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LETTER TO THE EDITOR

Diffusion Effects in the Radiolytic Grafting of Styrene on Polymethylpentene Film

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ABSTRACT

A mathematical analysis has been made of the interaction of diffusion and reaction kinetics during the radiolytic grafting of styrene on polymethylpentene film. The theory is only partially successful in predicting experimental values, but it does suggest possible relationships that are suitable for further investigation.

When a film of polymethylpentene (PMP) is immersed in liquid styrene and irradiated with gamma rays, the styrene diffuses into the film where it is consumed in a grafting reaction. The problem of mathematically relating the styrene diffusion rate and reaction rate is a specific example of a general problem involving the diffusion of any reactant into a solid film or sheet within which it is consumed. The differential equation expressing the general problem has been written [1] as

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial X^2} - k \qquad (1)$$

where C is the concentration of reactant in the film, k is the rate of reactant consumption in the film, X is the coordinate normal to the film surface, and t is time. This equation has been solved [1] by setting up suitable boundary conditions, writing the Laplace transformation of Eq. (1) and the boundary conditions, obtaining the solution of the transformed equation, and finally applying the Fourier-Mellin theorem to yield the following expression for concentration:

$$C = C_0 + \frac{k(X^2 - Xl)}{2D} + \frac{4kl^2}{\pi^3 D} \sum_{n=1,3,5}^{\infty} \frac{1}{n^3} \sin\left(\frac{n\pi X}{l}\right) \exp -\left\{\frac{Dn^2\pi^2 t}{l^2}\right\} \tag{2}$$

where C_0 is the saturation concentration of reactant in the film, l equals film thickness, and the other symbols have the definitions already given. At large values of t, Eq. (2) reduces to the simple form

$$C = C_0 + \frac{k(X^2 - Xl)}{2D} = C_0 + \frac{kl^2}{2D}\left[(X/l)^2 - (X/l)\right] \tag{3}$$

where the second form is convenient for use in computations.

The objective of the present analysis is to apply Eqs. (2) and (3) to the radiolytic grafting of styrene on PMP films, using the grafting rate data reported earlier [2]. Before doing this, it is necessary to consider the kinetics of the grafting reaction. The generally accepted equation for the rate of styrene polymerization in a homogeneous liquid phase can be written [3] as

$$\text{rate} = k_p \left(\frac{R_i}{k_t}\right)^{1/2} [M] \tag{4}$$

where k_p is the rate constant for propagation, k_t is the rate constant for termination, R_i is the rate of initiation, and [M] is monomer concentration. For a grafting reaction within a polymeric film, the highly viscous nature of the medium results in a very low value for k_t. Other investigators [4] have noted that absorbed monomer may plasticize a polymeric film, leading to an increase in k_t and a corresponding decrease in grafting rate. The earlier study [2] of styrene grafting showed that the rate of grafting on PMP, polypropylene, and polyethylene is approximately inversely proportional to the saturation concentration of styrene in these three polymers. If styrene concentration has a similar inverse effect on grafting rate within a PMP film, the rate in Eq. (4) should be multiplied by a correction factor, K/[M], where K is a proportionality constant, so that

$$\text{rate} = k_p \left(\frac{R_i}{k_t}\right)^{1/2} [M] \left(\frac{K}{[M]}\right) = k \tag{5}$$

Such a line of reasoning would indicate a grafting rate approximately independent of [M] within the film, and allow the application of Eqs. (1), (2), and (3) to the styrene/PMP grafting system.

In order to employ these equations, values of k, C_0, and D must be determined. Table I of Ref. 2 showed a styrene grafting rate of 0.47%/hr on PMP, corresponding to 4.7 g/kg/hr, giving

$$k = 7.53 \times 10^{-4} \text{ mole/kg/sec} \tag{6}$$

where units of mole/kg/sec are used for reasons given below.

Reference 2 showed that PMP film immersed in styrene at room temperature exhibits a weight gain of 19.6% at saturation, indicating a styrene concentration in the film of 196 g/kg of polymer, or

$$C_0 = 1.88 \text{ mole/kg} \tag{7}$$

The diffusion constant for styrene in PMP was determined using a technique suggested by McCall [5]. A PMP film sample of 0.0597 cm thickness was immersed in styrene until saturated, blotted dry, and then hung in air and weighed periodically on an automatic balance to determine the weight loss curve. Figure 1 shows the fraction of the original styrene retained, $Q/C_0 l$, plotted versus elapsed time, t.

