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Reaction Kinetics of the Radiation-Induced Grafting of Styrene on Polyethylene Film

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ABSTRACT

Based on rate data obtained previously, an analysis has been made of the reaction kinetics of the radiation-induced grafting of styrene on polyethylene film by using various concentrations of methanol in the styrene. A new feature of the work involves the use of internal film concentrations of styrene and methanol computed from the Flory theory of polymer/solvent interaction, which possibly improves the accuracy of calculations of termination rate constant k_t at various methanol concentrations. A graphical plot of k_t dependence on internal film viscosity is computed from an equation of Smoluchowski. Techniques are defined which may lead to improved accuracy in the computation of rate constants.

INTRODUCTION

The previous report [1] presented rate measurements for the radiation-induced grafting of styrene on polyethylene film, with various amounts of methanol added to the styrene. The essential data

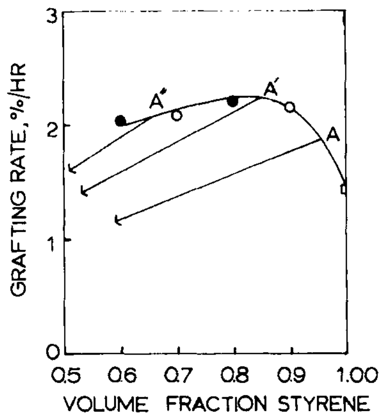

FIG. 1. Grafting rates on 0.012-in. polyethylene film of styrene solutions of several different δ values: (●) solution E; (○) ethanol; (□) no additive.

from the earlier report are presented in Fig. 1, with minor modifications in the method of graphing. The purpose of the present work is to analyze the rate data of Fig. 1, show how k_t can be computed at different methanol concentrations, and present a coherent hypothesis which explains the grafting kinetics and is consistent with the experimental data.

The cobalt-60 source and the techniques of monomer purification and film grafting have already been described in detail [1].

Table 1 presents the compositions of the grafting solutions employed in obtaining the rate data shown in Fig. 1. Solution E consists of a 36/64 volume ratio of benzene/methanol having a Hildebrand δ value of 12.7 (equal to that of ethanol). The original purpose of the data summarized in Fig. 1 was to show that the same curve is obtained regardless of whether pure ethanol (δ = 12.7) or a 36/64 solution of benzene/methanol (δ = 12.7) is added to styrene to form the grafting solution. The use of the Hildebrand δ value in the interpretation of film grafting, and methods of computing δ values for two or more components have been fully described [1].

Analysis of Fig. 1 reveals several interesting relationships. At any point on the curve, such as point A, it should be possible to hold the δ value of the grafting solution constant and make a sequence of rate measurements at different monomer concentrations that would

TABLE 1. Styrene–Polyethylene Runs: Variable Solubility Parameter

Run no.	Styrene (vol %)	Ethanol (vol %)	Solution E (vol %)	Grafting solution δ value	Run length (hr)	Grafting (%)
5P	60	0	40	10.8	21.3	43.3
6P	70	30	0	10.4	21.9	45.6
7P	80	0	20	10.0	22.2	49.0
8P	90	10	0	9.6	19.7	42.7
9P	100	0	0	9.2	25.0	35.8

fall on a straight line from A to the origin, in accordance with the demonstrated linear dependence of rate on monomer concentration. Such linear dependence has been observed for the styrene–nylon, styrene–polyethylene, and pentafluorostyrene–nylon systems [2]. It is reasonable to assume that point A could be located anywhere on the curve of Fig. 1, say at A' or A", and a straight line to the origin be constructed for the plot of grafting rate versus monomer concentration.

It was shown previously [1] that such straight lines to the origin can be constructed by regulating the grafting solution composition so as to hold the δ value of the solution constant, while allowing the monomer concentration to vary. The equation for all rates measured along the dotted line from A to the origin is

$$\text{Rate} = (\text{slope})(\text{volume fraction styrene}) \qquad (1)$$

For the point A shown in Fig. 1, the magnitude of the slope is 2.00. The slope will increase as point A moves to the left along the curve, and decrease as A moves along the curve to the right.

