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Rate-Controlling Factors in the Radiation-Induced Grafting of Pentafluorostyrene on Nylon and Polyethylene

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ABSTRACT

Radiation-induced grafting rates for pentafluorostyrene on nylon film were compared with those for pentafluorostyrene/polyethylene, styrene/nylon, and styrene/polyethylene. The effect of added methanol and/or acetone on grafting rate was determined for each system. Accelerating and retarding effects were interpreted in terms of how changes in the grafting solution affect termination rate and monomer concentration in the film. The effect of the grafting solution on termination rate appeared to depend upon the plasticizing efficiency of the grafting solution, as estimated from the difference in Hildebrand solubility parameters of the grafting solution and polymeric film. The grafting of minor amounts of pentafluorostyrene on nylon film greatly reduces its rate of water vapor absorption in a humid atmosphere, and considerably improves the clarity of the film.

INTRODUCTION

This report describes the continuation of the investigation of the radiation-induced grafting of fluorinated monomers on polyamide films.

Earlier work [4] showed that the radiation-induced grafting of pentafluorostyrene (PFS) on nylon 6 film is strongly accelerated by the addition of methanol to the PFS. Objectives of the present work included the investigation of the nature of the accelerating effect of methanol and the effect of added solvents in general. Another objective was to study the properties of nylon films containing grafted PFS.

Experimental approaches included the comparison of grafting rates for the PFS/nylon system with those for PFS/polyethylene, styrene/nylon, and styrene/polyethylene. The effect of added methanol and/or acetone on grafting rate was determined for each system. Using a semimicro balance, the saturation absorption of the various grafting solutions was measured for both nylon and polyethylene. Similar saturation absorption studies were made on polyethylene and nylon containing various amounts of grafted PFS. These studies helped to develop a possible explanation for the accelerating or retarding effects of added solvents.

EXPERIMENTAL TECHNIQUE

A 0.5-Ci ^{60}Co source was used as described previously [2, 4]. Each sample of film employed in an individual run measured about 0.4 by 1.0 cm. In making a run the film sample, together with monomer, was placed in a reaction cell or tube of about 0.5 cm i.d., which was reproducibly positioned in the horizontal center hole of the hollow cylindrical source as discussed earlier [2]. Careful positioning resulted in good reproducibility of rate measurements, with the curve of percent grafting vs time being linear in most cases. An exposure dose rate of 560 R/hr was determined by ferrous sulfate dosimetry [5].

The polyamide film was a nylon 6 film of 0.0080 in. thickness supplied by Nylonic Engineering, Herts, England. Since polymer films generally vary in thickness, the samples were cut from sections of the correct thickness after measurement with a micrometer. All nylon samples were stored in a desiccator prior to use to avoid a possible effect of water content on reaction rates. The polyethylene samples of 0.93 density and 0.0120-in. thickness 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.

Both styrene and PFS were freed of oxygen just prior to making a run by a freeze-thaw cycling in a vacuum system as already described [2, 3]. The reaction tube containing film and deoxygenated monomer 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 sample of nylon or polyethylene was extracted by stirring in warm acetone for 2 or 3 days. This was done to remove any PFS homopolymer from the film, since acetone had been shown to be a good solvent for polymeric PFS. Styrene-grafted nylon or polyethylene samples were freed of polystyrene homopolymer by stirring in warm benzene for 2 or 3 days.

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 weight after grafting and drying to constant weight (P_g) by the use of:

$$\text{percent grafting} = \left[\frac{P_g - P_0}{P_0}\right] \times 100 \tag{1}$$

In most cases the weight of the monomer-swollen film (P_s) at the end of the 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 by

$$\text{percent swelling} = \left[\frac{P_s - P_0}{P_0}\right] \times 100 \tag{2}$$

In measurements of monomer or solvent uptake in the absence of radiation, and in water vapor absorption studies on PFS-grafted nylon, film weights were determined with a Mettler H2O semimicro balance, which gave weight readings to 0.01 mg.

