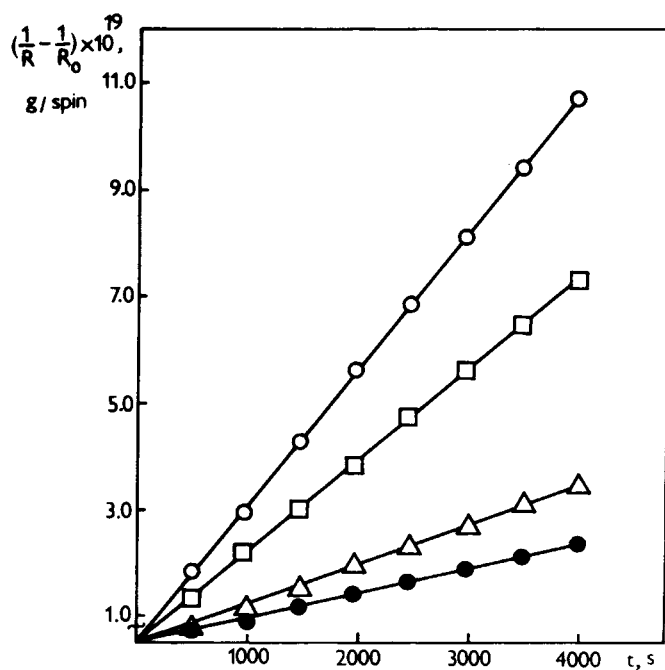Fig. 3. Decay curves for macroradicals in irradiated PVDF for radiation doses (MGy): (a) 0.406; (b) 0.982.

Fig. 4. Test of the second-order kinetics for 373 K in a series of irradiated PVDF samples for radiation doses (MGy): (○) 0.406; (□) 0.610; (△) 0.819; (●) 0.982.
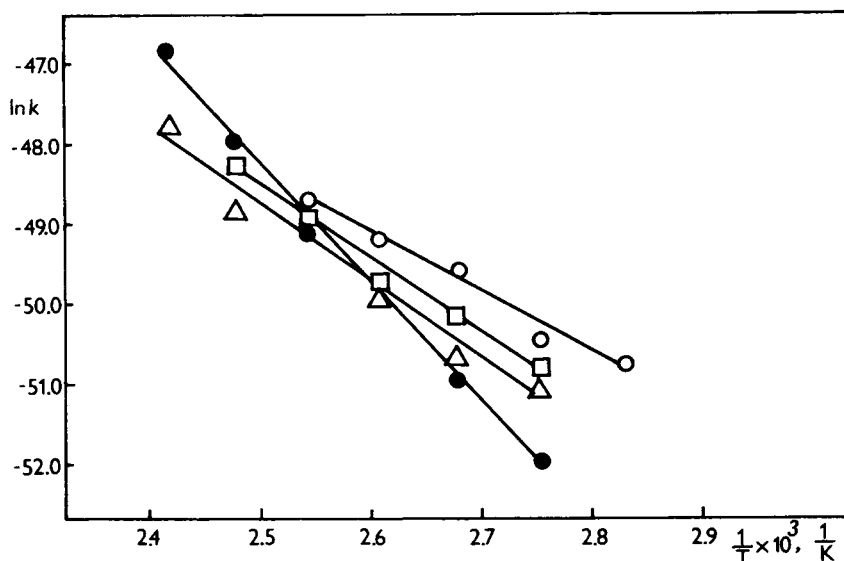
Fig. 5. Temperature variations of the rate constants for macroradical decay in irradiated PVDF in coordinates of Arrhenius equation for radiation doses (MGy): (○) 0.406; (□) 0.610; (△) 0.819; (●) 0.982.

no signal of peroxide macroradicals was observed. Consequently, PVDF resembles more polyethylene where ROO˙ center decays at a lower temperature[11] than polytetrafluoroethylene where peroxide macroradicals are very stable.[12] This fact is probably connected with the possibility of hydrogen abstraction in PVDF in contrast to PTFE; with the course of consecutive reaction during radiolysis as well as with great differences in T_g temperatures of the particular polymers ($T_{g,\,PE}$ = 203 K, $T_{g,\,PVDF}$ = 228 K, and $T_{g,\,PTFE}$ = 403 K).

