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# Viscosity Effects in the Radiation-Induced Grafting of Vinyl Monomers on Polyvinyl Chloride) Films

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# Viscosity Effects in the Radiation-Induced Grafting of Vinyl Monomers on Poly(vinyl Chloride) Films

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## ABSTRACT

Radiation-induced grafting rates of styrene on poly(vinyl chloride) (PVC) film were measured in a series of runs at various styrene concentrations, while holding constant the Hildebrand solubility parameter of the grafting solution, and therefore theoretically also holding internal film viscosity constant. The results show rate apparently proportional to the first power of styrene concentration, with an induction period of 15 hr at the particular (constant) dosage rate employed. The rate data are compared and contrasted with those obtained in earlier grafting studies by Takamatsu on styrene-PVC, in which styrene concentration within the film was varied and internal film viscosity was also varied. The rate of acrylonitrile grafting on PVC film was also measured, and overall grafting rates for styrene-PVC and acrylonitrile-PVC are compared on the basis of the calculated values of rates of initiation, rates of propagation, internal monomer concentrations, and rates of termination. Internal film viscosities for several monomer-polymer systems were estimated by using an equation derived by Smoluchowski, and the relation between internal film viscosity and the rate of termination by macroradical interaction is discussed.

## INTRODUCTION

The present work had two objectives: (1) to follow up from a different point of view the finding of Takamatsu [1] that the rate of styrene grafting on PVC film varies with the internal film viscosity, and (2) to estimate the internal film viscosity for several monomer-polymer grafting systems and to express the termination rate constant for such systems as a function of internal film viscosity.

In an important experiment, Takamatsu [1] carried out radiation-induced grafting on PVC films containing styrene at various concentrations and showed that the rate is greatest at an internal monomer concentration of about 3.5 mole/liter and is smaller at higher and lower concentrations. In order to explain the decrease in rate above 3.2 mole/liter, Takamatsu assumed that the rate constant for the termination reaction increases with styrene concentration. Termination involves the interaction of polymeric free radicals, and he reasoned that the absorbed styrene in the polymer works as a plasticizer and increases the molecular motion of the polymer, thus expediting macroradical interaction. He demonstrated the plasticizing action of styrene in PVC by measuring the elastic modulus of PVC containing various concentrations of styrene.

The writer approached the matter from a different point of view, attempting to hold the internal film viscosity constant by proper choices of grafting solution composition, thus enabling a study of grafting rate dependence on monomer concentration at constant internal film viscosity. This technique has been discussed in previous reports [2-4] and will only be summarized briefly. It involves the use of the Hildebrand solubility parameter $\delta$ to assess the plasticizing efficiency of the grafting solution [5]. Efficient plasticization corresponds to small values of $|\delta_p - \delta_s|$, while poor plasticization corresponds to larger values of $|\delta_p - \delta_s|$, where $\delta_p$ and $\delta_s$ are the Hildebrand solubility parameters for the polymer film and the grafting solution, respectively. By using a series of grafting solutions of constant $\delta$ value, the internal film plasticity (and viscosity) is theoretically held constant, allowing one to evaluate the effect of other variables such as monomer concentration. When the grafting solution $\delta$ value was held constant in this way, linear plots of grafting rate versus monomer concentration were obtained for styrene-nylon [3], pentafluorostyrene-nylon [3], and styrene-polyethylene [2].

One of the secondary objectives of the present work was to determine whether the constant $\delta$ value approach would lead to linear dependence of grafting rate on monomer concentration for the styrene-PVC system. The various factors affecting rate are contained in the conventional equation for the rate $R_p$ of free radical polymerization [6]:

$$R_p = k_p (R_i/k_t)^{1/2} [M] \qquad (1)$$

where $[M]$ 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.

It is evident that a linear dependence of rate on $[M]$ would not be observed unless the other factors on the right hand side of the equation are held constant. Since $k_t$ depends strongly on internal film viscosity, the above-mentioned approach was used in an attempt to hold the internal film viscosity constant. This contrasts with Takamatsu's approach, where the internal film viscosity was varied deliberately, in order to observe the effect on grafting rate.