RESULTS

PFS/Nylon System

Figure 1 presents percent grafting vs time for PFS/methanol at a 60/40-volume ratio on 0.008 in. nylon film. Earlier work had shown

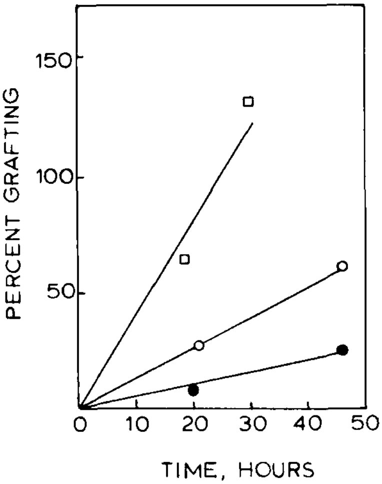

FIG. 1. Percent grafting vs time for PFS on 0.008 in. nylon film: (□) PFS/methanol, 60/40; (○) PFS/acetone/methanol, 60/20/20; and (●) PFS/acetone/methanol, 60/30/10.

that PFS will not graft on nylon in the absence of methanol [4].

Figure 1 also shows the effect of using 60/20/20 and 60/30/10 volume ratios of PFS/acetone/methanol. The addition of the acetone has a strong retarding effect on the grafting reaction. The reduction of methanol concentration to 50 and 25% of its original value reduces the grafting rate to 26 and 12% of its original value, respectively.

Figure 2 presents a plot of percent uncorrected swelling vs percent grafting for the PFS/nylon system. The curve is linear, indicating a constant swelling/grafting ratio of 1.29. Other studies have indicated a constant ratio of swelling to grafting in certain monomer/polymer systems, as in the grafting of styrene on polymethylpentene [2]. The new feature in Fig. 2 is that the constancy of the ratio is preserved regardless of the relative amounts of methanol and acetone in the grafting solution.

PFS/Polyethylene System

In the PFS/polyethylene system, grafting takes place when monomer alone is present without added solvent, as demonstrated in Fig. 3. In this system, however, the acetone accelerates grafting while methanol causes retardation.

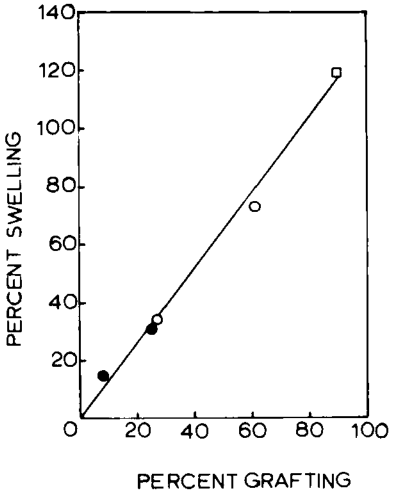

FIG. 2. Percent swelling vs percent grafting on 0.008 in. nylon film: (□) PFS/methanol, 60/40; (○) PFS/acetone/methanol, 60/20/20; and (●) PFS/acetone/methanol, 60/30/10.

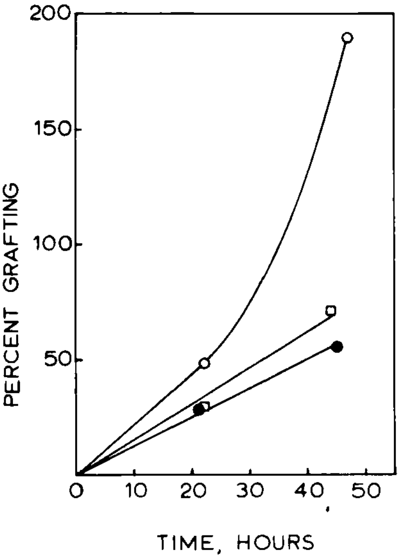

FIG. 3. Percent grafting vs time for PFS on 0.012 in. PE film: (□) PFS alone; (●) PFS/methanol, 60/40; and (○) PFS/acetone, 60/40.

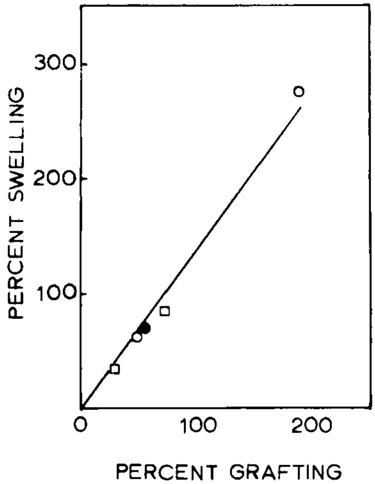

FIG. 4. Percent swelling vs percent grafting on 0.012 in. PE film; (□) PFS alone; (●) PFS/methanol, 60/40; and (○) PFS/acetone, 60/40.