Since the addition of ethanol or solution E has an equivalent effect, it is concluded that for this particular monomer–polymer grafting system, constancy of the δ value of the grafting solution appears to be a reliable indication of the constancy of k_t. That is, when the δ value is identical for two grafting solutions, k_t would appear to be identical for the two solutions regardless of their chemical compositions. Caution should be exercised in extrapolating this conclusion to other monomer–polymer pairs and other solvent additives until further examples of such behavior have been confirmed.

Equation (1) can be studied in more detail by the use of the general polymerization rate equation attributed to Chapiro and others:

$$R_p = \text{rate} = k_p(R_i/k_t)^{1/2}[M]_F \tag{2}$$

where $[M]_F$ is monomer concentration within the film, R_i is the rate of initiation, k_p and k_t are the rate constants for propagation and termination, respectively, and R_p is the rate of monomer consumption by grafting.

Let it be assumed that the monomer concentration within the film $[M]_F$, is proportional to that in the grafting solution, $[M]$, so that

$$[M]_F = q[M] \tag{3}$$

where the factor q is constant along the line from A to the origin.

Equation (2) then becomes

$$R_p = [qk_p(R_i/k_t)^{1/2}][M] \tag{4}$$

which can be expressed in the form of Eq. (1):

$$R_p = (S)[M] \tag{5}$$

where S is the slope of the rate versus $[M]$ plot. If attention is restricted to a single line such as AO, the constancy of the slope makes it very probable that q and the other components of the S factor are constant along AO.

CALCULATION OF k_t

It is theoretically possible to calculate k_t from Eq. (2), but it is first necessary to assign values to R_p, k_p, R_i, and $[M]_F$. Turning first to $[M]_F$, it is recognized that the styrene concentration within the film is quite different from $[M]$, the external styrene concentration in the grafting solution. In the prior article [1], a ternary diagram (Fig. 12) was presented, showing the equilibrium volume fraction relationships in the three-component system, styrene–methanol–polyethylene. These equilibrium relationships were computed from an equation derived by Krigbaum [3], based on Flory's [4] theories of polymer-solvent interaction.

The external volume fractions of styrene and methanol, corresponding to the curve of Fig. 1, are shown in the two left-hand columns of Table 2. For example, at an external styrene volume fraction of 0.80, the external volume fraction of methanol can be computed from the composition of solution E to be (0.20) × (64/100) = 0.128, as shown in the second column from the left. The third column from the left shows an external (styrene plus benzene) volume fraction of 1.000 - 0.128 = 0.872. In the fourth column from the left, the external S/(S + B) ratio is 0.80/0.872, which equals 0.917, and which is also assumed to be the ratio internal to the film since styrene and benzene have the same δ value.

TABLE 2. Internal and External Concentrations

External styrene volume fraction	External methanol volume fraction	External S + B volume fraction	External $\frac{S}{S+B}$ ratio	Internal S + B + M volume fraction	Internal methanol volume fraction	Internal styrene volume fraction
1.00	0	1.00	1.00	0.071	0	0.071
0.95	0.032	0.968	0.981	0.071	0.0030	0.0668
0.90	0.064	0.936	0.961	0.071	0.0063	0.0621
0.85	0.096	0.904	0.940	0.071	0.0095	0.0579
0.80	0.128	0.872	0.917	0.071	0.0124	0.0537
0.75	0.160	0.840	0.893	0.071	0.0148	0.0495
0.70	0.192	0.808	0.866	0.070	0.0173	0.0450
0.65	0.224	0.776	0.838	0.069	0.0198	0.0410
0.60	0.256	0.744	0.806	0.068	0.0220	0.0370