## EXPERIMENTAL TECHNIQUE

The cobalt-60 source and the method of placement of successive film samples in the same position in the source were discussed in an earlier report [7]. Reproducible positioning of the film sample duplicates the dosage rate precisely, and enables meaningful rate measurements to be obtained. The exposure dose rate at the film location was found to be 407 R/hr by ferrous sulfate dosimetry.

Poly(vinyl chloride) film samples about 0.02-0.03 g in weight were used in the grafting runs. The unplasticized PVC film was of 0.007 in. thickness and was supplied by W. R. Grace and Company. All film samples were extracted by stirring for 2 days in warm benzene and drying to constant weight prior to use.

The monomers, styrene and acrylonitrile, were washed several times with dilute aqueous sodium hydroxide solution, distilled, and stored over anhydrous calcium sulfate at refrigerator temperature prior to use. The solvent employed in some of the runs was reagent grade benzene, which was stored in its bottle over anhydrous calcium sulfate and always used from the same bottle.

Before each run the grafting solution was freed of oxygen by freeze-thaw cycling in a vacuum system as described in a previous report [7]. The small tube containing the film sample and grafting solution was frozen down and sealed from the vacuum line with a hand torch while pumping, then positioned in the cobalt-60 source for the start of the grafting run.

The styrene-grafted PVC samples were extracted by stirring for 2 days in warm benzene, then dried in air to constant weight. The acrylonitrile-grafted samples were extracted in a similar way in nitromethane saturated with water. The latter has been found to be an excellent solvent for removing homopolymeric acrylonitrile without dissolving the PVC. Each grafted PVC sample was accompanied by a PVC blank of similar size which was extracted and dried to constant weight (but not irradiated). This procedure enabled a correction to be made for any minor gain or loss in sample weight not attributable to grafting.

All grafting runs were made at 23 ± 1° C; Eq. (2) was used,

$$\text{Percent grafting} = [(P_g - P_0)/P_0] \times 100 \qquad (2)$$

where $P_0$ is the film sample weight before grafting and $P_g$ is the weight of the same sample after grafting, extracting, and drying to constant weight.

Saturation absorption of styrene or acrylonitrile by (ungrafted) PVC was determined by immersing a film sample in the monomer for about 24 hr, blotting dry with filter paper, and weighing in a closed weighing bottle. The blotting and weighing was repeated several times at 0.5-hr periods to yield an average weight of swollen film $P_s$, from which the weight percent swelling was computed by Eq. (3).

$$\text{Percent swelling} = [(P_s - P_0)/P_0)] \times 100 \qquad (3)$$

## RESULTS

### Grafting of Styrene on PVC Film

The intention in studying styrene grafting on PVC film was to hold the $\delta$ value of the grafting solution constant in a series of runs while varying the styrene concentration. This can be done by progressively reducing the volume percent styrene in the grafting solution and replacing it with benzene. Thus the selected grafting solutions contained styrene/benzene volume ratios of 100/0, 75/25, 50/50, and 25/75. Since the δ value is 9.2 for both styrene and benzene, the δ value of the grafting solution remained constant at 9.2 in all of the runs.

Experimental data for the individual runs are summarized in Table 1. The percent grafting vs. time curves for the various styrene concentrations are presented in Fig. 1. There was an induction period of about 15 hr before the grafting started. The presence of the induction period appears to be a general characteristic of grafting on PVC, because it was also observed by Takamatsu [1] and others. Takamatsu employed several dosage rates and found that the length of the induction period is a function of the dosage rate, the period decreasing as the dosage rate increases. Only one dosage rate was used in the present work, producing the same induction period of about 15 hr in all runs.