A plot of percent uncorrected swelling vs percent grafting is presented in Fig. 4. Again, the swelling/grafting ratio remains the same regardless of the relative amounts of acetone and methanol. In this case the swelling/grafting ratio equals 1.38, which is not greatly different from the value for the PFS/nylon system.

Styrene/Nylon System

Grafting vs time plots for the styrene/nylon system are presented in Fig. 5. This is another system in which no grafting takes place in the absence of methanol. Replacement of 50% of the methanol with acetone reduces the rate to about 41% of its original value.

Swelling vs grafting (Fig. 6) for the styrene/nylon system is seen to be linear. The swelling/grafting ratio equals 1.53, which is much larger than the corresponding value for PFS/nylon or PFS/polyethylene.

Styrene/Polyethylene System

Grafting curves for styrene alone on polyethylene, and for styrene containing acetone or methanol, are presented in Fig. 7. Methanol has a strongly accelerating effect, with a steeply rising curve

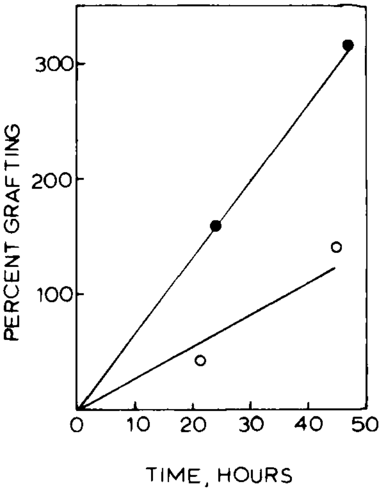

FIG. 5. Percent grafting vs time for styrene on 0.008 in. nylon film: (●) styrene/methanol, 80/20; and (○) styrene/methanol/acetone, 80/10/10.

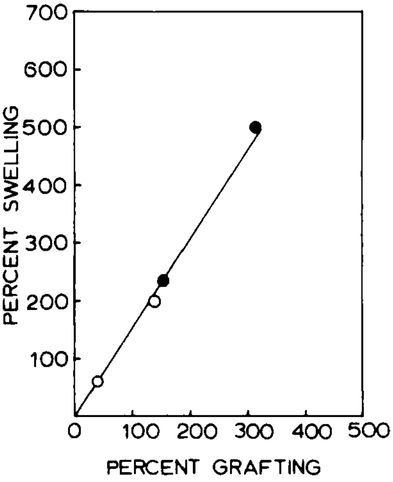

FIG. 6. Percent swelling vs percent grafting on 0.008 in. nylon film: (●) styrene/methanol, 80/20; and (○) styrene/methanol/acetone, 80/10/10.

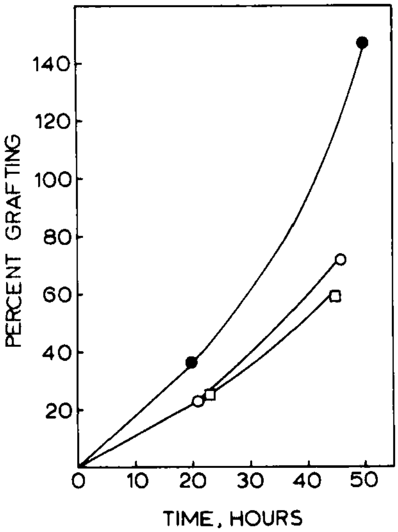

FIG. 7. Percent grafting vs time for styrene on 0.012 in. PE film: (□) styrene alone; (●) styrene/methanol, 80/20; and (○) styrene/acetone, 80/20.

suggesting an autocatalytic reaction. Acetone has little or no effect on the rate. The slight acceleration observed with acetone is probably within the limits of experimental error.

A plot of percent uncorrected swelling vs grafting (Fig. 8) again shows a linear shape. The swelling/grafting ratio of 1.67 is not much different from that for styrene/nylon, but is much larger than the value for PFS on either polyethylene or nylon.

