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Solvent Effects on the Rate of Radiation-Induced Grafting of Vinyl Monomers on Polymeric Films

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Solvent Effects on the Rate of Radiation-Induced Grafting of Vinyl Monomers on Polymeric Films

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ABSTRACT

Earlier work indicated that in the radiation-induced grafting of vinyl monomers on polymeric films, the plasticity of the film being grafted is determined by the Hildebrand solubility parameter of the grafting solution. Film plasticity affects the termination step of the grafting reaction, and thus strongly influences the overall rate of monomer grafting on the polymeric film.

In the grafting of styrene on nylon film, a sequence of irradiation runs was made at selected volume ratios of styrene/benzene/methanol, all grafting solutions having a constant solubility parameter value of 9.5 Under these conditions, a linear plot of grafting rate vs volume percent styrene in the grafting solution was obtained. A similar sequence of runs grafting pentafluorostyrene on nylon film at constant solubility parameter also produced a linear plot of grafting rate vs volume percent PFS.

Styrene was grafted on polyethylene film in a sequence of four

runs using styrene dissolved in methanol, ethanol, 1-propanol, and 1-butanol, each solution having the same solubility parameter of 10.4. A straight-line plot of grafting rate vs volume percent styrene was obtained under these conditions.

INTRODUCTION

The writer recently developed [1] a new theoretical approach to the rate of radiation-induced grafting of vinyl monomers on polymeric films which assesses the plasticizing efficiency of the grafting solution in terms of its Hildebrand solubility parameter. The purpose of this report is to compare the experimental grafting rate results for several monomer/polymer systems with the predictions of the theory.

Before discussing the experimental methods, it is necessary to present a brief summary of the new theory, which can be based on the following conventional equation for the rate of free radical polymerization (grafting):

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

where k_t and k_p are the rate constants for termination and propagation, respectively, R_i is the rate of initiation, and $[M]$ represents average monomer concentration within the film. Assuming that R_i is rather constant because it is based on radiation intensity, and that k_p is relatively constant because it involves the diffusion velocity of small molecules, it is deduced that the principal causes for grafting rate variation are 1) changes in $[M]$ or 2) changes in k_t due to viscosity increase or decrease within the polymeric medium.

An increase in $[M]$ can take place when a solvent is added to the monomer which causes increased penetration of the monomer into the interior of the film. A change in k_t results when a solvent is added to the grafting solution which changes the plasticizing efficiency of the grafting solution, thus changing the viscosity of the polymeric medium (film interior) where the grafting reaction takes place.

The theory postulates that the plasticizing efficiency of the grafting solution is related [2] to its cohesive energy density (CED), which is the energy of vaporization per unit volume in cal/cc:

$$CED = \frac{\Delta H_{298} - RT}{M/d} \qquad (2)$$

where ΔH_{298} is the latent heat of vaporization at 298°K, T is the absolute temperature, R is the gas constant, M is the molecular weight, and d is the density of the liquid at 298°K. Hildebrand [3] defined the solbuility parameter, δ, as the square root of the CED:

$$\delta = (CED)^{1/2} \qquad (3)$$

Mutual solubility of two substances will be observed [4] if the free energy of mixing is negative:

$$\Delta H - T\Delta S = \Delta F < 0 \qquad (4)$$

Since ΔS is always positive for polymer/solvent systems, the sign of ΔF is determined by the sign and magnitude of ΔH, the heat of mixing. If there is a strong interaction between polymer and solvent, such that ΔH is negative, the polymer will dissolve since ΔF will be negative. If there is no strong polymer/solvent interaction, ΔH being positive, the magnitude of ΔH will determine whether or not the solvent will dissolve the polymer. Only solvents that produce small ΔH values will dissolve the polymer, and the smaller ΔH the better the solvent [4, 5]. In selecting an effective solvent (or plasticizer), one tries to make ΔH as small as possible by minimizing $|\delta_p - \delta_s|$, since ΔH is proportional to $(\delta_p - \delta_s)^2$ according to Hildebrand [3]. In these expressions, δ_p and δ_s are the parameter values for polymer and solvent, respectively. Since efficient plasticization is correlated with large k_t, the rate of grafting should become larger as $|\delta_p - \delta_s|$ increases, other things being equal. In other words, for efficient plasticization one attempts to minimize $|\delta_p - \delta_s|$, but for faster grafting one attempts to maximize $|\delta_p - \delta_s|$.