For each external styrene volume fraction, the corresponding internal polyethylene volume fraction can be read from Fig. 12 and Table 6 of the prior report [1]. For example, an external styrene volume fraction of 0.80 corresponds to an internal PE volume fraction of 0.929, which would indicate an internal volume fraction of 0.071 for all absorbed liquids (styrene plus benzene plus methanol). The two right-hand columns of Table 2 show internal methanol and internal styrene volume fractions of 0.0124 and 0.0537, respectively, as read from Fig. 12 of the prior report [1]. The internal volume fraction of styrene is not read directly from Fig. 12, but rather (styrene plus benzene) is read directly and multiplied by S/(S + B) to yield the internal styrene volume fraction. It should also be noted in reading Fig. 12 of the prior report for the purposes of this calculation, that an indicated 80/20 external ratio of styrene/methanol would correspond to an external total of 80 parts of (styrene plus benzene) to 20 parts of methanol. Smoothed curves of internal styrene and internal methanol volume fractions have been prepared as functions of external styrene volume fraction and are presented in Fig. 2.

In the present work no attempt is made to distinguish between styrene concentrations in the amorphous and crystalline portions of the film. In diffusion theory, a type of average diffusion constant known as the "effective diffusion constant" is sometimes used, and

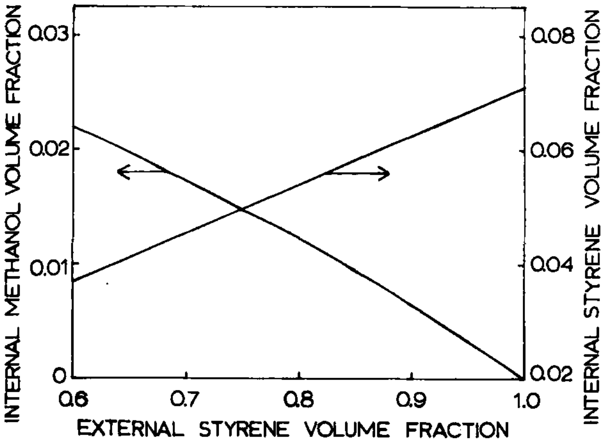

FIG. 2. Internal styrene and internal methanol volume fraction plotted as functions of external styrene volume fraction.

in a similar way the internal styrene concentration in the right-hand column of Table 1 can be considered as an "effective styrene concentration" within the polyethylene film. A related and controversial question is whether the grafting takes place in the crystalline or amorphous domains of the polyethylene, with some authors [5] concluding that grafting takes place in the amorphous areas only, and others observing that the amount of grafting is proportional to the percent crystallinity [6]. In any case, the Krigbaum equation employed in the present calculations refers to only one concentration of an absorbed component in the "polymer phase," and makes no distinction between crystalline and amorphous areas of the polymer phase.

Another factor appearing in Eq. (2) is the rate of initiation R_i, which must be estimated from the measured dosage rate. Ferrous sulfate dosimetry indicated a dosage rate of 477 R/hr [1], corresponding to 460 rad/hr, since one roentgen deposits 0.965 rad in water medium [7]. In order to compute the rate of radical formation in polyethylene, the corresponding dosage rate in polyethylene containing absorbed styrene, methanol, and benzene must be computed. For cobalt γ-radiation, as in the present case, the task is simplified by the fact that γ-rays of this energy are generally absorbed almost entirely by the Compton effect, for which the absorption coefficient of an element is proportional to Z/A, where Z is the atomic number and A is the atomic weight of the element. An average value of Z/A is used for compounds, so that for water and polyethylene [7],

$$(\overline{Z/A})_{H_2O} = [(2)(1) + 8]/18 = 0.556 \tag{6}$$

$$(\overline{Z/A})_{PE} = (6 + 6 + 4)/28 = 0.572 \tag{7}$$

For polyethylene containing absorbed styrene, methanol, and benzene, an average $(\overline{Z/A})_{mix}$ for the composite would be obtained by summing the weight fractions of all components times their $(\overline{Z/A})$ values. In the present case, the dose absorbed by the swollen composite can be computed from the dose absorbed by the water of the dosimeter as follows:

$$D_{mix} = (460 \text{ rad/hr}) \frac{(\overline{Z/A})_{mix}}{(\overline{Z/A})_{H_2O}} \tag{8}$$