The swelling/grafting ratios for all of the monomer/polymer systems investigated are summarized in Table 1. In all four systems the swelling/grafting ratios are essentially independent of the acetone/methanol ratio. The value of uncorrected swelling was determined for each film just at the end of the run when absorbed monomer and unextracted homopolymer were still present in the film. Hence the constancy of the swelling/grafting ratio in all systems implies either that essentially all homopolymer was removed by the extraction technique, or else that a consistently constant fraction of homopolymer was removed in all extractions and that the ratio of homopolymer/graft polymer was constant for each monomer/polymer system. In this connection it is worth noting that the extraction time was not constant but ranged from 2 to 3 days in duration.

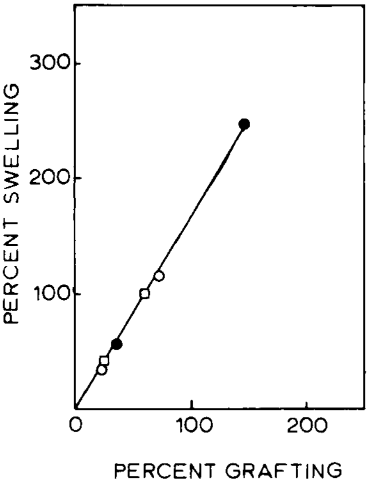

FIG. 8. Percent swelling vs percent grafting on 0.012 in. PE film; (□) styrene alone; (●) styrene/methanol, 80/20; and (○) styrene/acetone, 80/20.

TABLE 1. Swelling/Grafting Ratios

Monomer/polymer system	Swelling/grafting ratio
PFS/nylon	1.29
PFS/PE	1.38
Styrene/nylon	1.53
Styrene/PE	1.67

Effect of Grafting on Film Properties

The water vapor absorption of a series of PFS-grafted nylon films was measured by placing suitable 0.01 g samples in a desiccator at 57% relative humidity. The atmosphere in the desiccator was maintained at this relative humidity at room temperature by means of a saturated aqueous solution of sodium bromide in the bottom of the desiccator. The film samples were dry when placed in the desiccator, and were weighed periodically on the semimicro balance as they gradually absorbed water.

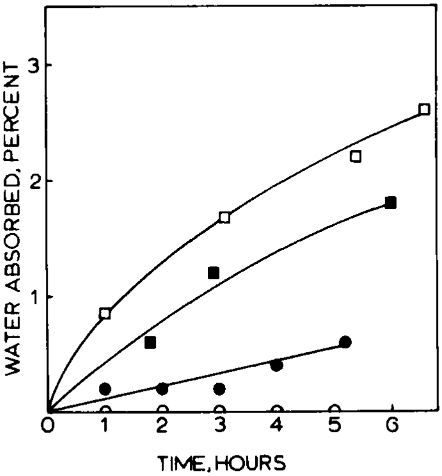

FIG. 9. Percent water absorbed vs time for 0.008 in. nylon film in 57% relative humidity at room temperature: (□) ungrafted nylon; (■) nylon plus 8% PFS; (●) nylon plus 26% PFS; (○) nylon plus 61% PFS.

Figure 9 presents plots of weight per cent water absorbed vs time for nylon films containing 8, 26, and 61% grafted PFS, and for the ungrafted nylon control film. Even 8% grafted PFS produced a significant retardation of water absorption, while the sample having 61% grafted PFS had absorbed no detectable amount of water after 5 hr. After 1 day at 57% relative humidity, the film with 26% grafted PFS had absorbed only 1.8 wt% of water, as compared to 3.9% for the ungrafted nylon control film.

These effects can be explained in terms of the δ values for PFS and water, employing theories outlined below in the Discussion Section. In brief, the low δ value for PFS ($\delta = 6.7$) makes it highly incompatible with water which has a very high δ value ($\delta = 23.4$). Hence, as increasing amounts of PFS are grafted on the nylon, it becomes less capable of absorbing water. Similar comments would apply concerning the grafting of other fluorinated monomers on polymeric films. Grafting of such monomers would be advantageous on films like polyvinyl alcohol, which has many desirable properties but lacks water resistance.

The grafting of a few percent of PFS appeared to improve the transparency of both nylon and polyethylene films.