Work with δ values and CED values is facilitated by the fact that lists of such values for many substances have been compiled by Hildebrand [3], Immergut [4], and others [2, 5].

In many radiation-induced film grafting studies described in the literature, irradiation runs were made with various amounts of solvent added to the monomer, and then grafting rate was plotted as a function of monomer concentration in the grafting solution. The resulting curve often passed through a maximum at a particular concentration of added solvent. Examples of such behavior include the radiation-induced grafting of methyl acrylate on polyethylene in the presence of added methanol [6]; pentafluorostyrene on polyethylene with added acetone [1]; pentafluorostyrene on nylon with added methanol [1]; tert-butylaminoethylmethacrylate on polyethylene with added n-hexane [6]; and styrene on nylon with added methanol [1].

The complicated shape of such rate vs concentration curves is probably due to the simultaneous variation of [M] and k_t in Eq. (1). More simple kinetic behavior might result in some cases if k_t were held constant, which could be accomplished by adjusting the compositions of the grafting solutions so as to hold the δ value constant (since k_t depends on the internal plasticity of the film, which depends in turn on the δ value of the grafting solution [5]). Experimental sequences of grafting runs at constant δ values are described below for the pentafluorostyrene/nylon and styrene/nylon systems.

EXPERIMENTAL TECHNIQUE

The ^{60}Co source and the method of reproducibily placing samples in the source has been described [7]. Careful positioning of film sample and grafting solution resulted in good reproducibility of rate measurements. An exposure dose rate of 540 R/hr was measured by ferrous sulfate dosimetry [8].

Film samples used in the individual runs weighed 0.01 to 0.02 g. The polyamide film was a nylon 6 film of 0.0080 in. thickness supplied by Nylonic Engineering of Herts, England. All nylon samples were stored in a desiccator before use to prevent any change in rate being caused by a variation in water content. The polyethylene film samples were of 0.93 density and 0.0120-in. thickness, and were supplied by Consolidated Thermoplastics of Woonsocket, Rhode Island.

The 2,3,4,5,6-pentafluorostyrene (PFS) from PCR Incorporated was washed three times with 10% aqueous sodium hydroxide solution, then three times with distilled water, and stored over anhydrous calcium sulfate at refrigerator temperature prior to use. Styrene was handled in the same way, and was also distilled at reduced pressure.

The following solvents of reagent grade were obtained for use in this work: methanol, ethanol, 1-propanol, 1-butanol, benzene, and pentafluorobenzene (PFB). Each solvent was stored in its bottle over anhydrous calcium sulfate for several days prior to use, and then always used from the same bottle throughout the course of the investigation. These precautions were necessary to produce comparable grafting rates, since the slightest change in water content of the grafting solution can sometimes cause a significant change in grafting rate.

Just prior to making a run, the grafting solution of styrene or PFS was freed of oxygen by freeze-thaw cycling in a vacuum system already described [7]. The reaction tube containing film and deoxygenated grafting solution was frozen down and sealed from the vacuum system while pumping, then placed inside the ^{60}Co source in the predetermined position.

After making a run, the PFS-grafted samples of nylon were extracted by stirring in warm acetone for 2 days, while styrene-grafted samples were extracted by stirring in warm benzene. Such extractions were carried out to remove homopolymer formed within the films. In each extraction a blank film sample was extracted which had not been grafted, and any weight loss observed was used to correct the percent grafting computation for the corresponding grafted film.