If W_{PE} equals the weight fraction of PE in the swollen composite, the fraction of the dose absorbed by the composite which is absorbed by the PE equals

$$D_{PE}/D_{mix} = W_{PE}\,(\overline{Z/A})_{PE}/(\overline{Z/A})_{mix} \tag{9}$$

so that the dose absorbed by the PE is given by

$$D_{PE} = (460\text{ rad/hr})\,\frac{(\overline{Z/A})_{mix}}{(\overline{Z/A})_{H_2O}}\,W_{PE}\,\frac{(\overline{Z/A})_{PE}}{(\overline{Z/A})_{mix}}$$

$$= (460\text{ rad/hr})\,W_{PE}\,\frac{(\overline{Z/A})_{PE}}{(\overline{Z/A})_{H_2O}} \tag{10}$$

When the polyethylene is immersed in pure styrene, the polyethylene absorbs 7.4% styrene by weight corresponding to a PE weight fraction of 0.933, so that the dose absorbed per hour by the PE is

$$D_{PE} = (460\text{ rad/hr})\,(0.933)(0.572)/(0.556)$$

$$= 442\text{ rad/hr}$$

The rate of initiation R_i can now be computed from an equation used by Takamatsu [8] and others:

$$R_i = G\rho\phi/6.02 \times 10^{25} \tag{11}$$

where G or "G value" is number of PE free radicals produced per 100 eV of absorbed radiant energy, ρ is the weight (grams) of PE per liter of PE–styrene–methanol–benzene composite, and ϕ is the radiation dosage absorbed by PE (in eV/g-sec). The above dosage of 442 rad/hr absorbed by PE can be multiplied by a conversion factor of 1.75×10^{10} to give $\phi = 774 \times 10^{10}$ eV/g-sec. The value of ρ at each styrene concentration can be computed from the internal volume fraction of PE shown in Table 2. Thus, in Table 2 the immersion of PE in pure styrene gives a PE volume fraction of 0.929 at equilibrium, corresponding to 929 cc PE/liter of the swollen composite.

Since the density of PE is 0.93 g/cc, there is 0.93 × 929 = 864 g/liter of the swollen composite. The value of G is taken equal to 7 as employed by Odian [5], based on radical yields from low molecular weight models of polyethylene. Substitution of these values in Eq. (11) gives the rate of initiation:

$$R_i = \frac{(7)(864)(774 \times 10^{10})}{(6.02 \times 10^{25})}$$

$$= 7.77 \times 10^{-10} \text{ mole/liter-sec}$$

All of the values of R_i in Table 2 were computed by using the same value of ϕ, which does not vary significantly over the styrene concentration range considered. The slight change in ρ must be taken into account in computing R_i at different styrene concentrations, resulting in a slight change in R_i as styrene concentration changes.

While it does introduce an error, an estimate of the value of the propagation rate constant k_p can be obtained by assuming that it has the same value in the film as in the free radical polymerization of pure liquid styrene at room temperature. The value of the latter, 44 liter/mole-sec, determined by Matheson [9], is the figure generally accepted by most investigators. The actual value of the propagation constant in the film is probably lower, because the movement of the reactants is slowed somewhat due to the very high viscosity of the interior of the film. (Note: When the δ value of the grafting solution is held constant, the value of k_p should not vary for the same reason that k_t does not vary.)

It is evident that the rate of monomer consumption in grafting can be converted from units of %/hr to mole/liter-sec by the relation,

$$R_p = \left(\frac{\%/\text{hr}}{100}\right)(a)\left(\frac{1 \text{ mole}}{104.1 \text{ g}}\right)\left(\frac{1 \text{ hr}}{3600 \text{ sec}}\right) = \text{mole/liter-sec} \tag{12}$$

where a is weight (g) of PE per liter of swollen composite. For PE film in pure styrene the grafting rate is 1.43%/hr from Fig. 1, and a is 864 from the above computation of R_i, yielding

$$R_p = \left(\frac{1.43}{100}\right) (864) \left(\frac{1}{104.1}\right)\left(\frac{1}{3600}\right)$$

$$= 3.07 \times 10^{-5} \text{ mole/liter-sec}$$

When PE is immersed in styrene, 1 liter of the swollen composite contains 71 cc of styrene at equilibrium (Table 2). Since the density of styrene is 0.907 g/cc, this corresponds to 64.4 g styrene/liter of swollen film, or a styrene concentration within the film of 0.619 M.