DISCUSSION

Previous Work

The accelerating effect of certain solvents on various monomer/polymer grafting pairs has been known for a long time. Previous investigators have explained solvent accelerating effects by postulating that the solvent does one or more of the following things:

1. Absorbs radiation energy and efficiently transfers energy to the grafting system, in the manner of a sensitizer.
2. Aids penetration of monomer into polymer.
3. Produces a Trommsdorf effect, whereby the solvent tends to immobilize or curl up the growing polymer chains inside the polymer film, thus slowing down termination by radical combination and increasing the overall polymerization rate.

In regard to Hypothesis 1, it is difficult to accept methanol as a sensitizer that accelerates the grafting of PFS on nylon (Fig. 1) but retards the grafting of PFS on polyethylene (Fig. 3). A similar difficulty arises in the case of acetone, which accelerates the grafting of PFS on polyethylene (Fig. 3) but retards the grafting of PFS on nylon (Fig. 1).

Hypothesis 2 has some experimental support, but is probably not always the dominant factor. For example, PFS/acetone grafts more rapidly on polyethylene than PFS alone (Fig. 3), even though the percent of PFS/acetone absorbed by polyethylene is less than the percent of PFS alone absorbed (Table 2). Furthermore, styrene/methanol grafts more rapidly on polyethylene than styrene alone (Fig. 7), although the percent of styrene/methanol absorbed by polyethylene is less than the percent of styrene alone that is absorbed (Table 2).

In considering Hypothesis 3, there is no doubt that a Trommsdorf effect exists in a medium as highly viscous as the interior of a polymeric film. The significant question is whether the grafting solution intensifies or diminishes the existing Trommsdorf effect, thus causing acceleration or retardation of grafting, respectively.

Takamatsu [6] was perhaps the first to note that absorbed monomer can plasticize the polymeric film and hence expedite the termination reaction. In studying the radiation-induced grafting of styrene on polyvinyl chloride (PVC), he prepared films containing various styrene concentrations and found that the rate of grafting is small at low styrene concentration, becomes larger as the concentration increases, and again decreases at higher concentrations. It was shown that the maximum rate of grafting occurs at a styrene concentration of 3.2 mole/liter and is smaller for both lower and higher

TABLE 2. Acceleration and Retardation Data

Polymer	Solution	δ Polymer	δ Solution	$\lvert \delta_p - \delta_s \rvert$	Acceration or retardation	Saturation abs (%)
Nylon	PFS/methanol, 60/40	13.6	10.4	3.2	Acc[a]	23.0
Nylon	PFS/acetone/methanol, 60/30/10	13.6	Large	Small	Ret	13.5
PE	PFS/methanol, 60/40	8.5	10.4	1.9	Ret	10.2
PE	PFS	8.5	6.7	1.8	-	10.2
PE	PFS/acetone, 60/40	8.5	Large	Large	Acc	9.2
Nylon	Styrene/methanol, 80/20	13.6	10.5	3.1	Acc[a]	34.7
Nylon	Styrene/acetone/methanol, 80/10/10	13.6	9.9	3.7	Ret	18.3
PE	Styrene/methanol, 80/20	8.5	10.5	2.0	Acc	6.5
PE	Styrene	8.5	9.2	0.7	-	7.5
PE	Styrene/acetone, 80/20	8.5	9.4	0.9	None	5.7

[a] Acceleration in the sense that no grafting takes place on dry nylon plus monomer alone.

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 recombination of polymeric free radicals, and there is some plausibility to the theory that the styrene plasticizes the PVC and facilitates the molecular motion of the polymer so that radical recombination is expedited. He demonstrated the plasticizing action of styrene in PVC by measuring the elastic modulus of PVC containing various concentrations of styrene.

In this connection, the work of Machi [7] is of interest. Machi studied the radiation-induced grafting of styrene on polyethylene, employing several volume ratios of styrene/methanol. Since most of the grafting appeared to take place in the amorphous portion of the polyethylene, he stressed the effect of the various grafting solutions on the viscosity of the amorphous region. He postulated that the methanol reduces the concentration of styrene in the amorphous region of the polyethylene, which results in a higher viscosity and therefore a decrease in termination rate.