All grafting runs were made at the temperature of the irradiation room, 23 ± 1°C. Percent grafting was calculated from original film weight (P_0) prior to grafting, and the weight after grafting and drying to constant weight (P_g) by use of

$$\text{percent grafting} = \left[\frac{P_g - P_0}{P_0}\right] \times 100 \qquad (5)$$

The weight of the monomer-swollen film (P_s) at the end of each run was measured by quickly blotting the film between filter papers and then weighing it in a closed weighing bottle. The percent swelling (uncorrected for homopolymer content) was computed as

$$\text{percent swelling} = \left[\frac{P_s - P_0}{P_0}\right] \times 100 \qquad (6)$$

EXPERIMENTAL RESULTS

PFS/Nylon System

When an attempt is made to graft dry PFS on nylon film, little or no grafting takes place [9]. Addition of methanol to the PFS aids penetration of the nylon film and produces a large and easily measured rate of grafting [1]. This behavior is similar to that of many monomer/polymer systems, with the rate vs concentration curve passing through a maximum at some particular concentration of added solvent.

According to the theory outlined above, the observed behavior should be simpler if the δ value of the grafting solution (and hence k_t) could be held constant, which should not be difficult to arrange.

Suppose it is first decided to hold methanol concentration constant at 10 vol% throughout a planned sequence of runs. Assuming a δ value of 6.7 for PFS and 14.3 for methanol [2], the δ value for a 90/10 volume ratio of PFS/methanol can readily be estimated:

$$\text{CED} = (0.9)(6.7)^2 + (0.1)(14.3)^2 = 60.9 \tag{7}$$

$$\delta = (60.9)^{1/2} = 7.8 \tag{8}$$

In order to hold the δ value of the solution constant at 7.8, it would be necessary to replace various amounts of the PFS by an auxiliary solvent having the same δ value as the PFS. While the δ value for PFB is not known, it is known that the δ value for benzene, 9.2, is the same as the value for styrene. Hence, it is reasonable to assume that the δ value for PFB is approximately the same, 6.7, as for PFS.

Table 1 shows a planned sequence of grafting solution compositions (Runs 1F-10F) in which the methanol concentration is held constant at 10 vol%, while the PFS concentration is varied from 25 to 90 vol%,

TABLE 1. PFS/Nylon Runs

Run no.	PFS (vol%)	PFB (vol%)	Methanol (vol%)	Solution δ value	Run length (hr)	Grafting (%)
1F	25	65	10	7.8	21.5	11.9
2F	25	65	10	7.8	28.8	15.1
3F	25	65	10	7.8	44.7	28.9
4F	45	45	10	7.8	22.2	21.2
5F	45	45	10	7.8	29.3	31.5
6F	45	45	10	7.8	48.5	51.3
7F	70	20	10	7.8	22.7	30.8
8F	70	20	10	7.8	29.2	44.8
9F	90	0	10	7.8	18.9	35.9
10F	90	0	10	7.8	28.5	80.5
11F	40	0	60	11.9	19.2	58.5
12F	60	0	40	10.4	17.7	62.7
13F	80	0	20	8.8	17.5	45.6

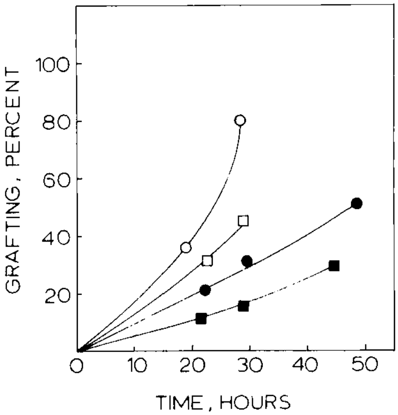

FIG. 1. Percent grafting of PFS on 0.0080 in. nylon 6 film vs hours of irradiation. (■) 25% PFS; (●) 45% PFS; (□) 70% PFS; (○) 90% PFS (see Table 1).

in each case adding enough PFS so that the total of PFS plus PFB equals 90 vol%. The key to the method is the choice of the auxiliary solvent, PFB, which has the same δ value as PFS and can replace any reduction in PFS to give overall constancy in δ value for the total solution.