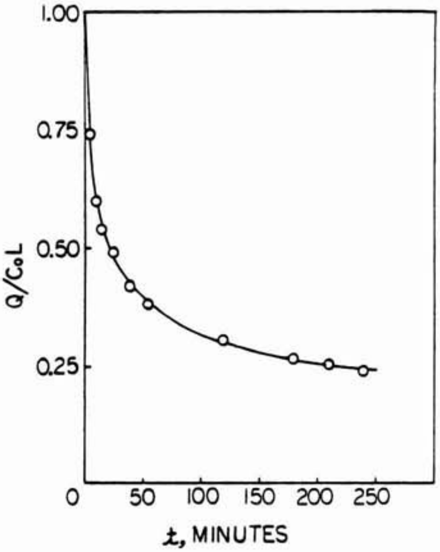

FIG. 1. Plot of Q/C_0l versus time for styrene diffusion from 0.0597 cm polymethylpentene sheet at 23°C.

McCall expressed the diffusion constant, D, as a function of fractional concentration, C/C_0,

$$D = D_0 \exp(aC/C_0) \qquad (8)$$

where D_0 and a are constants. McCall computed theoretical Q/C_0l versus t curves for small integral values of a, and the curve in Fig. 1 shows the best fit with the McCall curve for $a = 5$.

An experimental plot of ln Q against t was found to approach asymptotically at large values of t to a straight line having a slope of 1.67×10^{-5} sec^{-1}. McCall showed that D_0 can be computed from the slope of the asymptote,

$$D_0 = \frac{(\text{slope})(l)^2}{\pi^2} \qquad (9)$$

so that

$$D_0 = \frac{(1.67 \times 10^{-5})(5.97 \times 10^{-2})^2}{(3.1416)^2} = 6.04 \times 10^{-9}\ \text{cm}^2\ \text{sec}^{-1} \qquad (10)$$

To determine a suitable value of D for use in the present computations, it was estimated from the lowest curve of Fig. 2 that the average styrene concentration in the film equals approximately $0.35C_0$. (The average concentration for the lowest curve of Fig. 2 always equals $0.35C_0$, regardless of the values of k and D.) Substitution in Eq. (8) yields

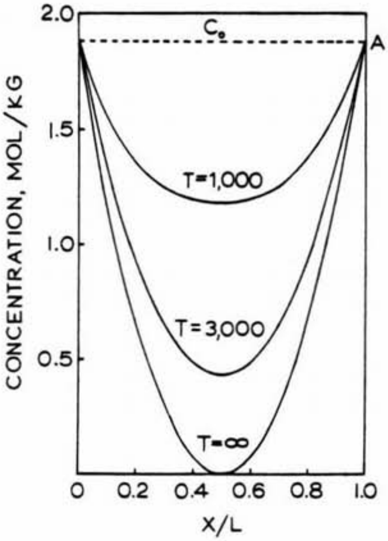

FIG. 2. Theoretical concentration curves for styrene in 0.0265 cm film of polymethylpentene at 23°C, assuming $D = 3.5 \times 10^{-8}$ cm² sec⁻¹, $k = 7.53 \times 10^{-4}$ mole/kg/sec in Eq. (2).

$$D = (6.04 \times 10^{-9})(e^{5 \times 0.35}) = 3.5 \times 10^{-8}\ \text{cm}^2\ \text{sec}^{-1} \qquad (11)$$

which was the value of D selected for use in the present work.

At this point it is possible to employ the selected values of k,

C_0, and D in the theoretical equations to calculate 1) critical film thickness, 2) induction period, and 3) grafting rate versus film thickness curve.

CRITICAL FILM THICKNESS

The critical film thickness is that thickness above which the grafting rate per unit surface area becomes constant (or decreases) as film thickness continues to increase. A more quantitative definition is that thickness for which the steady-state monomer concentration becomes zero in the center of the film, but only in the center of the film. Hence, the critical thickness can be computed by setting C = 0 and X/l = 0.5 in Eq. (3) and solving for l, giving

$$l^2 = 8DC_0/k \tag{12}$$

$$l^2 = \frac{(8)(3.5 \times 10^{-8})(1.88)}{(7.53 \times 10^{-4})}$$

$$l = \text{critical thickness} = 0.0265 \text{ cm} \tag{13}$$

The theoretical value of 0.0265 cm (0.0104 in.) may be compared with the experimental value of 0.008 in. obtained previously [2]. The agreement is good, especially when it is noted that k, C_0, and D were determined in separate and independent experiments.

