

## Correlation of Molecular Motion and Free-Radical Decay in Irradiated PMMA

### INTRODUCTION

Free-radical decay in poly(methyl methacrylate) (PMMA) has been studied during the past two decades.<sup>1</sup> Rate constants and activation energies were determined over a wide temperature range *in vacuo* and at atmospheric pressure of various gases and vapors. In recent years, papers describing the pressure effect on the kinetics of free radicals have appeared. It has been found that the stability of free radicals depends on the external pressure effect on a polymer.<sup>2,3</sup>

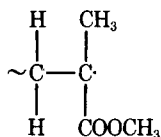
In the present paper, we tried to point to the correlation between molecular motion and kinetics of free-radical decay. The sample chosen for this study is PMMA, with defined dynamic-mechanical and dielectric properties. On this basis, the proper temperature region has been selected to demonstrate the assumed correlation.

### EXPERIMENTAL

The PMMA samples produced by Röhm G.m.b.H., Darmstadt, trade name Plexiglas 233 ( $\bar{M}_w = 3.10^6$ ), were used. The samples 6 mm in diameter and 6 mm in length were prepared by turning, and then  $\gamma$ -irradiated with a total dose of 5 Mrad. The initial spectrum of free radicals was measured at room temperature using an X-band ESR spectrometer. The sample was then transferred to a pressure device,<sup>3</sup> subjected to pressure, heated to the required temperature, and held at this temperature for 30 min. The time of heating and cooling was negligible compared with the time of annealing. Upon cooling the pressure device to room temperature, the pressure was released and the sample was transferred to the ESR spectrometer to record the resultant spectrum. The changes in the intensity of the spectrum during transfer of the sample from the ESR spectrometer to the pressure device and the reverse were negligible. The rate constant for free-radical decay was determined from the difference between the initial and the resultant concentrations of free radicals.

### RESULTS AND DISCUSSION

Before and after annealing of the samples, the well-known nine-line spectrum of PMMA was observed (Fig. 1a). The shape of the spectrum does not change during annealing; its nine-line character is preserved. The considered nine-line part of the spectrum belongs to the end radicals



Besides the mentioned dominating end radicals, the chain radicals<sup>5</sup> also contribute to the observed spectrum (Fig. 1). Their total concentration does not reach 10%. In addition, we observed that the stability of chain radicals, mainly at high pressures, is greater than that of the end radicals.<sup>5</sup> The observed changes in the intensity of the spectrum correspond to the changes in the concentration of the less stable end radicals.

Figure 2 shows the pressure dependence of the rate constant for the end radical decay ( $k$ ) determined according to second-order kinetics. At lower temperatures (50–70 °C),  $k$  is only slightly dependent on pressure. Above 80 °C, strong pressure dependence of  $k$  is observed at low pressures.

Information on physical properties of PMMA employed was obtained from a detailed description by the manufacturer;<sup>3</sup> here, the temperature dependence of the logarithmic decrement  $\Lambda$  and shear modulus  $G$  at 10 sec<sup>-1</sup> is given. The  $\alpha$  process starts at about 80 °C based on the temperature dependence of the shear modulus  $G$ .<sup>3</sup> According to Gall and McCrum,<sup>6</sup> the beginning of the main-chain relaxation for both syndiotactic and conventional PMMA is at about 80 °C.

