

Concept of mobile voids in the interpretation of decay of free radicals in solid polymers

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An alternative idea of decay of free radicals in solid polymers based upon a concept of voids existing in each polymer with the mobility induced by the motion of respective polymer segments and vice versa has been put forward taking into account formal reaction kinetics. It has been shown that this approach enables the qualitative interpretation of second-order decay, stepwise decay of free radicals initiated by a stepwise increase of temperature as well as the effect of high pressure on the overall rate constant of the decay process.

(Keywords: mobile voids; free radicals; solid polymers)

INTRODUCTION

The kinetics of decay of free radicals generated in a polymer matrix is usually interpreted in terms of the second-order equation

$$1/[R] - 1/[R]_0 = k't$$

where t is the time, $[R]_0$ and $[R]$ are the concentrations of the decaying radicals at time zero and time t and k' is the second-order rate constant. Although the second-order decay fits the experimental observations in numerous cases^{1,2}, there are exceptions to such kinetics. It has not, for example, been clarified whether deviation from second-order kinetics results from a peculiarity of the diffusion-controlled process of free-radical decay or from the mechanism of recombination itself. The solution proposed by Grozdic *et al.*² assumes that, in a mixture of free radicals generated in a polymer matrix by gamma irradiation, some recombine according to a bimolecular mechanism while others move by a first-order process to locations in the solid polymer where they cannot react at a given temperature.

In studies by Tiño *et al.*³⁻⁵, free radicals statistically dispersed in a solid polymer were subjected to the motion of segments carrying the radical site and the theoretical decay in concentration of radicals governed by such a process was investigated. Several types of radical chain motion were shown to exist for a free-radical decay, namely crank, crankshaft and kink⁶. Such a model based on a Monte Carlo simulation was performed on a computer and corresponding curves of free-radical decay were thus constructed and compared with experimental results.

In the present paper, a formal kinetic approach has been used for the interpretation of the kinetics of free-radical decay connected with the concept of mobile voids as reacting particles. This approach enables a simple interpretation of most aspects of free-radical decay in solid polymers, for example, variability in the formal

reaction order, the existence of a stepwise decay and the effect of high pressure on the stability of the relevant types of radicals.

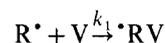
EXPERIMENTAL

Experimental measurements of free-radical decay in gamma-irradiated samples of poly(vinyl acetate) have been performed using an e.s.r. spectrometer Varian E 4 working in the 3 cm band (9.5 GHz). The overall dose of radiation was 6 kGy, the temperature of irradiation 77 K. Irradiated samples were kept in liquid nitrogen.

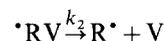
The system of differential equations modelling the decay of free radicals has been solved on a personal computer using the Runge-Kutta method of the fourth order.

RESULTS AND DISCUSSION

The mobile void should be understood as a free space, the size of which is determined by the state of the polymer matrix, which renders some degree of motional freedom to polymer segments. The motion of polymer segments enables the void to move a given distance. In a formalism which we develop further we assume that mobile voids V in a polymer behave as reacting particles, the physical catalysts of free-radical decay. Their overall amount can then be expressed in concentration units and will depend on temperature. When encountering the migrating void, free radicals R^* which are originally immobilized in a polymer matrix:



can migrate with it through the polymer together as a moiety *RV in which a radical site is considerably more mobile. Due to fluctuations of the segmental motions the void may abandon these radicals



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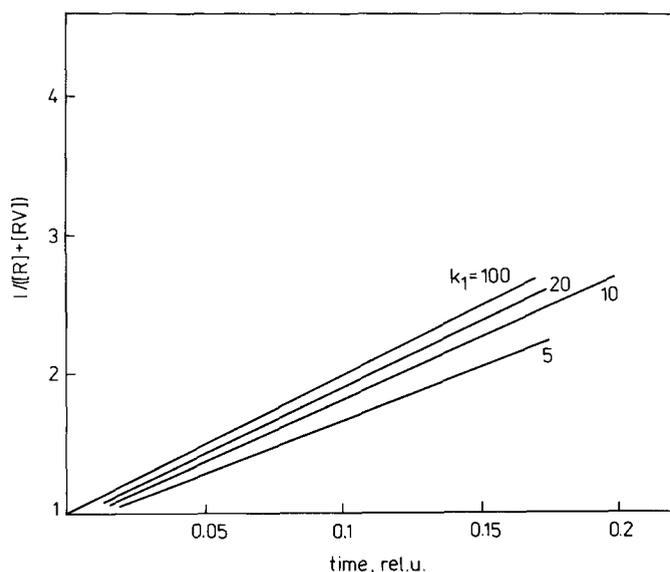