Grafting runs on 0.0080 in. nylon 6 films were carried out using the grafting solution compositions of Table 1, and the results are presented as percent grafting vs time plots in Fig. 1. The highest rate of grafting is for the solution containing 90% PFS, and the lowest rate is for the 25% PFS solution. All of the curves show a change in rate as irradiation continues, which is not surprising because the substrate film composition is changing as grafting proceeds. A study of the curves shows that the faster the grafting proceeds, generally speaking, the faster the rate of grafting changes.

Only the initial grafting rates in Fig. 1 are valid for substitution in Eq. (1), because only the initial rate applies to grafting on pure nylon. The dotted line with open points in Fig. 2 is a plot of initial grafting rate in percent/hour vs PFS concentration in volume percent in the grafting solution. The upper solid curve through filled points corresponds to Runs 11F, 12F, and 13F made at variable δ values with only PFS and methanol in the grafting solution. The solid curve through the maximum represents the typical plot that is obtained when only methanol is added to the monomer and no attempt is made to hold the δ value constant. The peak in this latter curve was delineated by the use of single 1-day runs, the rate in each case being taken as the

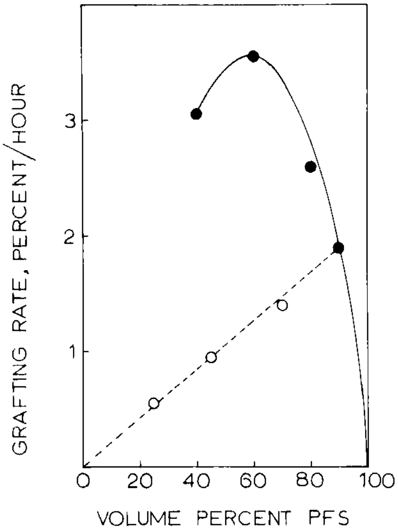

FIG. 2. Grafting rate of PFS on 0.0080 in. nylon 6 film vs volume % PFS. (--) constant methanol concentration and δ value constant at 7.8. (——) Variable methanol concentration and variable δ value (see Table 1).

percent grafting divided by the run duration in hours (Runs 11F, 12F, and 13F).

Knowing the slope of the dotted line in Fig. 2, the proportionality between rate and PFS concentration becomes

$$\%/\text{hr} = 0.0198[\text{PFS}] \qquad (9)$$

where [PFS] is the volume percent concentration of PFS in the grafting solution. If it is assumed that the average concentration of PFS in the film is proportional to its concentration in the solution, then the grafting rate is proportional to the first power of monomer concentration in the film, in agreement with the conventional polymerization kinetics indicated by Eq. (1).

A plot of percent swelling vs percent grafting for Runs 1F-10F of Table 1 is shown in Fig. 3. Most of the data points fall close to the straight line. Minor deviations from the line may be the fault of the experimental technique in removing too much or too little monomer from the swollen film prior to weighing. It is of interest that the linear

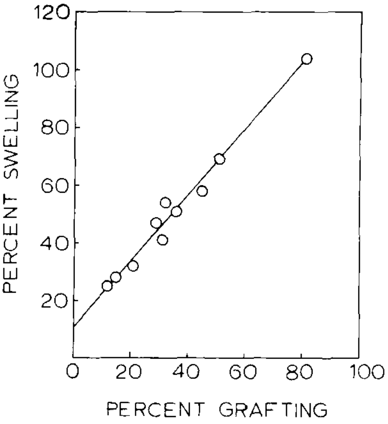

FIG. 3. Percent swelling vs percent grafting for PFS/nylon samples; δ value of 7.8 for all grafting solutions (see Table 1).

plot in Fig. 3 results in spite of the wide variations in composition of the grafting solution (at constant δ). This behavior is in agreement with the comments of Doolittle [5], who theorized that the extent of swelling of the polymer depends on the δ value of the surrounding solution rather than on its composition.