INDUCTION PERIOD

The induction period can be estimated by employing Eq. (2) to compute styrene concentration across the thickness of the film for several values of t. Figure 2 presents theoretical concentration curves in a 0.0265-cm film at t = 0, t = 1,000 sec, t = 3,000 sec, and at "infinite" time. The rate of monomer diffusion into the film is proportional to the slope of the concentration curve, dC/dX, at point A in Fig. 2. As time passes, the slope at A and the rate of monomer consumption increase until both become constant when the curve reaches its lowest position, corresponding to a steady-state concentration function. Inspection shows that the concentration curve has almost reached its final position after 3,000 sec, so the theoretical induction period due to diffusion is of the order of 1 hr. If such an induction period did exist, it was too short to detect experimentally in runs of 24 to 72 hr duration [2].

GRAFTING RATE AT VARIOUS FILM THICKNESSES

While the theoretical equations do not predict absolute reaction rates, it is possible to use Eq. (3) to derive grafting rates at other thicknesses from the fact that the rate is 0.0274 mg/hr/cm² of surface for a film 0.0055 in. (0.01397 cm) thick, as shown in Ref. 2. (This would correspond to 0.0548 mg/hr/cm² of film of the same thickness.) For such a thin film the monomer penetration depth is simply equal to half the film thickness, so that

$$0.0274\ \mathrm{mg/cm^2/hr} = (3.93)(0.00698\ \mathrm{cm})$$

$$\mathrm{mg/cm^2\ surface/hr} = (3.93)(\text{penetration depth, cm}) \qquad (14)$$

Above the critical thickness it is necessary to solve Eq. (2) with $C = 0$ to obtain the penetration depth, X, giving

$$X = \frac{kl \pm (k^2l^2 - 8kC_0D)^{1/2}}{2k} = \frac{l \pm (l^2 - h^2)^{1/2}}{2} \qquad (15)$$

in which the symbol h is used to indicate the critical thickness, where the penetration depth X is obtained by taking the negative sign of the square root.

Table 1 presents a comparison of observed rates and theoretical rates. For the critical thickness and below, Eq. (14) was used in computing the theoretical rates with penetration depth taken as half the film thickness. Above the critical thickness, Eq. (15) was used to compute the penetration depth, X, which was then substituted in Eq. (14) to give the theoretical rate. The agreement between observed and theoretical rates is not good enough to support the theory convincingly, nor is it poor enough to rule the theory out.

It is of interest to note some further implications of the theory. From Eq. (12) it is seen that critical thickness is proportional to

TABLE 1

Film thickness (in.)	Film thickness (cm)	Penetration depth (cm)	Theoretical rate[a] $(mg/cm^2/hr)$	Observed rate[a] $(mg/cm^2/hr$
0.0055	0.0140	0.0070	0.022	0.027
0.0090	0.0228	0.0114	0.045	0.033
0.0104	0.0265	0.0133	0.052	-
0.0150	0.0381	0.00535	0.021	0.034
0.0240	0.0610	0.00300	0.012	0.035

[a] These are rates per unit surface area and are equal to one-half of the rates per unit film area.

$D^{1/2}$ and inversely proportional to $k^{1/2}$. Hence, a large diffusion constant and small k (low radiation dosage rate) should result in a large value for critical thickness and vice versa. Figure 3 presents theoretical curves for grafting rate versus film thickness for several values of D/k, the curve on the right representing the present computations for the grafting of styrene on PMP. The predicted rate always goes through a peak at the critical film thickness. A search of the literature fails to reveal a report of such grafting behavior for any monomer/polymer system. However, very few quantitative studies have been made of the effect of film thickness on grafting rate.

