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# Physical Chemistry

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**Abstract**

**Full Text**

## Physical Chemistry

**R. S. Maslovskaya, A. B. Taubman, L. P. Yanova**

# Diffusion Permeability of Polymers during Their Radiation Destruction in Different Physical States

*(Presented by Academician P. A. Rehbinder, May 4, 1964)*

In studying the radiation destruction of polymethyl methacrylate (PMMA) and polybutyl methacrylate (PBMA) ([1 2]), as well as of low-molecular-weight compounds ([3]), we established that the amount of gaseous radiolysis products formed changes sharply with irradiation temperature in the temperature range close to the glass-transition temperatures ($T_c$) and viscous-flow temperatures of polymers ($T_t$), and to the melting temperatures of low-molecular-weight substances.

The mechanism of this effect was interpreted on the basis of the assumption that, owing to the low rate of diffusion in the glassy state, the gases formed create high local supersaturations, which inhibit further gas evolution and shift the quasi-equilibrium state of the destruction  recombination reactions of free radicals to the right.

In the high-elastic and viscous-flow states, the increased diffusion rate, by promoting the dissipation of local supersaturations, creates favorable conditions for the growth of nuclei of a new phase and thereby for the intensification of gas evolution.

The aim of the present work was to measure the diffusion and permeability coefficients of the indicated polymers in different physical states, which could provide direct confirmation of the correctness of the proposed mechanism.

Measurements were carried out both on unirradiated polymers and on polymers irradiated with electrons at doses of $1 \cdot 10^{21}$ eV/g in the case of PMMA and $0.3 \cdot 10^{21}$ eV/g for PBMA. Comparatively thick PMMA and PBMA films (0.4-0.5 mm) were used as the objects of study, because when polymers are irradiated in the high-elastic state their surface layers turn into a sponge ([2]). The diffusion constants ($D$), permeability ($P$), and also solubility were determined by the Daynes method ([4]), which was further developed in the works of Barrer ([5]), Reitlinger ([6]), and Amerongen ([7]), and which makes it possible to estimate all three quantities simultaneously. The films under study were glued to the flanges of a diffusion cell; to prevent them from being pressed through when gas was

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

admitted, a mesh was welded to the cell on the vacuum side. The cell was placed in a jacket into which a cooling mixture from a Höppler thermostat was supplied, or in a furnace whose temperature fluctuations did not exceed $\pm 1^{\circ}$. The cell was evacuated to $10^{-6}$ mm Hg, after which carbon dioxide was admitted into one of its chambers. The pressure of the gas that had diffused through was measured with a MacLeod manometer with an expanded measuring range. The permeability was calculated from the formula:

$$P = \frac{dp}{dt} \cdot \frac{l}{a} \cdot \frac{273}{p} \left( \frac{V_{\text{cell}}}{T_{\text{cell}}} + \frac{V_{\text{syst}}}{T_{\text{syst}}} \right), \tag{1}$$

where $dp/dt$ is the rate of pressure change in the second chamber per 1 sec; $l$ is the film thickness; $a$ is its area; $p$ is the pressure of the gas being admitted; $V_{\text{cell}}$ and $T_{\text{cell}}$ –

volume and temperature of the cell; $V_{\text{syst}}$ and $T_{\text{syst}}$ are the volume and temperature of the system. The diffusion coefficient is determined from Daynes' equation:

$$D = \frac{l^2}{6\theta}, \tag{2}$$

where $\theta$ is the time lag. This quantity was determined graphically from the dependence $P = f(t)$ as the intercept on the time axis formed by the point of intersection of the extension of the rectilinear portion of the $P - t$ curve with the abscissa axis and the origin, corresponding to the moment when the diffusing gas comes into contact with the film. The time lag in the glassy state for such comparatively thick films is large and amounts to 9-15 h. To establish diffusion equilibrium, a time approximately equal to three time-lag periods is required; therefore, to avoid leakage of air into the system and distortion of the measurement results, intermittent evacuation with freezing out of the diffused carbon dioxide gas was carried out.

Fig. 1. Temperature dependence of the diffusion coefficient of polymethyl methacrylate. 0–unirradiated polymer; 1–irradiated at $t < T_c$; 2–irradiated at $t > T_c$

Fig. 2. Temperature dependence of the diffusion coefficient of polybutyl methacrylate. 0–unirradiated polymer; 1–irradiated at $t < T_c$; 2–irradiated at

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$t > T_c$

The experimental data are summarized in Table 1 and are presented in Figs. 1-2 in the form of curves of the dependence $\lg D$—$1/T$.