Styrene/Nylon System

A planned series of runs for styrene/nylon was also carried out, similar to the series for PFS/nylon in that the δ value for the grafting solution was held constant while monomer concentration was varied. The solution compositions for the runs are presented in Table 2. Benzene was chosen as the auxiliary solvent because it has the same δ value, 9.2, as styrene. Methanol concentration was held constant at 5% by volume for Runs 1S through 8S. In these eight runs the δ value of the grafting solution was held constant at 9.5, which can readily be verified by the computational methods already described.

Percent grafting vs time plots at the different styrene concentrations are shown in Fig. 4. As in the PFS/nylon system, the slope of each curve changes with time, and the more rapid the grafting the more rapid the change in the rate of grafting (corresponding to the more rapid change in the composition of the substrate film).

The initial grafting rates computed from Fig. 4 are plotted against styrene concentration in Fig. 5, resulting in a straight-line plot (dotted line with open points). The upper solid curve with filled

TABLE 2. Styrene/Nylon Runs

Run no.	Styrene (vol%)	Benzene (vol%)	Methanol (vol%)	Solution δ value	Run length (hr)	Grafting (%)
1S	25	70	5	9.5	28.5	29.5
2S	25	70	5	9.5	45.7	58.5
3S	50	45	5	9.5	21.1	40.7
4S	50	45	5	9.5	44.4	133
5S	70	25	5	9.5	18.1	42.6
6S	70	25	5	9.5	28.8	122
7S	95	0	5	9.5	21.4	79.0
8S	95	0	5	9.5	28.2	152
9S	80	0	20	10.4	23.7	158
10S	60	0	40	11.5	21.7	120

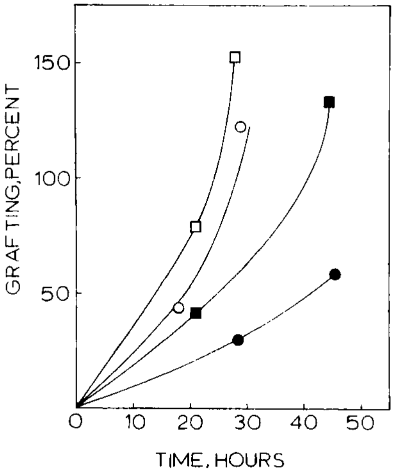

FIG. 4. Percent grafting of styrene on 0.0080 in. nylon 6 film vs hours of irradiation. (●) 25% styrene; (■) 50% styrene; (○) 70% styrene; (□) 95% styrene (see Table 2).

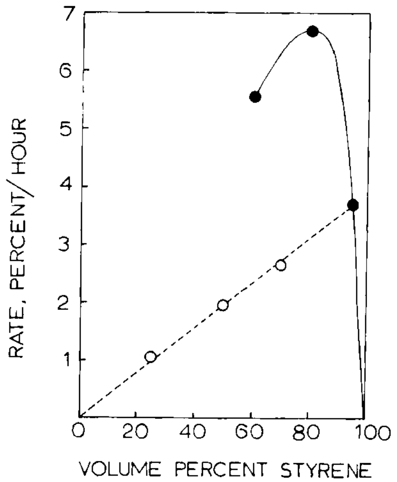

FIG. 5. Grafting rate of styrene on 0.0080 in. nylon 6 film vs volume % styrene. (--) Constant methanol concentration and δ value constant at 9.5. (——) Variable methanol concentration and variable δ value (see Table 2).

points corresponds to runs 9S and 10S, made at variable δ values with only styrene and methanol in the grafting solution. The solid curve illustrates the behavior commonly observed when no attempt is made to hold the δ value of the grafting solution constant. From the slope of the line in Fig. 5, the rate dependence on styrene concentration can be expressed as

$$\%/\text{hr} = 0.0387\,[\text{styrene}] \qquad (10)$$

where [styrene] is the volume percent concentration of styrene in the grafting solution. If it is assumed that the average concentration of styrene in the film is proportional to its concentration in the grafting solution, then the grafting rate is again proportional to the first power of monomer concentration in the film.