Figure 3 shows curves for the decay of all macroradicals in the two limiting samples where polyenyls dominate. Each point on the curves represents the number of macroradicals which survived gradual thermal processing 15 min at each temperature.

The decay of macroradicals depends generally on the chemical structure of centers and external factors including physical conditions of the decay process. To determine the constancy of the chemical factor, we used the fact that allyl centers are less stable than polyenyl centers. For this reason detailed kinetic measurements were done in the temperature interval between 353 and 423 K for radiation doses from 0.4 to 1.0 MGy. Figure 4 shows the test of the

TABLE II
The Kinetic Parameters of the Decay of Polyenyl Macroradicals in Crosslinked PVDF

D (MGy)	T (K)	$k_{0,\,eff}$ (g/spin s)	E_{eff} (kJ/mol)	k_0 (g/spin s)
0.406	353–403	1.53×10^{-13}	62.6	1.53×10^{-13}
0.610	353–413	6.69×10^{-12}	75.8	1.18×10^{-13}
0.819	363–423	2.91×10^{-11}	81.4	0.93×10^{-13}
0.982	363–423	2.89×10^{-5}	125.5	1.26×10^{-13}

second-order kinetic for the representative temperature 373 K for a series of four radiation doses.

Figure 5 illustrates the temperature dependences of the rate constants in coordinates of Arrhenius form and the parameters $k_{0,\text{eff}}$ and E_{eff} are summarized in Table II.

DISCUSSION

The decay curves from Figure 3 deliver following information. First, it is obvious that there are differences in the course of curves within the low temperature region. They consist in different beginnings of the relative steep decrease in the number of macroradicals (at 0.406 MGy at ca. 303 K vs. 0.982 MGy at ca. 333 K) and consequent shift of the curve b with respect to higher temperatures with the increasing radiation dose. This phenomenon is evidently conditioned by the dominant effect of radiation crosslinking of the amorphous phase on the stability of macroradicals at low temperatures (see Table I, column 2). On the other hand, at higher temperatures near T_m we can observe gradual approach of both curves and finally, at about 438 K both curves coincide. At this temperature, macroradical centers in both samples completely disappear. After considering thermal parameters $T_{m,i}$ and $T_{m,p}$ it is obvious that in the high-temperature region the phase transition of the crystalline phase to the amorphous state contributes to the decay of radical centers (see Table I, columns 3 and 4).

Kinetic data may be discussed either in view of rate constants k (in temperature, dose) or after Arrhenius expression of the rate constants in terms of the effective preexponential factors $k_{0,\text{eff}}$ and effective activation energies E_{eff}.

The first approach represented by Figure 5 shows different courses of $\ln k = f(1/T)$ with the radiation dose. At lower temperatures, when the doses are 0.41–0.82 MGy, the decay rate constant of polyenyl macroradicals increases with temperature. However, at higher temperatures the decay of polyenyl macroradicals accelerates in the sample irradiated to the maximum dose. These facts might be connected with the course of the two phenomena.

The first might be the decomposition reaction of ROOH at high temperatures. These reactants might be formed by binding the molecule O_2 to polyenyl center R˙ accompanied by the temporary formation of ROO˙ centers transformed to ROOH products with relatively short lifetime at higher temperatures. As long as this complex process is decisive, the kinetics of free-radical decay should be of pseudomonomolecular character with respect to polyenyls. The validity of the second-order kinetics for the decay of polyenyls shows that this decay process is not the dominant one.