Outline of the Present Theory

The theory to be outlined in this article is more in accord with the concepts of Takamatsu [6] and Machi [7] than with those of previous investigators. The conventional equation for the rate of free radical polymerization can be used as a basis for the discussion:

$$\text{rate} = k_p \left(\frac{R_i}{k_t} \right)^{1/2} [M] \tag{3}$$

where k_t and k_p are the rate constants for termination and propagation, respectively, R_i is the rate of initiation, and $[M]$ is monomer concentration. The main precaution in using this equation as an expression for grafting rate in a polymeric medium of high viscosity is to take into account the slowness of reactant diffusion in the high viscosity medium. If it is assumed that R_i is based on radiation intensity and is therefore rather constant, and that k_p is relatively constant because it involves the diffusion velocity of small molecules, then the main reasons for grafting rate variation are 1) changes in $[M]$ or 2) changes in k_t due to viscosity increase or decrease.

In considering the first reason, there is considerable evidence that grafting rate increases with $[M]$ under some conditions. As an example, the grafting of PFS alone on dry nylon film will not take place, but the dilution of PFS with methanol aids penetration of PFS into the film and provides a sufficient concentration, [M], within the film to allow grafting to occur. Other examples of the effect of monomer concentration on grafting rate are discussed below.

The second reason for change in grafting rate involves the effect of the viscosity of the polymeric medium on k_t. The effect of increased viscosity of a liquid medium in slowing the termination step of a free radical polymerization has been known for a long time. One investigation which revealed the phenomenon was the study of Benson [8] concerning rates of the termination step in the polymerization of several vinyl monomers. Also, Matheson showed that k_p/k_t increases as the percent conversion and viscosity increases during the polymerization of styrene [9].

In the radiation-induced grafting of a monomer solution on a polymeric film, the magnitude of k_t will be determined by the effectiveness of the particular solution in plasticizing the specific film, and thus lowering the viscosity of the medium (film interior) where the grafting reaction takes place. Therefore it becomes necessary to select a method of assessing plasticizer efficiency. A plasticizer has been defined as a lubricant which facilitates movement of the resin macromolecules over each other, thus providing internal lubricity [10]. Hence it is quite reasonable that a plasticizer in the film should expedite macroradical combination, the magnitude of the effect depending upon the efficiency of the plasticizer. For partially crystalline resins, plasticization affects primarily the amorphous regions or the regions of crystal imperfections [10].

The method of assessing plasticizer efficiency and compatibility should be a general one which can be applied to any polymer and any grafting solution. The method selected for use here is based on cohesive energy density (CED), defined as the energy of vaporization per unit volume in calories per cubic centimeter. Hildebrand defined the solubility parameter δ as the square root of the CED:

$$\delta = (\mathrm{CED})^{1/2} = (\Delta E/V)^{1/2} \qquad (4)$$

where ΔE is the energy of vaporization and V is the molal volume.

Mutual solubility of two substances will occur if the free energy of mixing is negative:

$$\Delta H - T\Delta S = \Delta F < 0 \qquad (5)$$

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. 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. 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 $|\delta_p - \delta_s|$.

Estimation of Solubility Parameters

The CED value for a liquid can be estimated [11] by

$$\text{CED} = \frac{\Delta H - RT}{M/d} \tag{6}$$

where ΔH is the latent heat of vaporization, T is the absolute temperature, R is the gas constant, M is the molecular weight, and d is the density of the liquid. The value of ΔH can be closely estimated from Hildebrand's equation [12],

$$\Delta H = 23.7\, T_b + 0.020\, T_b^2 - 2{,}950 \tag{7}$$

where T_b is the boiling point of the liquid in degrees absolute.

Using styrene as an example,

$$\Delta H = (23.7)(418) + (0.020)(418)^2 - 2{,}950 = 10{,}451 \text{ cal}$$

$$\text{CED} = \frac{10{,}451 - (1.987)(298)}{104.15/0.902} = 85.36 \text{ cal/cc} \tag{8}$$

$$\delta = (85.36)^{1/2} = 9.2 \qquad (9)$$

the latter value appearing in Table 2.