Figure 1 Plot of reciprocal value of concentration of free radicals versus time for decay of free radicals according to the model represented by equations (1)–(3) for different values of k_1 . ($[V]_0 = 5$, $[R]_0 = 1$, $k_2 = 1$, $k_3 = 5$, $k_4 = 5$ RU)

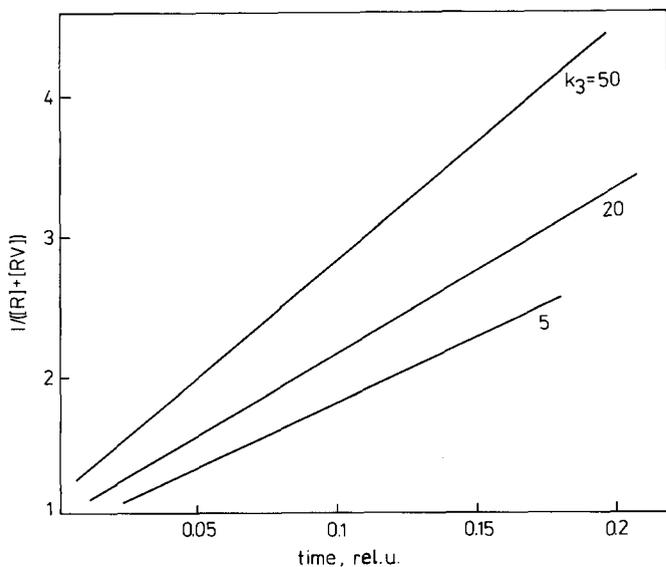
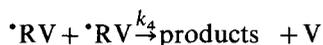
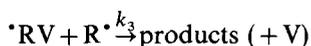


Figure 2 Plot of reciprocal value of concentration of free radicals versus time for decay of free radicals according to the model represented by equations (1)–(3) for different values of k_3 . ($[V]_0 = 5$, $k_1 = 10$, $k_2 = 1$, $k_4 = 5$ RU)

which lose mobility, and the probability of encountering another radical R^* is thus reduced. The decay of free radicals may take place only when the collision of *RV with R^* radicals or two *RV particles occurs.



The idea has been put forward that whenever free radicals in moieties *RV disappear by combination, a mobile void disappears, too, because of the formation of a new bond. On the other hand, if disproportionation is a prevailing route of free radical termination, the concentration of mobile voids remains constant; if

radicals R^* undergo fragmentation, the concentration of mobile voids increases.

The differential equations describing the rate of free-radical decay and the change of concentration of mobile voids are:

$$d[R^*]/dt = -k_3[^*RV][R^*] + k_2[^*RV] - k_1[R^*][V] \quad (1)$$

$$d[V]/dt = -k_1[R^*][V] + k_2[^*RV] + k_4[^*RV]^2 \quad (2)$$

$$d[^*RV]/dt = k_1[R^*][V] - k_2[^*RV] - k_3[^*RV][R^*] - 2k_4[^*RV]^2 \quad (3)$$

The rate of free radical disappearance is then expressed by the sum of the rates of equations (1) and (3).

For the selected set of parameters, such that the initial concentration of mobile voids (in relative units (RU)) $[V]_0 = 5$ RU, the initial concentration $[R]^*$ of free radicals was equal to 1 RU, $[RV]_0 = 0$, and given rate constants k_1 , k_2 , k_3 and k_4 , the graphical representation of free-radical decay plotted in coordinates $1/([R] + [RV])$ versus time is shown in Figures 1, 2 and 3.

It may be seen that for a given set of parameters, the agreement with the second-order fit appears to be rather good except for the start of the process, where deviation from the straight line can be observed. It is not, however, difficult to find the parameters for which the second-order fit can be successfully applied throughout the whole time interval investigated (Figures 1 and 2). Within given parameters, the most significant effect on the rate constant k' of free-radical decay, which is identical with the slope of a plot $1/([R] + [RV])$ versus t , can be observed for the constant k_4 (Figure 3).