The second explanation is based on the correlation of kinetic and thermodynamic results. At a particular temperature of the lower temperature region between 353 and 383 K, the rate constant decreases with radiation dose throughout the range of doses. Table I and Figure 7 show that regions of linear rise of the decay rate constants with temperature between radiation doses 0.41 and 0.82 MGy and the steep increase at 0.98 MGy belong to the areas of initial lines of DSC thermograms, i.e., below $T_{m,i}$. The decay of polyenyls takes mostly place in the amorphous zones of PVDF matrix at low
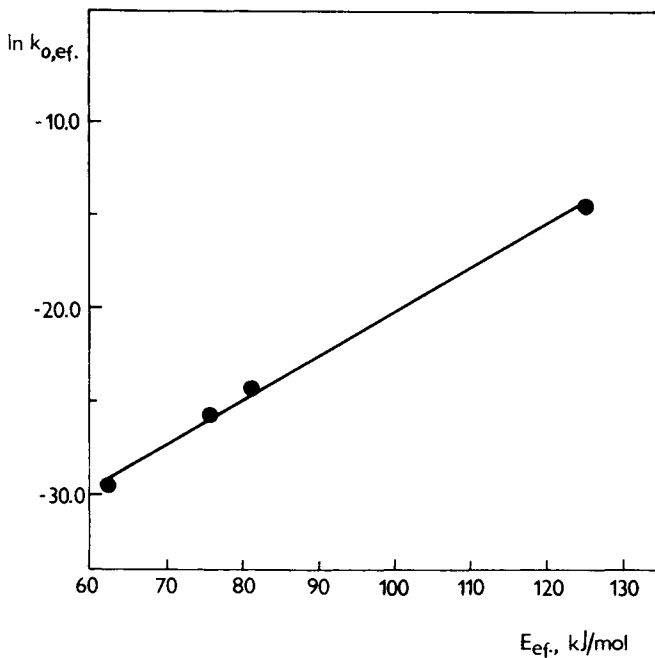
Fig. 6. The dependence of effective kinetic parameters for macroradical decay in crosslinked PVDF.

temperatures. A decrease in rate constants with the increasing radiation dose reflects either the increasing hindering influence of radiation-induced crosslinkings in polymer amorphous regions on the physical migration of polyenyls through molecular motions or/and the rising steric hindrances in the final stage of the decay process.

At the particular temperature in the region of the temperatures above 383 K, the sequence of the rate constants for polyenyl decay remains constant except for the maximally crosslinked sample. The decay of polyenyls is more rapid in this system than in other less crosslinked PVDF samples. A comparison of these temperature regions with DSC thermograms shows their overlaps with endotherms of melting the crystalline phase in the irradiated PVDF samples. The higher reactivity of polyenyls at higher temperatures correlates with phase transformation of the crystalline phase which, at the same time, leads to a release of steric hindrances or/and to an increase in the mobility of chains in the migration stage of decay. Changes in kinetic constant for free-radical decay are thus associated with the changes in endotherms of melting with radiation dose.

The reasons may be explained by the model of melting of lamellar crystallite[13] and concept of melting of the distribution of lamellar crystallites.[14] Accordingly, the decrease of $T_{m,p}$ and $T_{m,i}$ with radiation does is caused by raising the surface energy of lamellas in relatively wide distribution of the crystallite size under the effect of radiation crosslinking as well as increasing imperfection of crystalline regions.[15] On this ground, the enhanced rate of the decay of macroradicals followed is considered to be conditioned by melting of
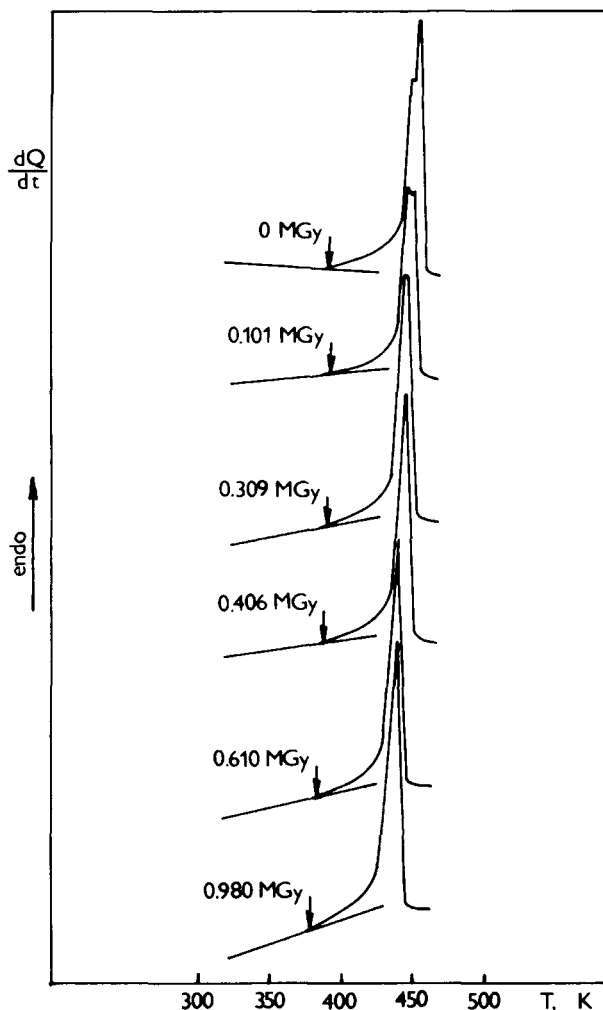
Fig. 7.   DSC thermograms of irradiated PVDF for radiation doses (MGy).