Grafting rates computed from Fig. 1 are shown as a function of external styrene concentration (vol %) in Fig. 2. The linear plot obtained would indicate rate proportional to [M] in conformity with

TABLE 1. Summary of Styrene-PVC Runs

| Run no. | Styrene (vol %) | Benzene (vol %) | Solution value | Run length (hr) | Grafting (%) |
|---|---|---|---|---|---|
| 1S | 100 | 0 | 9.2 | 23.7 | 2.0 |
| 2S | 100 | 0 | 9.2 | 45.1 | 5.6 |
| 3S | 100 | 0 | 9.2 | 70.6 | 9.1 |
| 4S | 75 | 25 | 9.2 | 28.2 | 1.2 |
| 5S | 75 | 25 | 9.2 | 47.9 | 4.3 |
| 6S | 75 | 25 | 9.2 | 69.9 | 7.2 |
| 7S | 50 | 50 | 9.2 | 47.0 | 2.8 |
| 8S | 50 | 50 | 9.2 | 71.3 | 4.9 |
| 9S | 25 | 75 | 9.2 | 45.7 | 1.3 |
| 10S | 25 | 75 | 9.2 | 68.3 | 2.5 |

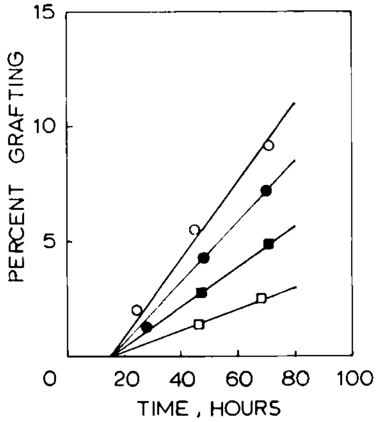

FIG. 1. Grafting vs. time for styrene on PVC film at 23° C for various grafting solution compositions: ( ○ ) 100% styrene; ( ● ) 75% styrene; ( ■ ) 50% styrene; ( □ ) 25% styrene.

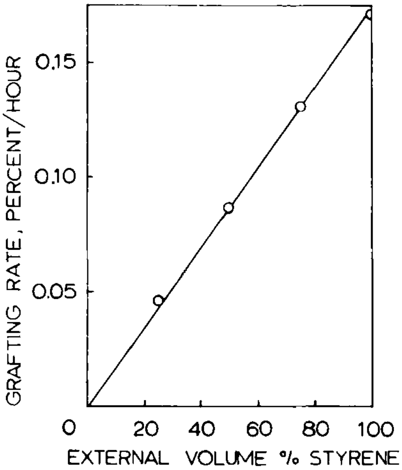

FIG. 2. Grafting rate for PVC-styrene vs. styrene in the grafting solution.

Eq. (1), providing it is assumed that the monomer concentration within the film, [M], is proportional to the external styrene concentration in the grafting solution. This assumption is reasonable, since an identical $\delta$ value for styrene and benzene indicates that the styrene/benzene ratio is the same inside and outside the film, according to Hildebrand's theory. Takamatsu [1] varied the dosage rate by a factor of about $10^3$ and found grafting rate proportional to the one half power of the dosage rate. Since $R_i$ is proportional to dosage rate, this would indicate another point of experimental agreement with Eq. (1) for the styrene-PVC grafting system.

By the use of Eq. (1) it is possible to compute an approximate value of $k_t$ for the PVC-styrene grafting system. In order to do so, values must be assigned to [M], $R_i$, $R_p$, and $k_p$. To determine [M], the saturation absorption of styrene by PVC film was measured and found to be 125.9% by weight of the original film. Assuming densities of 0.907 and 1.40 for styrene and PVC, respectively, it is estimated that 100 g PVC plus 125.9 g styrene has a volume of 210.1 cc (assuming zero volume change on mixing). Hence, the concentration of styrene equals

$$125.9 \times (1000/210.1) = 598 \text{ g/liter}$$

This corresponds to 5.74 mole/liter of styrene, and compares with a maximum concentration of 5.2 mole/liter obtained by Takamatsu [1]. The difference is not surprising, in view of the known variation in resin properties from sample to sample.