As is seen from the figures, the diffusion rate of both polymers increases with increasing temperature, as in any activated process. However, all the curves—which is especially important to emphasize—exhibit a break at certain temperatures corresponding to the transition points of PMMA and PBMA from the glassy to the highly elastic state, analogous to what we previously established for thermomechanical curves ([2]). The position of these points in the irradiated specimens, owing to the decrease in the molecular weight of the polymers as a result of degradation, proves to be shifted somewhat toward lower temperatures in comparison with the transition points of unirradiated specimens ($T_c = 95°$ for PMMA and $T_c = 8°$ for PBMA) ([2]). Thus, to each temperature region below and above $T_c$ there corresponds its own rectilinear segment of the curves $\lg D = f(t)$, the differences in whose course are characterized by changes in the quantities $D$ and $P$ by approximately two decimal orders of magnitude (Table 1, No. 1). At the same time, the looser packing and weaker

**Table 1**

| Specimen No. | Irradiation temperature, °C | Measurement temperature, °C | $D \cdot 10^9$, $\text{cm}^2/\text{s}$ | $P \cdot 10^9$, $\frac{\text{cm}^3}{\text{cm}^2 \cdot \text{s} \cdot \frac{\text{cm}}{\text{atm}}}$ | $E_D$, kcal/mol | $\Delta H$, kcal/mol | $\Delta S$ |
|---|---|---|---|---|---|---|---|
| 1 | PMMA (unirradiated) ($T_c = 95°$) | 25 | 1.6 | 1.0 | 13.2 | −3.6 | −13.5 |
| 1 | PMMA (unirradiated) ($T_c = 95°$) | 40 | 3.6 | 1.6 | | | |
| 1 | PMMA (unirradiated) ($T_c = 95°$) | 110 | 110 | 60 | 22.8 | −2.1 | −6.9 |

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| Specimen No. | Irradiation temperature, °C | Measurement temperature, °C | $D \cdot 10^9$, $cm^2/s$ | $P \cdot 10^9$, $\frac{cm^3}{cm^2 \cdot s} \cdot \frac{cm}{atm}$ | $E_D$, kcal/mol | $\Delta H$, kcal/mol | $\Delta S$ |
|---|---|---|---|---|---|---|---|
| 1a | PMMA (irradiated at $t < T_c$) | 25 | 6.3 | 4.2 | 9.0 | −2.0 | −4.3 |
| 1a | PMMA (irradiated at $t < T_c$) | 110 | 570 | 285 | 16.8 | −1.2 | −2.1 |
| 1b | PMMA (irradiated at $t > T_c$) | 25 | 170 | 120 | 5.8 | −1.05 | −3.2 |
| 1b | PMMA (irradiated at $t > T_c$) | 110 | 4460 | 2660 | 11.8 | −0.7 | −1.2 |
| 2 | PBMA (unirradiated) ($T_c = 8°$) | −26 | 23 | 30.6 | 7.7 | −1.0 | −3.2 |
| 2 | PBMA (unirradiated) ($T_c = 8°$) | −6 | 72 | 81 | | | |

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| Specimen No. | Irradiation temperature, °C | Measurement temperature, °C | $D \cdot 10^9$, $cm^2/s$ | $P \cdot 10^9$, $\frac{cm^3}{cm^2 \cdot s} \cdot \frac{cm}{atm}$ | $E_D$, kcal/mol | $\Delta H$, kcal/mol | $\Delta S$ |
|---|---|---|---|---|---|---|---|
| 2 | PBMA (unirradiated) ($T_c = 8°$) | 44 | 1400 | 1750 | 12.4 | −0.8 | −2.05 |
| 2a | PBMA (irradiated at $t < T_c$) | −23 | 44.5 | 62.2 | 6.6 | −0.9 | −2.9 |
| 2a | PBMA (irradiated at $t < T_c$) | 40 | 1600 | 2400 | 9.4 | −0.65 | −1.6 |
| 2b | PBMA (irradiated at $t > T_c$) | −25 | 68.2 | 99 | 5.9 | −0.8 | −2.2 |
| 2b | PBMA (irradiated at $t > T_c$) | 45 | 4100 | 6500 | 7.8 | −0.55 | −0.85 |

interactions of the main chains of PBMA macromolecules determine its significantly greater diffusion permeability in comparison with PMMA. This agrees with the data of work ([8]) on the diffusion of water and lower alcohols in these same polymers.