smaller crystallites and the decrease of thermodynamic parameters and the increase of rate constants to be controlled by the same factors. In other words, the increased concentration of chemical crosslinkings together with the increased possibility of the occurrence of radiation defects of physical and chemical nature in the crystalline phase lower the melting temperature and, consequently, increase the rate of the decay of polyenyls.

It follows from the second way of interpretation of kinetic parameters based on the application of the Arrhenius equation that the values of $k_{0,\mathrm{eff}}$ and E_{eff} increase with radiation dose. At the radiation doses between 0.41 and 0.82 MGy both parameters increase rather slowly; $k_{0,\mathrm{eff}}$ reaches reasonable values (after correction with the value $\rho = 1.74$ g/cm^3) in comparison with the typical values of radical reactions in the gas and liquid phases (10^{-15}–10^{-10} cm^3/s). On the other hand, an anomalous high value $k_{0,\mathrm{eff}}$ was found in the maximally irradiated PVDF sample. We expect that with the growing concen-

tration of the crosslinking of the matrix, of course, depending on crosslinking density, with the increasing steric hindrances and limited mobility the preexponential factor should remain the same or decrease and the activation energy should remain constant or should increase. In fact, not only E_{eff} but also $k_{0,eff}$ rise and, moreover, both parameters are in linear relationship typical of the compensation effect (see Fig. 6). The essence of the anomalous value of $k_{0,eff}$ and trend of both parameters as well as the existence of the compensation effect can be explained as follows. We can here apply Lebedev's approach[16] with regard to the character of the reaction system and conditions; this approach assumes the temperature dependence of the true activation energy, i.e., it varies with the increasing temperature in the region of phase transition.

The suitability of the application of this interpretation is also supported by DSC measurements. These indicate that the decay of polyenyls proceeds near the region of melting of the arranged regions in PVDF. Relations between the experimentally found apparent effective activation energy and the apparent effective preexponent and their true values E and k_0 are[16]

$$E_{eff} = E - T(\Delta E/\Delta T) \tag{1}$$

$$k_{0,eff} = k_0 \cdot e^{-1/R \cdot (\Delta E/\Delta T)} \tag{2}$$

For a strict application of these equations we have to know the true value of E, which is impossible. Therefore, for the verification of the above-mentioned concept and for the estimate of true values of k_0 we introduce the assumption. Let the true activation energy be approximately equal to the effective activation energy for the decay of polyenyls in minimally irradiated PVDF sample $E \doteq E_{eff(0.4\,MGy)}$. This assumption is supported by the fact that in this system $k_{0,eff}$ and E_{eff} reach reasonable values in view of their physical acceptability. The application of eqs. (1) and (2) for $\bar{T} = 393$ K leads to reasonable values of k_0, especially for maximally irradiated PVDF sample (see Table II). The true value of activation energy E would rather increase with the increased radiation dose. The results from this approximate analysis of kinetic parameters for decay indicate the validity of the assumption on slight decrease of the true activation energy for the decay of polyenyl macroradicals with temperature $\Delta E/\Delta T$ as a result of the course of the structural change. Then this approach provides the reliable argument concerning the effect of the structural change on the course of kinetic decay constants.

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