In order to compute $R_i$ it is first necessary to note that a dosage rate of 407 R/hr corresponds to 393 rad/hr, since one roentgen deposits 0.965 rad in water medium [8]. The $\gamma$-rays from cobalt-60 are 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, which may be computed for water and PVC [8] as shown in Eqs. (4) and (5):

$$(\overline{Z/A})_{H_2O} = [(2 \times 1) + 8]/18 = 0.556 \tag{4}$$

$$(\overline{Z/A})_{PVC} = (6 + 6 + 3 + 17)/62.5 = 0.512 \tag{5}$$

It can readily be shown [9] that for PVC swollen with styrene absorbed by the PVC equals

$$D_{PVC} = (393 \text{ rad/hr})W_{PVC} \left[(\overline{Z/A})_{PVC}/(\overline{Z/A})_{H_2O}\right] \qquad (6)$$

where $W_{PVC}$ is the weight fraction of PVC in the swollen film. Hence,

$$D_{PVC} = (393)\,(0.442)\,[(0.512)/(0.556)] = 160.3 \text{ rad/hr}$$

It is now possible to compute $R_i$ from the equation used by Takamatsu,

$$R_i = G\rho\phi/(6.02 \times 10^{25}) \qquad (7)$$

where G denotes the "G value", defined as the number of PVC free radicals per 100 eV absorbed, $\rho$ is the weight of PVC (g/liter) of PVC in styrene, and $\phi$ is the dosage absorbed by PVC (eV/g-sec). The dosage rate of 160 rad/hr can be multiplied by the conversion factor of $1.75 \times 10^{10}$ to give an absorbed dosage of $281 \times 10^{10}$ eV/g-sec. From the saturated absorption figures quoted above it is calculated that $\rho$ for the swollen film equals 476 g of PVC per liter. The G value of 3.2 is employed as was done by Takamatsu, based on the work of Nitta [10]. Substitution of these values in Eq. (7) yields

$$R_i = \frac{(3.2)(476)(281 \times 10^{10})}{(6.02 \times 10^{25})} = 0.710 \times 10^{-10} \text{ mole/liter-sec}$$

Again following Takamatsu [1], an approximate value for $k_p$ can be obtained by assuming it has the same value within the film, 44 liter/mole-sec, as it does in the homopolymerization of liquid styrene at room temperature [11].

If there is 476 g of PVC per liter of PVC-styrene swollen film, the rate of monomer consumption in grafting can be converted [9] from %/hr to mole/liter-sec by use of the equation,

$$R_p = \frac{0.171\%/\text{hr}}{100} \times 476 \times \frac{1}{104.2} \times \frac{1}{3600} = 2.17 \times 10^{-6} \text{ mole/liter-sec} \qquad (8)$$

For PVC immersed in 100 vol % styrene the various quantities are now available for substitution in Eq. (1), thus yielding the value of $k_t$:

$$2.17 \times 10^{-6} = 44(0.710 \times 10^{-10}/k_t)^{1/2}\ 5.74$$

$$k_t = 0.963 \times 10^{6} \text{ liter/mole-sec}$$

This result may be compared with Takamatsu's [1] values of $1.15 \times 10^{6}$ and $4.27 \times 10^{6}$ liter/mole-sec at 5.0 and 5.2 mole/liter of styrene, respectively. This degree of agreement exists in spite of the fact that Takamatsu's dosage rate was over 100 times as large as that used in the present work, which appears to indicate that Eq.(1) holds fairly well over a wide range of dosage rate. A slight difference in the computations also results from Takamatsu's use of $k_p$ equal to 55 liter/mole-sec.