Figure 6 presents a graph of percent swelling vs percent grafting for Runs 1S through 8S. Again the points lie close to a straight line, just as was observed for the PFS/nylon system.

Styrene/Polyethylene System

The PFS/nylon and styrene/nylon systems both involve acceleration in grafting by methanol owing to the improved penetration of

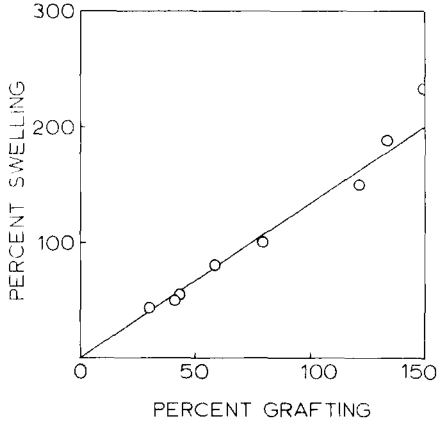

FIG. 6. Percent swelling vs percent grafting for styrene/nylon samples. δ value of 9.5 for all grafting solutions (see Table 2).

monomer into the film in the presence of methanol. Another type of acceleration is exhibited when methanol is added to the styrene/polyethylene grafting system. In the latter system, according to the theory, the high δ value (14.3) of methanol increases the δ value of the grafting solution, thus increasing $|\delta_p - \delta_s|$, since δ_p for polyethylene is 8.5. The increased value of $|\delta_p - \delta_s|$ corresponds to reduced plasticizing efficiency of the grafting solution, which reduces k_t, thereby increasing the overall rate according to Eq. (1).

It is also possible to raise the δ value of the grafting solution by adding ethanol to styrene, but more ethanol than methanol must be used for an equivalent effect because the δ value for ethanol is only 12.7. In order to compare the effects of adding different alcohols, a selected sequence of grafting solution compositions was prepared as shown in Table 3, in which the δ value of the grafting solution is held constant at 10.4 by adjusting the alcohol/styrene ratio. Each grafting solution in the table contains 20 vol% benzene to insure mutual solubility of all components during the irradiation run, including any homopolymer formed from the styrene.

A single 1-day run was carried out for each grafting solution in Table 3, the grafting rate being taken as the percent grafting divided by the duration of the run in hours. Figure 7 presents a plot of the computed grafting rate vs the volume percent styrene in the grafting solution, which shows a linear relation between grafting rate and

TABLE 3. Styrene/Polyethylene Runs

Run no.	Styrene (vol%)	Benzene (vol%)	Auxiliary solvent[a]	Auxiliary solvent (vol%)	Solution δ value	Run length (hr)	Grafting (%)
1A	60	20	methanol	20	10.4	22.2	36.8
2A	49	20	ethanol	31	10.4	20.7	26.9
3A	38	20	1-propanol	42	10.4	21.4	21.7
4A	27	20	1-butanol	53	10.4	20.9	16.9

[a] The following δ values were employed: methanol, 14.3; ethanol, 12.7; 1-propanol, 11.9; 1-butanol, 11.4.

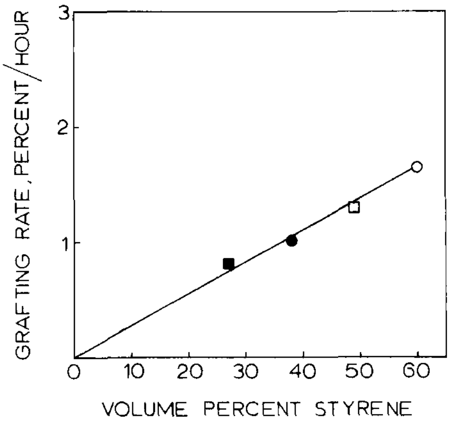

FIG. 7. Grafting rate of styrene on 0.0120 in. polyethylene film vs volume percent styrene. Added solvents as follows: (○) methanol; (□) ethanol; (●) 1-propanol; (■) 1-butanol (solution compositions in Table 3).