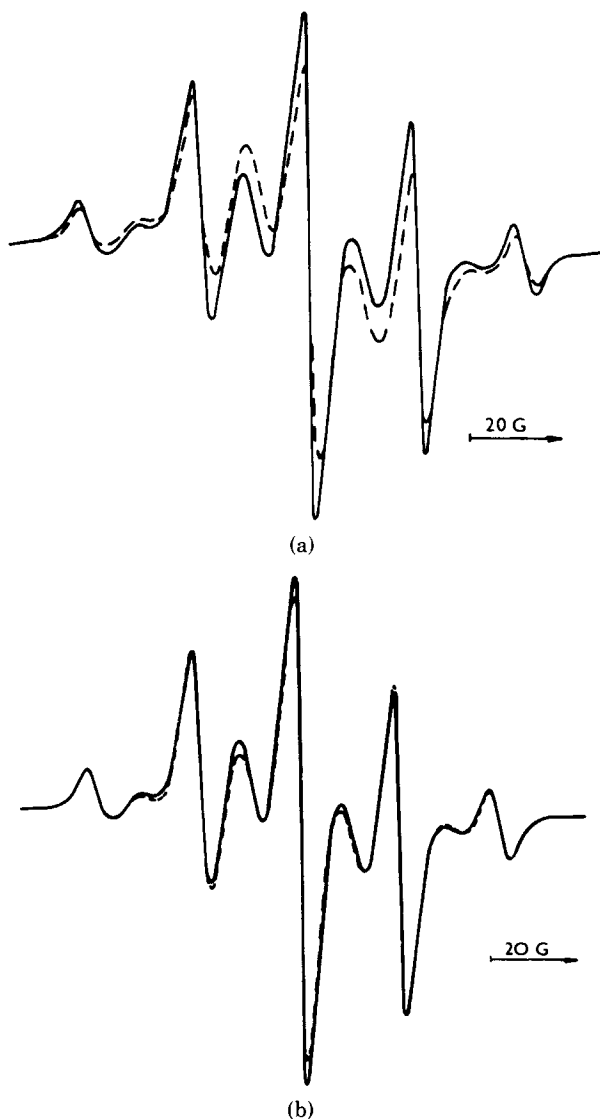


Fig. 1. ESR spectrum of  $\gamma$ -irradiated PMMA measured at room temperature: (—) before annealing (Gain = 1); (- - -) after 30 min annealing; (a) at 70°C and 1 atm (Gain = 2.5); (b) at 80°C and 8000 atm (Gain = 1).

In the  $\alpha$  relaxation region, chain backbone motions prevail. Such motions enable transport of free valences to the neighboring places until recombination of two close radicals occurs. The backbone motion can take place because there is a sufficient free volume around segments in the polymer. As soon as the free volume decreases, segment motion of the macromolecule is retarded and, therefore, the transport of free valences is reduced. A marked pressure dependence of the rate constant above 80°C shows that the decay is controlled by molecular motions which can be retarded by decreasing the free volume. Such molecular motions are mainly the segment motion of main chains beginning to participate in free-valence transport at 80°C. When subjecting the polymer to pressure, its  $T_g$  is shifted to a higher temperature.<sup>7</sup> As the temperature approaches  $T_g$ , segment motions are released and the effective transport mechanism for free valences starts to work. If the system is far from  $T_g$  at the given pressure, i.e., if it is beyond the  $\alpha$  relaxation region, the free-valence transport is slow. The boundary between the  $\alpha$  dispersion and the  $\beta$  dispersion is at about 80°C

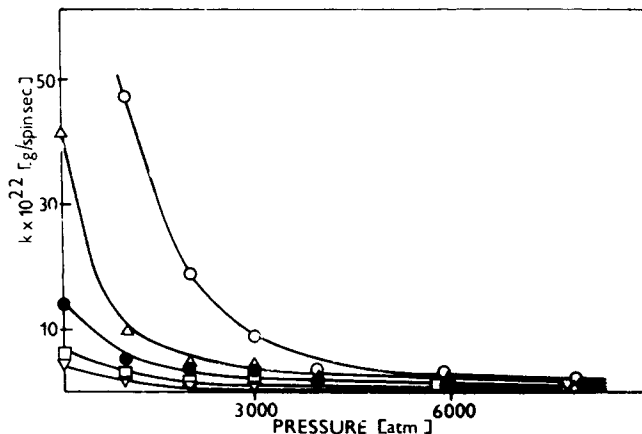


Fig. 2. Pressure dependence of the rate constant for free-radical decay in PMMA: (▽) 50°C; (□) 60°C; (●) 70°C; (△) 80°C; (○) 90°C.

at atmospheric pressure.<sup>6</sup> The effect of pressure causes a shift of this boundary to a higher temperature. The intensive radical decay is observed only in the  $\alpha$  relaxation region, where the segment motions predominate. These motions can be retarded by pressure which stops free-radical decay. In the  $\beta$  relaxation region, different types of molecular motions not very sensitive to pressure prevail. That is why in the  $\beta$  region the rate constant of free-radical decay is only slightly affected by pressure.

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