## Effect of Viscosity on Termination Rate

While some value of $k_p$ must be known or assumed to compute $k_t$, it is possible to compute $k_p^2/k_t$ from the measured values of $R_p$, $[M]$, and $R_i$, with no assumption about the magnitude of $k_p$. Rearranging Eq. (1) yields Eq. (9):

$$k_p^2/k_t = R_p^2/[M]^2 R_i \tag{9}$$

Substitution of the appropriate data from the above calculations yields $20.1 \times 10^{-4}$ liter/mole-sec for $k_p^2/k_t$, compared with the corresponding figure of $7.1 \times 10^{-4}$ liter/mole-sec computed by Takamatsu [1] for styrene-saturated PVC. These figures are not far from the literature value [11] of $0.95 \times 10^{-4}$ liter/mole-sec for the homopolymerization of liquid styrene, which led Takamatsu to conclude that at such high concentrations of styrene in PVC the graft polymerization reaction may take place in a manner similar to the polymerization reaction in pure styrene. This conclusion is strengthened by the fact that Eq. (1), originally derived for bulk monomer polymerization, seems to hold reasonably well for styrene-saturated PVC film.

Investigators of film grafting generally agree that changes in internal film viscosity have a tremendous effect on the magnitude of $k_t$. In a preliminary study of the viscosity effect [9], Eq. (10), originally derived by Smoluchowski [12] for any two reactants, was adapted to the specific case of macroradical interaction:

$$k_t = (4\pi N_0/1000)\,(D_1 + D_2)A_{12} \tag{10}$$

where $k_t$ is taken to be the rate constant (in liter/mole-sec) of the diffusion-controlled reaction between two macroradicals, $N_0$ is Avogadro's number, $D_1$ and $D_2$ are the diffusion constants for the two reactants (in $cm^2$/sec), and $A_{12}$ is the approach distance (in cm) between the centers of the reactants when they react.

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

$$D = RT/N_0 f \tag{11}$$

where f is the frictional force on a reactant moving through the medium at unit velocity, R is the ideal gas constant, and T is the absolute temperature. Furthermore, according to Stokes' law, f can be expressed as a function of the viscosity of the medium,

$$f = 6\pi\eta r \tag{12}$$

where $\eta$ equals the viscosity coefficient and r is the radius of the moving reactant. Substituting Eqs. (11) and (12) into Eq. (10) yields

$$k_t = \frac{4\pi N_0}{1000}\left(\frac{RT}{6N_0\pi\eta r_1} + \frac{RT}{6N_0\pi\eta r_2}\right)(A_{12}) \tag{13}$$

where $r_1$ and $r_2$ are the radii of reactants 1 and 2, respectively.

On applying Eq. (13) to the termination reaction in styrene grafting on PVC, it is noted that reaction takes place between two growing styrene chains. Hence, it is reasonable to assume that $r_1 = r_2 = r$, and $A_{12} = 2r$, so that

$$k_t = \frac{4\pi N_0}{1000}\left(\frac{2RT}{6N_0\pi\eta r}\right)(2r) \tag{14}$$

Making cancellations and noting that R = 8.31 × $10^7$ erg/°K/mole and T = 296°K, we have

$$k_t = (8)(8.31 \times 10^7)(296)/(3 \times 1000\eta)$$

$$= 6.55 \times 10^7/\eta \qquad (15)$$

Equation (15) indicates an inverse relationship between $k_t$ and $\eta$ and enables an estimation of $\eta$ for any $k_t$ value. For $k_t$ equal to 0.963 $10^6$ liter/mole-sec the corresponding value of $\eta$ would be 68.0 poise. The location of this point is shown as a filled circle in Fig. 3, which presents the hyperbolic plot of $k_t$ versus $\eta$. Figure 3 also shows open circle points corresponding to Takamatsu's $k_t$ values of 1.15 × $10^6$ and 0.112 × $10^6$ liter/mole-sec. Corresponding values of $k_t$ and $\eta$ for various monomer/polymer systems are summarized in Table 2.