PFS belongs to the group of fluorinated hydrocarbons, a group having very unusual CED properties according to Hildebrand [13]. The large molal volumes of the fluorinated hydrocarbons compared with the corresponding hydrocarbons lead to remarkably low internal pressures (cohesive energy densities), while their molecular weights aid in maintaining them in the liquid state. The net result is to make many of their solutions with ordinary liquid hydrocarbons deviate from Raoult's law to such an extent as to form two liquid phases. Theoretical equations developed by Hildebrand [14] indicate that the δ value for a fluorinated hydrocarbon should be about 2.5 units less than the value for the corresponding ordinary hydrocarbon. Since δ (styrene) is about 9.2, the δ (PFS) value should be approximately $9.2 - 2.5 = 6.7$, the latter value appearing in Table 2.

The literature lists δ values of 14.3 for methanol [14] and 10.0 for acetone [11]. In the present work the CED values for solutions of two or more components were estimated as simple averages based on volume percentages, neglecting any volume change on mixing. For example, the CED of a 60/40 volume ratio solution of PFS/methanol was estimated as

$$\text{CED} = (0.6)(6.7)^2 + (0.4)(14.3)^2 = 108.7 \text{ cal/cc} \qquad (10)$$

$$\delta = (108.7)^{1/2} = 10.4 \qquad (11)$$

The δ (nylon) value of 13.6 given by Immergut [11] was employed in Table 2. The δ value for a solid polymer cannot be calculated by Eq. (6) because such a polymer has no heat of vaporization or boiling point. Several methods of estimating δ values for polymers have been devised, which may lead to slightly different values for the same polymer. In this work the δ value for polyethylene was estimated from original swelling data of Richards [15] after editing by Hildebrand [12]. The method involves measuring the swelling of PE in a series of solvents covering a range of δ values, then constructing a plot of swelling vs δ value as in Fig. 10. The maximum point of the curve indicates a δ value of about 8.5 for polyethylene. The imprecision of the method is indicated by the scatter of the data points. Also, "polyethylene" is not one polymer but a class of polymers, the observed properties varying widely and depending upon density, molecular weight, and molecular weight distribution. The δ value indicated in Fig. 10 is therefore only a rough estimate, but adequate for discussion purposes.

The above comments on CED and δ values apply to solutions having a positive deviation from Raoult's law. When a negative deviation is observed, the attraction between the components of the solution, A and B,

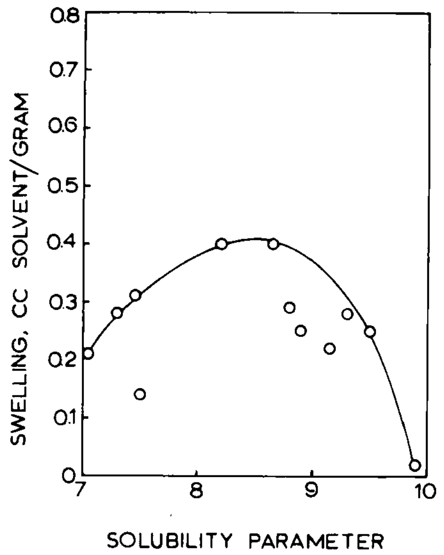

FIG. 10. Swelling of PE in cc solvent/g vs solubility parameter for various solvents; data of Richards [15].

is stronger than between A and A or between B and B. The classical example of such interaction is for solutions of chloroform in acetone, and halogenated hydrocarbons in general exhibit strong interaction or tendency toward association with acetone [16]. This type of behavior would be expected for PFS/acetone solutions.

The behavior of such solutions involving strong association of components cannot be described by simple equations leading to numerical values for δ and CED [16]. In qualitative terms the strong attraction between components would indicate large CED values, and hence the word "large" is recorded for the δ value of PFS/acetone solutions in Table 2. In determining $|\delta_p - \delta_s|$ for nylon and PFS/acetone, it should be noted that nylon has one of the highest δ values, 13.6, of any polymer, so that $|\delta_p - \delta_s|$ for this polymer/solution combination should be relatively "small" as recorded in Table 2. On the other hand, δ (PE) has the rather small value of 8.5, so that $|\delta_p - \delta_s|$ for PE in PFS/acetone should have a relatively "large" value, as indicated in Table 2.

Interpretation of Experimental Results

Table 2 compares the accelerating or retarding effects of several grafting solutions with the $|\delta_p - \delta_s|$ values for the corresponding polymer/solution combinations. The table also gives percent saturation absorption for the (ungrafted) polymeric films in the various grafting solutions. The latter data were obtained by immersing a 0.01-g sample of the film in a 1.0-ml sample of the grafting solution in a small stoppered bottle, storing for about 1 day at room temperature, blotting the film sample dry with filter paper, and quickly weighing on the semimicro balance.

