

# Decay of Free Radicals in Irradiated PMMA at High Pressures Studied by ESR

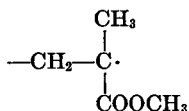
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## Synopsis

The decay of free radicals in irradiated PMMA subjected to high pressures has been studied by the method of ESR. The rate constants and activation energies has been determined for the decay of free radicals at the pressures of 5000 and 10,000 atm over the temperature range of 100–170°C. It has been found that the rate of decay was reduced essentially by the effect of high pressure. The mechanism of the decay of free radicals in solid polymers is being discussed. The important influence of the motion of macromolecule segments on the course of radical reactions in solid phase is printed out.

## INTRODUCTION

The first ESR spectrum in irradiated poly(methyl methacrylate) (PMMA) was recorded by Schneider and colleagues<sup>1</sup> in 1950. Further studies were focused mainly on the interpretation of the observed nine-line spectrum. On the basis of further investigations,<sup>2,3</sup> the idea prevailed that the observed nine-line spectrum belonged to a growth radical,



But other types of free radicals are present in a smaller concentration, too, and effect certain changes in the intensity ratio of individual spectral lines during their decay.<sup>4</sup>

Fewer papers are devoted to the study of kinetics of free-radical decay. Ohnishi and Nitta<sup>5</sup> studied the decay of free radicals in PMMA irradiated under vacuum. They reported an activation energy of 28 kcal/mole for the free-radical decay over the temperature range of 25°–55°C. Bresler and co-workers<sup>6</sup> generated free radicals in PMMA by mechanical destruction and determined the rate constants and activation energies for the free-radical decay. They quoted an activation energy of 29 kcal/mole for the temperature region of 60°–100°C under vacuum. They found that the temperature dependence of the rate constant  $k$  did not follow the Arrhenius

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TABLE I  
Rate Constants and Activation Energies of Free-Radical Decay

Pressure, atm	Temperature, °C	Rate constant, cm <sup>3</sup> spin <sup>-1</sup> sec <sup>-1</sup>	Activation energy kcal/mole
1	100	$3.0 \times 10^{-21}$	30
	89	$3.0 \times 10^{-22}$	
	76	$6.0 \times 10^{-23}$	
	60	$1.4 \times 10^{-23}$	
5,000	100	$2.8 \times 10^{-23}$	23
	110	$5.0 \times 10^{-23}$	
	120	$1.0 \times 10^{-22}$	
	130	$3.4 \times 10^{-22}$	
	140	$5.0 \times 10^{-22}$	
10,000	105	$1.0 \times 10^{-23}$	22
	120	$3.2 \times 10^{-23}$	
	130	$6.6 \times 10^{-23}$	
	140	$1.0 \times 10^{-22}$	
	150	$2.8 \times 10^{-22}$	
	155	$4.6 \times 10^{-22}$	

equation exactly and that, in case of free-radical decay, the quoted activation energy applied to a more narrow temperature interval.

The deviations from the law of Arrhenius observed aroused a great deal of discussion. A search was made to find such a mechanism for the free-radical decay which could clear up satisfactorily the anomalies in the kinetics of free-radical decay in the solid phase. Some papers suggested an essential influence of molecular motions on the course of radical reactions in solid polymers.<sup>7</sup> It was also found by the study of the analogous decay of free radicals in PGMA that the rate of free-radical decay was ten times greater in specimens without crosslinking than in crosslinked ones.<sup>8</sup>

All measurements have hitherto been made under vacuum or in inert atmosphere not exceeding the pressure of 1 atm. The decay of free radicals in solid polymers at high pressures, which is the topic of this paper, has not been studied before.

## EXPERIMENTAL

PMMA samples produced by Röhm and Haas, GmbH, under the brand name Plexiglas 233 ( $M_w = 3.10^6$ ) were used for measurements. Their shape was cylindrical, diameter as well as length being 5 mm. They were irradiated with a total dose of 4 Mrad of 1 MeV Van de Graaf electrons at room temperature and under nitrogen.

After irradiation, the ESR spectrum of the samples was recorded. The samples were then subjected to pressure at various temperatures outside the cavity resonator. The pressure device was as follows: A hole with a diameter of 5 mm was bored into the center of an iron cylinder having a diameter of 5 cm. The samples were placed into this hole in a cooled state.

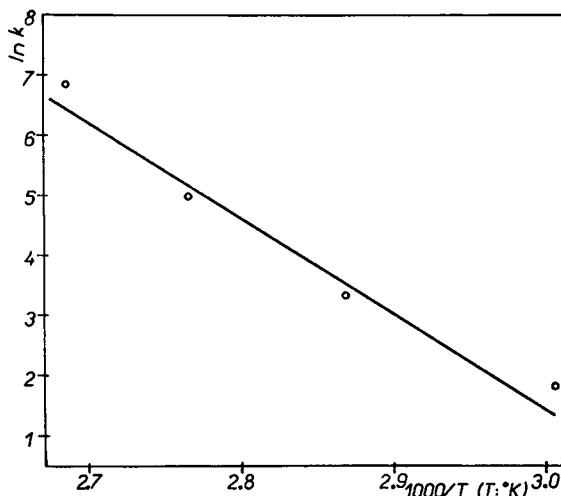


Fig. 1. Variation of  $\ln k$  with  $1/T$  for free-radical decay in irradiated PMMA at 1 atm.