Takamatsu's other $k_t$ values cover such a wide viscosity range that they cannot be shown in Fig. 3. In order adequately to represent

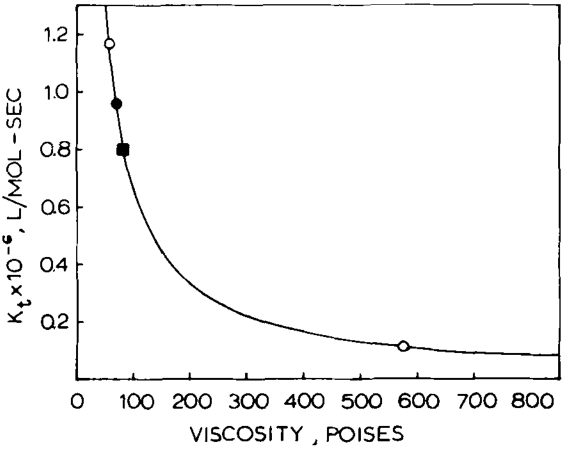

FIG. 3. Plot of termination rate constant vs. internal film viscosity for: ( ○ ) PVC-ST, data of Takamatsu and Shinohara [1]; ( ● ) PVC-ST, this report; ( ■ ) PVC-AN, this report.

TABLE 2. Summary of $k_t$ and Viscosity Values

| Viscosity (poise) | log $\eta$ | $k_t$ (l./mole-sec) | log $k_t$ | System | Reference |
|---|---|---|---|---|---|
| $1.53 \times 10^1$ | 1.19 | $4.27 \times 10^6$ | 6.63 | PVC-ST | [1] |
| $5.70 \times 10^1$ | 1.76 | $1.15 \times 10^6$ | 6.06 | PVC-ST | [1] |
| $6.80 \times 10^1$ | 1.84 | $9.6 \times 10^5$ | 5.98 | PVC-ST | This report |
| $8.15 \times 10^1$ | 1.91 | $8.0 \times 10^5$ | 5.91 | PVC-AN | This report |
| $5.85 \times 10^2$ | 2.77 | $1.12 \times 10^5$ | 5.05 | PVC-ST | [1] |
| $2.34 \times 10^3$ | 3.37 | $2.8 \times 10^4$ | 4.45 | PVC-ST | [1] |
| $4.31 \times 10^3$ | 3.64 | $1.52 \times 10^4$ | 4.18 | PVC-ST | [1] |
| $5.90 \times 10^3$ | 3.77 | $1.11 \times 10^4$ | 4.05 | PVC-ST | [1] |
| $1.07 \times 10^5$ | 5.03 | $6.1 \times 10^2$ | 2.79 | PE-ST | [9] |

the extended viscosity range, it is convenient to recast Eq. (15) in logarithmic form,

$$\log k_t + \log \eta = 7.816 \qquad (16)$$

A plot of Eq. (16) is presented in Fig. 4, which includes all of Takamatsu's $k_t$ data points for PVC-styrene as open circles.

## Grafting of Acrylonitrile on PVC Film

The radiation grafting of acrylonitrile on PVC film was also investigated. A graphical plot of percent grafting versus time is shown in Fig. 5. It is interesting that an induction period of 15 hr is observed, since this is the same as the induction period for styrene-PVC, and suggests that the period depends upon some property of the PVC film and is independent of the particular monomer used.

Values of $k_t$ and $\eta$ for the acrylonitrile/PVC system can be computed by the methods discussed above. In this case an average saturation absorption of 41.1 wt % acrylonitrile on the PVC weight was observed. Since the density of acrylonitrile equals 0.806, the saturation absorption corresponds to a monomer concentration within the

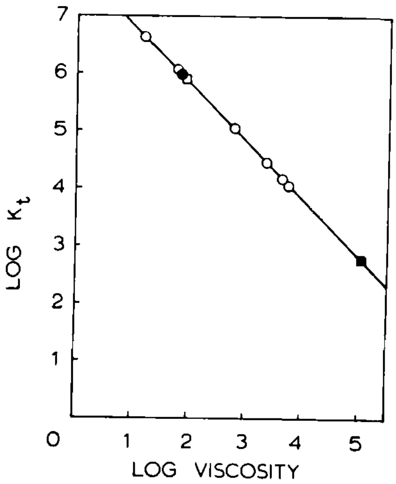

FIG. 4. Plot of log $k_t$ vs. log viscosity for the monomer-polymer systems of Table 2: ( ○ ) PVC-ST (Takematsu); ( ● ) PVC-ST ( Wilson); ( ■ ) PE-ST; ( □ ) PVC-AN.

film of 6.30 mole/liter a PVC weight fraction in the saturated film of 0.708, and a PVC content of 816 g/liter in the saturated film. Figure 5 indicates a grafting rate of 2.15 %/hr or $91.6 \times 10^{-6}$ mole/liter-sec.