styrene concentration. Computation of the slope of the line indicates that

$$\%/\text{hr} = 0.0278[\text{styrene}] \qquad (11)$$

where [styrene] is the volume percent concentration of styrene in the grafting solution. If the concentration of styrene in the film is proportional to its concentration in the grafting solution, then the grafting rate is again proportional to the first power of [M] as indicated in Eq. (1).

While the data of Fig. 7 are limited in scope to only four solvents, they would appear to indicate that the accelerating effect of the added solvent depends on its δ value rather than on its chemical composition or on some other property. It is evident that such simple behavior would not be shown by any added solvent which functions as a chemical retarder or accelerator of polymerization.

Figure 8 presents a plot of percent swelling vs percent grafting for the runs of Table 3. The data points fall close to a straight line in spite of the wide variation in composition of the grafting solutions. The fact that the points do not fall on the line may be due to the experimental error in the swelling measurement. The approximately linear plot shown in the graph is in accordance with Doolittle's [5]

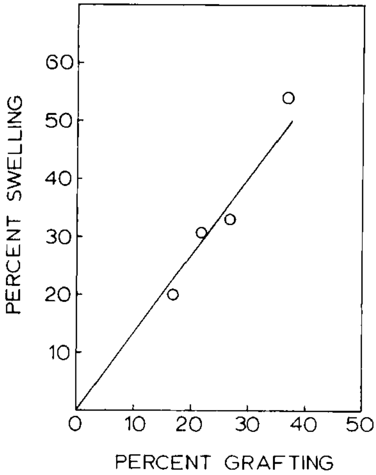

FIG. 8. Percent swelling vs percent grafting for styrene/PE samples. δ value of 10.4 for all grafting solutions (see Table 3).

comment that the amount of polymeric swelling depends on the δ value of the surrounding solution rather than on its chemical composition.

The fact that polyethylene contains both amorphous and crystalline regions does not disturb the application of the theory to the styrene/polyethylene system, providing [M] is considered to be an average concentration over both types of region. This can be shown by consideration of a hypothetical example in which f_a and f_c represent volume fractions of amorphous and crystalline material, respectively. Let $[M]_e$ equal monomer concentration in the external grafting solution, and assume that $C_a[M]_e$ and $C_c[M]_e$ represent monomer concentration in amorphous and crystalline regions, respectively, where C_a and C_c are proportionality constants. If the grafting rate equals K_a times monomer concentration in the amorphous region, and K_c times monomer concentration in the crystalline region, the total rate of grafting for unit film volume can be written

$$\text{total rate/unit volume} = f_aK_aC_a[M]_e + f_cK_cC_c[M]_e \qquad (12)$$

$$= (f_aK_aC_a + f_cK_cC_c)[M]_e \qquad (13)$$

indicating that the total rate is proportional to the styrene concentration in the grafting solution. The straight line plot in Fig. 7 tends to confirm the additivity of rates in the amorphous and crystalline regions indicated by Eq. (13). In connection with the use of an average value of [M], it should be noted that [M] may also represent an average across the thickness of the film, since the monomer concentration under some conditions is much less in the center of the film than it is at the film surfaces [10].

DISCUSSION

If the number of solvents used in constructing Fig. 7 were to be increased from four to eight or ten, the theories of Doolittle [5] and Hildebrand [3] indicate that the data points for all such solvents would fall close to the same straight line in Fig. 7, regardless of the chemical nature of such solvents. If any solvent data points deviated from the line, it would appear appropriate to correct the δ values for those solvents so as to cause their points to fall on the line. The calibration of solvent δ values could thus be based on grafting rates involving radical recombination in a viscous (polymeric) medium. Such a set of δ values would be self-consistent, and would probably be more valid for present purposes than δ values from the literature that were determined by some other method. (It has been noted that the δ value for a particular substance may vary considerably, depending on the method of measurement [1]). While such a set of δ values would be consistent for the monomer/polymer grafting system employed in their measurement, it would have to be determined by further experimentation whether the set would also be consistent for other monomer/polymer systems, or even for the grafting of other monomers on the same polymer.