Stepwise decay of free radicals at low temperatures

Let us assume that the concentration of free voids is lower than the initial concentration of free radicals. When all mobile voids are consumed in the recombination reaction, the concentration of free radicals is not zero, but attains a new lower level. Decrease of free radicals can be reinitiated by the introduction of an additional amount of mobile voids into the polymer due to, for example, an increase of temperature. In such a way,

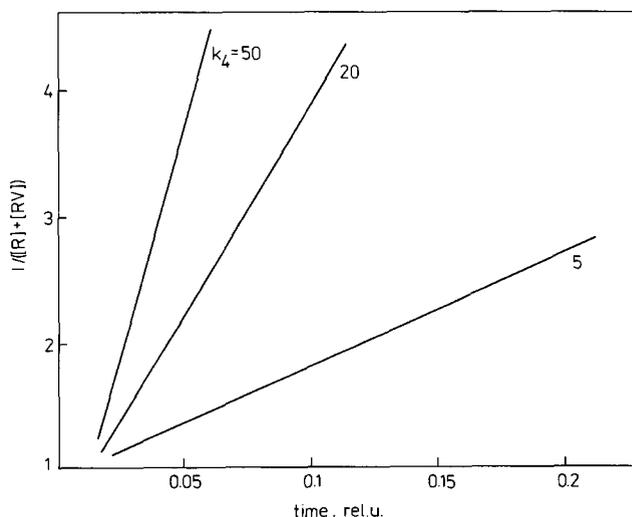


Figure 3 Plot of reciprocal value of concentration of free radicals versus time for decay of free radicals according to the model represented by equations (1)–(3) for different values of k_4 . ($[V]_0 = 5$, $[R]_0 = 1$, $k_1 = 10$, $k_2 = 1$, $k_3 = 5$ RU)

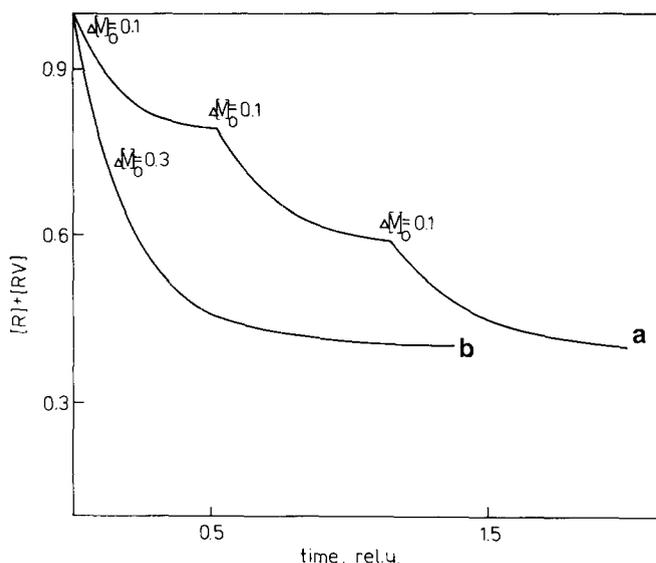


Figure 4 Stepwise decay of free radicals described by equations (1)–(3) for regular increments of a mobile void concentration $[V]$ indicated by respective relative units (curve a). Curve b represents a decay for initial mobile void concentration corresponding to the sum of the increments of curve a. ($[V]_0 = 0.1$, $[R]_0 = 1$, $k_1 = 10$, $k_2 = 10$, $k_3 = 50$, $k_4 = 5$)

Table 1 The concentration changes with temperature of free radicals generated in gamma-irradiated poly(vinyl acetate)

Time (s)	$[R] \times 10^{-15}$ (spins g^{-1})				
	30°C	40°C	50°C	60°C	70°C
0	0.924	0.760	0.507	0.301	0.145
180	0.904	0.712	0.474	0.279	0.134
360	0.897	0.693	0.453	0.259	0.125
540	0.883	0.669	0.431	0.242	0.113
720	0.864	0.647	0.410	0.225	0.104
900	0.856	0.625	0.377	0.208	0.095
1080	0.839	0.604	0.356	0.194	0.087
1260	0.828	0.582	0.342	0.180	0.081
1440	0.820	0.561	0.321	0.167	0.073
1620	0.814	0.550	0.302	0.153	0.069
1800	0.792	0.535	0.284	0.145	0.060

several steps can be observed on the curve of the free-radical decay, as shown on *Figure 4*. This is in accordance with experiments with free radicals in the poly(vinyl acetate) matrix where the temperature of the polymer was increased stepwise which initiated a stepwise decay of free radicals, as can be seen in *Table 1*. The existence of stepwise decay is also reported in the literature⁷.