Following the logic of the previous computation, the value of $k_p$ in the film is assumed to be the same as in the bulk polymerization of pure acrylonitrile. The latter has a value of $1.96 \times 10^3$ liter/mole-sec at 60° C and an activation energy of 3.9 kcal/mole [13]. Use of the Arrhenius equation would indicate a $k_p$ value of $9.37 \times 10^2$ liter/mole-sec at 23° C.

The remaining computations proceed as follows.

PVC Absorbed Dose:

$$D_{PVC} = 393 \times 0.708 \times (0.512/0.556)$$

$$= 256 \text{ rad/hr}$$

$$\phi = 256 \times 1.75 \times 10^{10}$$

$$= 448 \times 10^{10} \text{ eV/g-sec}$$

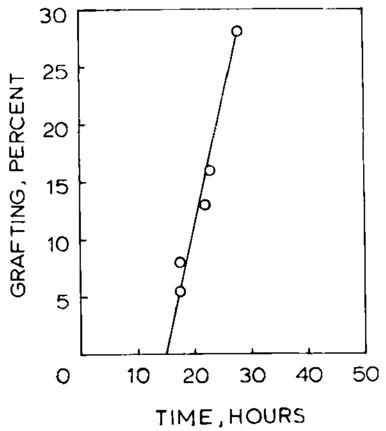

FIG. 5. Grafting vs. time for PVC-acrylonitrile at 23° C.

Rate of Initiation:

$$R_i = \frac{(3.2)(816)(448 \times 10^{10})}{(6.02 \times 10^{25})}$$

$$= 1.94 \times 10^{-10} \text{ mole/liter-sec}$$

Termination Rate Constant:

$$k_t = \frac{(9.37 \times 10^2)^2 (6.30)^2 (1.94 \times 10^{-10})}{(91.6 \times 10^{-6})^2}$$

$$= 0.804 \times 10^6 \text{ liter/mole-sec}$$

Internal Film Viscosity:

$$\eta = (6.55 \times 10^7)/(0.804 \times 10^6) = 81.5 \text{ poise}$$

The termination rate constant, $0.80 \times 10^6$ liter/mole-sec, is shown in Figs. 3 and 4 as an unfilled square at a viscosity of 82 poise. The previous report [9] indicated a $k_t$ value of $6.12 \times 10^2$ liter/mole-sec for styrene-polyethylene, corresponding to a viscosity of $1.07 \times 10^5$ poise. The viscosity point for the styrene-PE system cannot be included in Fig. 3 but is shown in Fig. 4 as a filled square.

## DISCUSSION

Figure 4 indicates a wide variation in film viscosity for the different grafting systems, ranging approximately from $10^1$ to $10^5$ poise. It is of interest that one system, styrene-PVC, covers most of this range ($10^1$ to $10^4$ poise) when the internal film concentration of the monomer is varied intentionally.

The viscosity values in Fig. 4 can be made more meaningful by reference to other types of materials of known viscosity. For example, ordinary honey has a viscosity of 115 poise at room temperature [14]. The extrusion viscosity of poly(ethylene terephthalate) at 270°C is about $2 \times 10^3$ poise [15]. Polymeric systems used as spinning solutions generally show a viscosity of about 3200 poise in the conduits leading to the spinnerets, about 2600 poise in the spinnerets, and between 900 and 100 poise in the spinning pumps [16]. At a viscosity of about $10^4$ poise a typical glass composition is in its "working range," meaning that it has enough flexibility and malleability to be worked, while retaining some firmness and strength [17].