A common practice in published monomer/polymer grafting studies has been to plot grafting rate vs added solvent concentration, generally producing a curve passing through a maximum and having a fairly complicated shape. Such curves are difficult to interpret in a quantitative way, and the present research indicates that their shape may depend on the simultaneous variation of [M] and k_t in Eq. (1).

It now appears that a simplified kinetics picture may be obtained in such cases by irradiating a selected sequence of grafting solution compositions having the same δ value (and hence the same k_t) but different values of [M]. The present work demonstrates that such a procedure may lead to a linear plot of grafting rate vs monomer concentration in some monomer/polymer systems. Following are some new interpretations of monomer/polymer grafting systems described in the literature, and suggestions for applying a modified experimental approach which may lead in each case to a linear plot of rate vs [M].

Methyl Acrylate/Teflon Plus Methanol [11]

The addition of methanol in this case gives a strong accelerating effect. The addition of methanol (δ value 14.3) to the monomer would tend to increase $|\delta_p - \delta_s|$, since Teflon has a δ value of only 6.2. It would be of interest to make a series of runs at constant methanol concentration, the balance of the solution being made up of various ratios of methyl acrylate to auxiliary solvent, the auxiliary solvent being chosen to have the same δ value as methyl acrylate.

Styrene/Polyethylene Plus 2-Propanol [12, 13]

The addition of 2-propanol (estimated δ value 11.5) accelerates the grafting of styrene (δ value 9.2) on polyethylene (δ value 8.5) corresponding to an increase in $|\delta_p - \delta_s|$. It might prove interesting to hold the propanol concentration constant at about 30%, while varying the ratio of styrene/benzene, using benzene as the auxiliary solvent (δ value 9.2).

Styrene/Polyethylene Plus Methanol [1, 14-17]

A number of investigators have studied this system, and have noted that the addition of methanol (δ value 14.3) accelerates the grafting of styrene (δ value 9.2) on polyethylene (δ value 8.5), probably due to an increase in $|\delta_p - \delta_s|$ according to the theory. A constant δ value series of runs could be set up by holding methanol at 20% concentration while varying the ratio of styrene/benzene, making use of benzene (δ value 9.2) as the auxiliary solvent. The probability of a straight line plot of grafting rate vs styrene is excellent for this system in view of the strong evidence from Fig. 7 that the grafting rate is first order in styrene concentration.

Acrylonitrile/Polyvinylchloride Plus Hexane [18]

The addition of hexane (δ value 7.3) to acrylonitrile was found to accelerate its radiation-induced grafting on PVC (δ value 9.7). In this system the hexane of very low δ value increases $|\delta_p - \delta_s|$ because of the relatively high δ value of the PVC. A sequence of constant δ value runs could be constructed by holding the hexane concentration constant, while varying the ratio of acrylonitrile to auxiliary solvent, the latter selected to have the same δ value as the acrylonitrile. (When an auxiliary solvent of correct δ value cannot be found, it is possible to use a combination of two solvents having the correct average δ value.)

2,2,2-Trifluoroethyl Methacrylate (TFEM)/Nylon Plus Methanol [9]

Addition of methanol (δ value 14.3) accelerates the grafting of TFEM on nylon (δ value 13.6). In this system the methanol probably acts to aid the penetration of TFEM into the nylon, just as in the grafting of PFS on nylon. A series of constant δ value runs could be prepared by holding the methanol concentration constant at 20% while varying the ratio of TFEM to an auxiliary solvent, the latter having the same δ value as the TFEM.

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