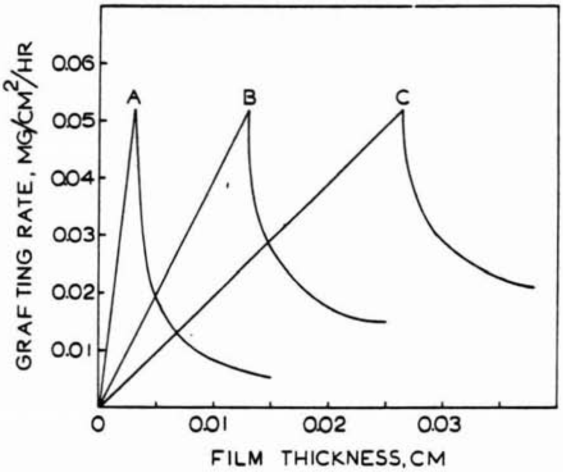

FIG. 3. Theoretical styrene grafting rates on polymethylpentene versus film thickness showing peak rates at A, B, and C, corresponding to D/k values of 5.99×10^{-7}, 1.12×10^{-5}, and 4.6×10^{-5}, respectively; values of k adjusted to give the same peak rate in each case.

Some of the reasons that the postulated diffusion model does not agree precisely with the experimental facts are 1) the variability of the diffusion constant, 2) the swelling of the film by the monomer, and 3) the complexity of the grafting reaction kinetics within the film.

VARIABILITY OF THE DIFFUSION CONSTANT

The simple Fick's laws of diffusion employ a diffusion constant, D, that is independent of the concentration of the diffusing substance. However, extensive studies of monomer/polymer systems have shown that the diffusion constant for monomer diffusion is almost always a function of monomer concentration [6, 7, 9]. Hence, Eq. (1), assuming constant D is not precise, can only approximate the behavior of an actual monomer/polymer system.

EFFECT OF SWELLING

As grafting proceeds, the film may absorb an increasing amount of monomer, resulting in a considerable swelling of the film. In the grafting of styrene on PMP, film swelling representing monomer absorption of 100 to 200% of original film weight was commonly observed [2]. Swelling is accompanied by dimensional change, so that the coordinate X in Eqs. (1) and (2) loses its original meaning.

A mathematical technique for overcoming this difficulty has been suggested by Crank [8]. In brief, a frame of reference must be selected that is fixed with respect to the substance of the film. The usual Fickian equations can be made to apply by departing from the orthodox linear scale (centimeters) for measurement of the coordinate usually denoted by X. Instead, one takes the basic unit volume of film to be its volume in the absence of absorbed monomer and employs a unit of length, X_B, such that unit X_B contains, per unit area, unit basic volume of the substance of the film, B. Then the thickness of the film, measured in these units, is constant and equal to the original unswollen thickness. Note that X_B must be measured so that equal increments of X_B include equal increments of amount of B, and the concentration of monomer, C, must be expressed as the amount of monomer per unit amount of B. In computational terms, this means that monomer concentration must be expressed in moles per kilogram of polymer rather than moles per liter of film.

While this approach may be mathematically satisfactory, it leaves unanswered questions about the side effects of high monomer concentrations that require further investigation.

It is significant that the properties of the film change as the grafting progresses. In the present case, the copolymer of styrene/methylpentene that is forming has a much stronger tendency to absorb styrene than does the original homopolymer. This type of phenomenon has been studied by Kawase [10] in the radiolytic grafting of various alkyl methacrylates on polypropylene. Evidently only the initial grafting rate applies to the original homopolymer.

COMPLEXITY OF GRAFTING REACTION KINETICS

The actual reaction kinetics within the film may be much more complex than indicated by Eq. (5). It is possible that the order of rate dependence on monomer concentration may be a function of monomer concentration. For example, rate may depend on $[M]^{-1.0}$ at high monomer concentration, on $[M]^{1.0}$ at low concentration, and on intermediate powers of $[M]$ at intermediate concentrations. The assumption of constant k in Eq. (5) may be as much of an oversimplification as the assumption of constant D in Eq. (1). In such a case, a solution based on Eq. (5) would be only a rough approximation.

In conclusion, while the theory is only partially successful in predicting experimental values, it provides useful interpretations of the facts and suggests possible new relationships that should be investigated. The above computations postulate a rate of grafting, k, that is approximately independent of the monomer concentration in the film. When grafting rate is proportional to monomer concentration, a different set of relations is predicted as indicated by Eq. (57) of Ref. 1. For k independent of concentration, the following remarkably simple relation between film thickness and critical film thickness can be derived from Eq. (15):

$$l^2 = h^2 + v^2 \tag{16}$$

where v is that thickness in the center of the film which contains no monomer after the steady state has been reached ("infinite" time).

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