In a model calculation, when the concentration of mobile voids increased to a final level in one step, there is also a one-step decay of free radicals ending at a level obtained by several subsequent steps (*Figure 4*). Regardless of the fact that in model calculations the level of free volume was increased by regular increments, the qualitative agreement with experiment is obvious. In a respective polymer matrix, the largest increments of mobile void concentration are expected at around the phase transition temperatures. Of interest may be the estimation of rate constant k' for each of the simulated steps of a free-radical decay; it increases linearly with decreasing level of initial concentration of free radicals $[R]_0$ (*Figure 5*). A twofold change of $[V]_0$ by 0.1 RU for

an initial value of free-radical concentration $[R]_0 = 1$ RU gave new equilibrium levels of $[R]$, namely 0.8 and 0.6 with the constants k' given in *Table 2*.

The value of k' for $\Delta[V]_0 = 0.3$, representing a one-step increase of concentration of mobile voids, indicates that there exists a tendency towards the additivity of rate constants k' according to the overall magnitude of concentration of mobile voids being available for several steps of the decay process. In the case of a stepwise decay of poly(vinyl acetate) radicals, the decline from linearity of the plot k' versus $[R]_0$ may be considered as being due to non-linear temperature dependence of mobile void concentration (*Figure 5*). As in previous cases, the values of k' were calculated from $1/([R] + [RV])$ versus t plots for data of the respective decay steps presented in *Table 1*.

The effect of high pressure on decay of free radicals in polymers

For a series of polymer free radicals generated chemically or by irradiation, the beneficial effect of high

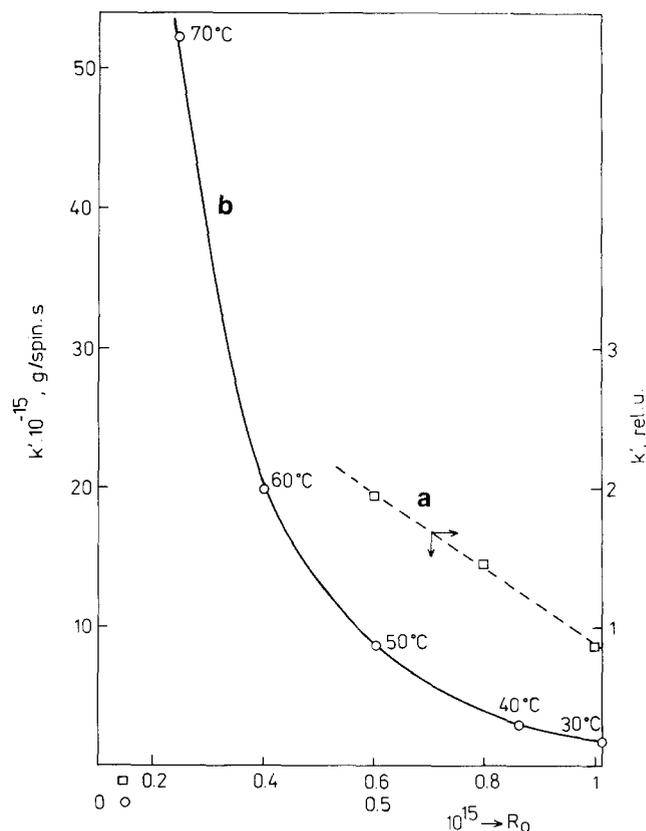


Figure 5 Plot of second-order rate constant k' against initial concentration of free radicals R^* . Curve a represents the stepwise decay shown in *Figure 4*, curve b the experimental decay of free radicals in irradiated poly(vinyl acetate)