For PE immersed in pure styrene, the various factors are now available for the calculation of k_t from Eq. (2).

$$3.07 \times 10^{-5} = 44\,(7.77 \times 10^{-10}/k_t)^{1/2}\ 0.619$$

Thus

$$k_t = 6.10 \times 10^{2} \text{ liter/mole-sec}$$

In similar fashion, values of k_t at other styrene concentrations were computed and are compiled in Table 3. Table 3 also shows the values of R_i, R_p, internal [M], and ρ employed in the calculation of k_t at each styrene concentration.

A graph of k_t versus external styrene concentration is presented in Fig. 3. As expected, the value of k_t drops rapidly as the first of the solution E is added, and then decreases much more slowly as the styrene concentration drops below 70 or 80 vol %. Because of the numerous assumptions introduced into the computation, the values of k_t in Fig. 3 are no better than approximations. Another error in the computation is introduced by the assumption that k_p is constant, when it must decrease as solution E is added for the same reason that k_t decreases.

TABLE 3. Summary of Termination Rate Constant Calculations

External styrene volume fraction	$R_i \times 10^{10}$ (mole/liter-sec)	$R_p \times 10^5$ (mole/liter-sec)	Internal styrene concn (mole/liter)	$k_t \times 10^{-2}$ (liter/mole-sec)	ρ (g PE/liter)
1.00	7.77	3.07	0.619	6.10	864
0.95	7.77	4.36	0.582	2.69	864
0.90	7.77	4.95	0.541	1.80	864
0.85	7.77	5.15	0.505	1.44	864
0.80	7.77	5.18	0.467	1.22	864
0.75	7.77	5.11	0.431	1.07	864
0.70	7.78	4.98	0.392	0.93	865
0.65	7.79	4.82	0.357	0.83	866
0.60	7.80	4.57	0.322	0.75	867

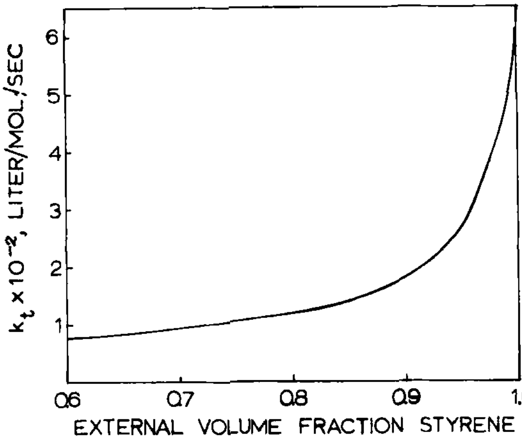

FIG. 3. Termination rate constant plotted as a function of external styrene volume fraction; data from Table 3.

EFFECT OF VISCOSITY ON k_t

Plasticity and viscosity are inverse functions, so that viscosity decreases as plasticity increases. Information concerning the effect of viscosity on k_t can be obtained through the use of an equation derived by Smoluchowski [10], which gives the reaction rate constant as a function of the diffusion constant for two reactants diffusing toward each other through the reaction medium:

$$k = (4\pi N_0/1000)(D_1 + D_2)R_{12} \tag{13}$$

where k is the second-order rate constant, D_1 and D_2 are the diffusion constants for the two reactants (free radicals in the present case), and R_{12} is the reaction distance in centimeters, that is, the distance between the centers of the reacting entities when they react.