Referring to Fig. 4, such wide variations in viscosity, through their influence on $k_t$, undoubtedly have a considerable effect on the overall rate of vinyl monomer grafting on polymeric films. However, other factors in the rate equation also have an important effect on rate, as shown by the summary in Table 3 of the kinetic data for PVC-styrene, PVC-acrylonitrile, and PE-styrene. Data for all three systems pertain to films saturated with monomer during grafting runs at 23°C. (Incident gamma radiation intensity was the same for PVC-ST and PVC-AN, but slightly greater for PE-ST than for the other two systems [9]).

Inspection of Table 3 shows that the overall grafting rate for PVC-AN is three times that for PE/ST, and the latter is 14 times that for PVC-ST. In the interpretation of these relative rate values, it should be noted that in Eq. (1) the factors $k_p$ and [M] appear to

TABLE 3. Factors Affecting Overall Grafting Rates

| | PVC-styrene[a] | PVC-acrylonitrile[a] | PE-styrene[b] |
|---|---|---|---|
| $R_p$ (mole/liter-sec) | $0.22 \times 10^{-5}$ | $9.2 \times 10^{-5}$ | $3.1 \times 10^{-6}$ |
| [M] (mole/liter) | 5.7 | 6.3 | 0.62 |
| $k_p$ (liter/mole-sec) | 44 | 937 | 44 |
| $R_i$ (mole/liter-sec) | $0.71 \times 10^{-10}$ | $1.9 \times 10^{-10}$ | $7.8 \times 10^{-10}$ |
| $k_t$ (liter/mole-sec) | $0.96 \times 10^{6}$ | $0.80 \times 10^{6}$ | $6.1 \times 10^{2}$ |
| $\eta$ (poise) | 68 | 82 | $1.1 \times 10^{5}$ |

[a] This report.
[b] Data of Wilson [9].

the first power, while $R_i$ and $k_t$ appear to the $\frac{1}{2}$ and $-\frac{1}{2}$ power, respectively. Hence, even though the PE-ST system enjoys the accelerating effect of a very high internal film viscosity, this effect is more than counterbalanced by the much larger values of $k_p$ and [M] for the PVC-AN system. On the other hand the high viscosity of the PE-ST system yields a higher grafting rate than for the PVC-ST system, because the magnitudes of [M] and $k_p$ for the latter system are not large enough to provide a counterbalancing effect.

The viscosity values presented in Table 3 are only approximately correct, partly because of the assumptions made in deriving Eq. (15), and partly because the use of the Smoluchowski equation in the first place involved the assumption that the termination step by macroradical interaction is a diffusion-controlled reaction. The latter assumption is incorrect to some extent, since the interaction of polymeric macroradicals is known [13] to require (small) activation energies of 2 to 5 kcal/mole. The interaction of macroradicals is quite a complicated reaction, as shown by the extensive studies of Schnabel [18-20]. It has been found that the rate depends in a complex way on radical size [21] and also in some way on chain flexibility and coil density [22]. Schnabel [20] has postulated that radical sites placed on loosely coiled chains will interact faster than tightly coiled macroradicals, and there is evidence for such behavior [23].

Schnabel has also used the Smoluchowski equation in studying macroradical reactions, not for estimating viscosity but for determining diffusion constants and reaction distances of the reactants [21]. His results seem to corroborate the concept of segmental diffusion as the rate-determining step in the interaction of macroradicals, a concept that has also been advanced by other investigators [24-27].

Further information of interest has been obtained by an investigation of the reverse reaction, chain scission, through fast kinetic studies carried out by the pulse radiolysis technique [28]. These studies showed that at least three different types of motion may contribute to the completion of chain scission: (1) translational motion of the center of mass, (2) segmental motion, and (3) disentanglement motion. The latter motion may be considered the reverse of overlapping or entanglement diffusion, and has been discussed by Horie [29] in connection with the mutual deactivation of macroradicals.

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