Pressure was applied with a piston of equal diameter. The necessary pressure having been reached, the iron cylinder with sample was quickly heated to the desired temperature and kept at constant temperature and pressure. The cylinder with the sample was in a nitrogen atmosphere. The iron cylinder was then quickly cooled, and after cooling the pressure was released. Then the cooled sample was put into the cavity resonator, and the spectrum was recorded by means of a commercial AEG spectrometer. The change in free-radical concentration due to the transfer of sample was negligible.

During the decay of free radicals, considerable changes in the spectrum take place. The relative intensities of individual lines change, a phenomenon that shall be discussed in a subsequent paper. The results given in this paper refer to the extinction of the nine-line spectrum of growth radical.

## RESULTS AND DISCUSSION

The rate constants and activation energies of free-radical decay at different pressures are given in Table I. The free radicals decay very quickly at temperatures near  $T_g = 108^\circ\text{C}$  when the pressure equals 1 atm. At a pressure of 1 atm and temperature of  $100^\circ\text{C}$ , the rate of decay is more than 100-fold that at  $100^\circ\text{C}$  and 5000 atm. Provided the pressure equals 5000 atm, free radicals can still be observed at  $160^\circ\text{C}$ . If the pressure is raised to 10,000 atm, the decay of free radicals is slowed down so much that the spectrum of free radicals can be recorded even after heating at  $190^\circ\text{C}$ .

The relationship between  $\ln k$  and  $1/T$  at different pressures is presented in Figures 1, 2, and 3. This relationship follows the law of Arrhenius rather well at high pressures. The changes in the modes of molecular motion are probably not so great at high pressures as they are at atmospheric pressure.

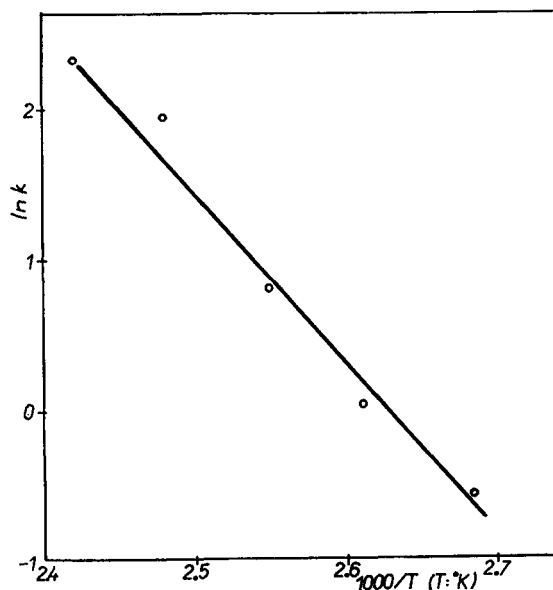


Fig. 2. Variation of  $\ln k$  with  $1/T$  for free-radical decay in irradiated PMMA at 5000 atm.

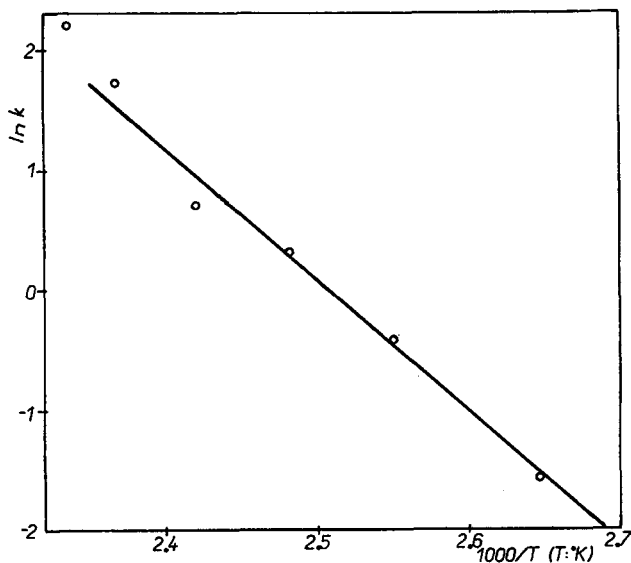


Fig. 3. Variation of  $\ln k$  with  $1/T$  for free-radical decay in irradiated PMMA at 10,000 atm.

The large influence of pressure on the rate of free-radical decay indicates that the decay is due to intermolecular migration of free radicals. The free radicals interact with neighboring segments of the macromolecule, are transferred, and vanish when meeting a partner for combination. It is

obvious that this mechanism is rather sensitive to the changes in segmental motions of the macromolecules. Under high pressure the motions are reduced, which results in a corresponding decrease in free-radical decay.

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