In the present case let it be assumed that

$$k = k_t \tag{14}$$

and that the diffusion constant is given by Einstein's equation,

$$D = RT/N_0 f \tag{15}$$

where f is the frictional force on a reactant moving through the medium at unit velocity, and R is the ideal gas constant.

According to Stokes' law [11], the frictional force f can be expressed as a function of the viscosity of the medium:

$$f = 6\pi\eta r \tag{16}$$

where η is the coefficient of viscosity of the medium and r is the radius of the moving reactant or particle (assumed spherical in the derivation). Combining Eqs. (15) and (16) yields

$$D = RT/6N_0\pi\eta r \tag{17}$$

Rewriting Eq. (13), on taking Eqs. (14) and (17) into account, yields

$$k_t = \left(\frac{4\pi N_0}{1000}\right)(R_{12})\left(\frac{RT}{6N_0\pi\eta r_1} + \frac{RT}{6N_0\pi\eta r_2}\right) \tag{18}$$

Hence,

$$k_t = \left[\left(\frac{4\pi N_0}{1000}\right)(R_{12})\left(\frac{RT}{6N_0\pi r_1} + \frac{RT}{6N_0\pi r_2}\right)\right]\left(\frac{1}{\eta}\right) \tag{19}$$

Setting the quantity in brackets equal to W,

$$k_t = W/\eta \tag{20}$$

where W is presumably a constant at a given temperature for a specific monomer–polymer grafting system and k_t is seen to be inversely proportional to η. After assigning an arbitrary value to W, a plot of k_t versus η was computed based on Eq. (20) and is presented in Fig. 4.

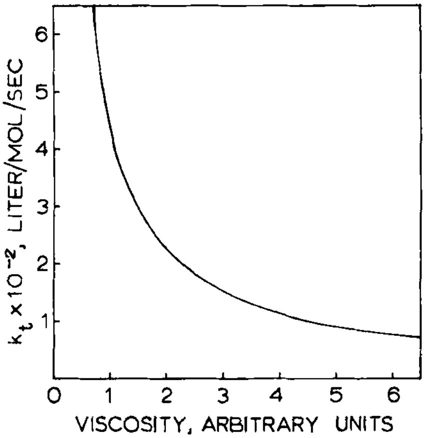

FIG. 4. Termination rate constant in customary units vs. viscosity in arbitrary units. Computation based on Eq. (20).

CONCLUSIONS

An hypothesis has been advanced to explain the kinetics of the radiation-induced grafting of styrene on polyethylene, taking into account the increase in grafting rate observed when methanol is added to the system. The data are consistent with the conventional rate expression for free-radical polymerization [Eq. (2)], provided it is assumed that k_t decreases as methanol is added, corresponding to a decrease in plasticity of the film interior and an increase in $|\delta_p - \delta_S|$. Points of agreement with Eq. (2) include grafting rate dependence on the first power of monomer concentration as shown in the previous report [1], and the grafting rate dependence on the one-half power of R_i as demonstrated by other investigators [12].

In the rate constant calculations carried out in this report, care has been taken to state all approximations clearly, so as to avoid giving the impression that precise computations are being made. While many approximations were employed in the present work, the study led to several conclusions regarding the method of analysis and the factors affecting the reliability of the results.

1. In order to check the dependence of rate on internal monomer concentration, the internal film plasticity must be held constant by some suitable method while [M] is varied.

2. Whether a solvent has been added to the monomer or not, a kinetic analysis requires the determination of monomer concentration within the film under all relevant conditions.

3. If the length of a run is short in comparison with the time required for all liquids to reach equilibrium concentration within the film, Eq. (2) cannot be used because it is based on the attainment of a steady state.

4. In testing adherence to Eq. (2), the initial rates of grafting for each set of conditions must be employed, because the rate generally changes as the run proceeds due partly to the change in composition of the substrate film (caused by grafting).

5. The free radical yield in polyethylene employed above, $G_R = 7$, is probably only a rough approximation, since the value of G_R would be expected to depend on percent crystallinity, molecular weight distribution, and other PE properties that have not been taken into account in the choice of this G_R value.

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