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Irradiation produces a characteristic and still stronger increase in permeability, its effect becoming especially pronounced at temperatures above $T_c$. This is clearly shown by a comparison of the data in Table 1 (Nos. 1a and 1b). If, in the sequence: unirradiated polymer–irradiated at $t < T_c$–irradiated at $t > T_c$, the value of $D$, measured at $t = 25^\circ$ (i.e., below $T_c$), is respectively $1.6 \cdot 10^{-9}$, $6.3 \cdot 10^{-9}$, and $170 \cdot 10^{-9}$ cm$^2$/s, then in the case of measuring it at $t = 110^\circ$ (i.e., above $T_c$) we have the sequence: $110 \cdot 10^{-9}$, $570 \cdot 10^{-9}$, and $4460 \cdot 10^{-9}$ cm$^2$/s.

All these effects are evidently associated with the formation of gaseous products of radiolysis, causing the appearance of microdefects in the polymer structure, and not with a decrease in its molecular weight, which, as was shown ([9–11]), does not affect the diffusion properties of the material over a wide range of values. A similar increase in the permeability of polytetrafluoroethylene was also found in ([12]).

Indeed, the influence of gas formation, relatively weak upon irradiation of PMMA and PBMA in the glassy state, should be considerably intensified if radiolysis occurs in the highly elastic state, when the volumes of the gases formed increase by a factor of 5–7 ([2]). This corresponds, as indicated, to the increase in the values of $D$ and $P$ by approximately two orders of magnitude. An even sharper increase in them, observed when the measurements are also carried out at $t > T_c$, is due to the fact that here there is an additional influence of the increased mobility of the polymer chains in the highly elastic state. Similar quantitative dependences were also found for PBMA (Table 1, Nos. 2–2b).

From all that has been said it follows that in the diffusion properties of a polymer, as in its mechanical properties ([2]), a change in its physical state during radiolysis manifests itself incomparably more sharply than a change in temperature by itself within the limits of a single state. An indication of the presence, in the structure of irradiated polymers, of microdefects responsible for their increased permeability is given by the magnitude of the activation energy ($E_D$) of the diffusion process. The increase in $E$ when the temperature is raised with passage through the point $T_c$ can be explained by analogy with the data of Meyer ([13]), who, using polyvinyl acetate as an example, showed that the path length for a unit act of diffusion is 10 Å at $t < T_c$ and 25 Å at $t > T_c$.

This indicates that at higher temperatures a larger number of segments participates in the formation of "holes." The same conclusion also follows from the data in Table 1 on the heat of dissolution of the gas ($\Delta H$), which has negative values owing to the exothermicity of the process; moreover, as can be seen, its absolute values are higher in the highly elastic state both for irradiated and nonirradiated polymers. Evidently, in the glassy state polymers contain more "holes" than their equilibrium number for a liquid with the same density of bonding energy between chains, as a result of which the dissolved gas molecules will be located in "holes" already existing in the polymer mass, and the heat release will be greater [14]. The circumstance that in the glassy state there exist "frozen-in" holes [15,16] apparently makes it possible to explain why the entropy changes of the process ($\Delta S$) not only have negative values, but also decrease in abso-

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lute magnitude upon passing through the point $T_c$. In irradiated films ($\Delta S$) increases somewhat, indicating diffusion in a medium of more flexible chains, where gas molecules can be arranged in a larger number of ways.

The material presented may serve as confirmation of the viewpoint we expressed earlier: that the process of gas evolution during the radiolysis of polymers at the stage of formation of gaseous radicals may be regarded as a quasi-reversible process. The data of this work on the dependence of the diffusion permeability of PMMA and PBMA on their physical state convincingly show that, in the glassy state, the direct reaction of liberation of degradation products is inhibited, whereas in the highly elastic state it is, on the contrary, greatly facilitated.

In conclusion, we consider it our duty to express our deep gratitude to S. A. Reitlinger and A. N. Pravednikov for a number of valuable suggestions and for their interest in the work.

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