Table 2 Dependence of rate constant k' on free radical concentration, $[R]_0$

$\Delta[V]_0$ (RU)	$[R]_0$ (RU)	k' (RU)
0.1	1	0.855
0.1	0.8	1.459
0.1	0.6	1.920
0.3	1	3.69

RU, relative units

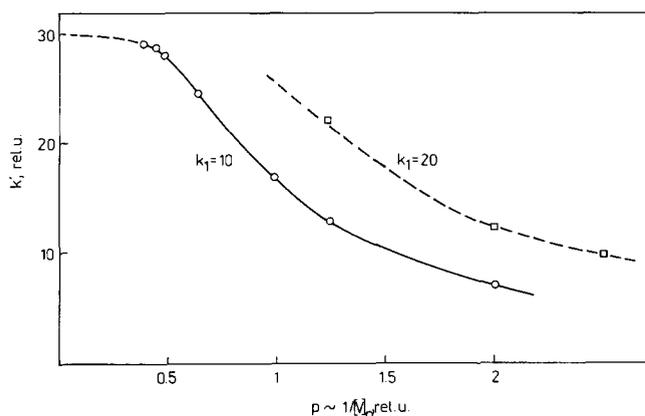


Figure 6 Pressure dependence of constant k' of free-radical decay for equations (1)–(3) ($k_2=10$, $k_3=50$, $k_4=5$, $[R]_0=1$)

pressure on their stability has been reported. The substantial reduction of concentration of mobile voids due to high pressure can explain this observation on a purely kinetic basis. According to the equation of state, the concentration of mobile voids in a polymer sample is inversely proportional to the pressure. When applying sufficiently high pressure, this concentration is reduced so that a considerably lower rate constant of free-radical decay is obtained and the stability of free radicals in a polymer matrix is thus apparently higher (Figure 6). It is also evident that free radicals which undergo fragmentation should be considerably less stabilized by increased pressure than free radicals which simply combine in the termination process, which corresponds to the fact that fragmentation of free radicals can act as a potential generator of mobile voids.

An examination of the dependence of decay constant k' on $1/[V]_0 \approx p$ on a linear scale yields qualitatively the same plot as was observed, for example, for the case of decay of free radicals in polycarbonate⁸, poly(vinyl

acetate)⁹, polyamide¹⁰ and other polymers. It may be of interest that at low pressures the plot exhibits some saturation of k' values, a fact which was not found experimentally. This flattening of the curve, however, appears to be quite obvious, indicating that an important increase of free-radical stability can be attained only when a sufficiently high pressure is applied to the polymer. Only sufficient pressure applied to the condensed matrix of a polymer allows for a reduction of the mobile void concentration to a level corresponding to the initial concentration of free radicals.

CONCLUSIONS

The kinetic approach based on a more or less restricted motion of voids induced by the segmental motion existing in a polymer matrix gives a supplementary view on the formalism of the free-radical decay in solid polymers. A migration of voids and the molecular motion of a radical centre attached to such voids leading to the disappearance of free radical sites does not require any particular assumption about the types of molecular motion. The latter are averaged in the values of the respective rate constants.

REFERENCES

- 1 Dole, M. *J. Phys. Chem.* 1987, **91**, 3117
- 2 Grozdic, N., Basheer, R., Mehta, M. and Dole, M. *J. Phys. Chem.* 1981, **85**, 1536
- 3 Tiño, J., Urban, J. and Klimo, V. *Chem. Papers* 1990, **44**, 711
- 4 Tiño, J., Urban, J. and Klimo, V. *Polymer* 1989, **30**, 2136
- 5 Tiño, J., Urban, J. and Klimo, V. *Chem. Papers* 1992, **46**, 154
- 6 Bartoš, J. and Tiño, J. *Polymer* 1984, **25**, 274
- 7 Emanuel, N. M. and Buchachenko, A. L. 'Chemical Physics of Ageing and Stabilization of Polymers', Nauka, Moscow, 1982 (in Russian)
- 8 Plaček, J., Szocs, F. and Borsig, E. *J. Polym. Sci., Polym. Chem. Edn* 1976, **14**, 1549
- 9 Szocs, F. and Rostašová, O. *J. Appl. Polym. Sci.* 1974, **18**, 2529
- 10 Szocs, F., Tiño, J. and Plaček, J. *Eur. Polym. J.* 1973, **9**, 251