The following is an attempt to apply the theory to the interpretation of the experimental grafting results for each monomer/polymer system in turn.

PFS/Nylon

Because of its low δ value, PFS will not swell nylon at all unless diluted by methanol (or other suitable solvent), thus raising its δ value and allowing penetration and swelling of the nylon film to take place. At 40 vol% methanol, δ for the grafting solution is only 10.4, corresponding to a large $|\delta_p - \delta_s|$ value of 3.2, in line with the observed high grafting rate of 4.1%/hr (Fig. 1).

The retarding effect of PFS/acetone/methanol is more difficult to assess because of the vague nature of the "small" rating for the $|\delta_p - \delta_s|$ value. Taking the "small" rating at face value would indicate efficient plasticization with resulting fast termination and low grafting rate. However, the retardation observed may result simply from a reduction in monomer concentration in the film, since replacement of 75% of the methanol with acetone reduces saturation absorption by the film from 23.0 to 13.5%. This does not imply that the observed rate is simply proportional to methanol concentration in the film, nor does it imply that the liquid actually absorbed by the film contains PFS/acetone/methanol in a 60/30/10 volume ratio. The liquid actually absorbed may contain much less than 60 vol% PFS.

PFS/Polyethylene

In this system a reversal of the effect for PFS/nylon is observed, with acetone now accelerating and methanol retarding the grafting reaction. If one accepts the "large" value of $|\delta_p - \delta_s|$ for PFS/acetone at face value, this would explain the acceleration as due to the low plasticizing efficiency of the grafting solution.

In comparing PFS alone with PFS/methanol, it is observed that both exhibit the same saturation absorption and the same $|\delta_p - \delta_s|$ values, within the limits of experimental error. The apparent "retarding" effect of added methanol may result from the lower concentration of monomer in the absorbed liquid, caused by the 40% dilution with methanol.

Styrene/Nylon

Methanol "accelerates" the grafting on nylon in the sense that little or no grafting takes place on dry nylon film when styrene alone is present. The lack of penetration by styrene alone correlates with the large difference in δ values between styrene and nylon.

The apparent "retardation" by acetone may be due to a decrease in monomer concentration in the film, since the saturation absorption of styrene/acetone/methanol is only 18.3% compared to 34.7% for styrene/methanol (Table 2). There is no simple way to translate these figures into comparable monomer concentrations in the film, but it would appear that acetone causes enough reduction in [M] to account for the observed decrease in grafting rate.

Styrene/Polyethylene

Added methanol accelerates grafting in this system, in line with the increase observed in $|\delta_p - \delta_s|$ in going from pure styrene to styrene/methanol. Addition of acetone to the styrene causes little effect on grafting rate, the slight observed rate increase probably being within the limits of experimental error. If the increase is taken to be real, it could be explained by the increase in $|\delta_p - \delta_s|$ in going from pure styrene to styrene/acetone.

Other Rate-Determining Factors

The above discussion of the application of the theory to the interpretation of Table 2 is an oversimplification of the total picture since a number of factors were temporarily omitted from consideration. Throughout the discussion the references to "monomer concentration" in the film should be replaced by "average monomer concentration." As monomer diffuses into the film it is consumed in the film, resulting in a relatively low value for [M] in the center of the film as compared to the surface layers. Both theoretical [1, 3] and experimental [17] studies suggest a monomer concentration vs film thickness curve in the shape of a catenary, with its minimum at the center of the film.

Theoretical arguments can be presented that the same steady-state or equilibrium concentration curve should be attained in the film, regardless of whether the initial concentration was zero or a constant value, C_0, throughout the film at the start of irradiation, in much the same way that the equilibrium state is the same in a chemical reaction regardless of the direction of approach. Monomer diffusion effects introduce a number of complicating factors that were ignored in the above discussion of Table 2. Such factors were minimized by using the same thickness of each polymeric film for all comparative studies on different grafting solutions.

Another factor not considered was the relative amounts of crystalline and amorphous material in the films. Most investigators have concluded that for partially crystalline polymers such as polyethylene, the grafting reaction takes place mainly in the amorphous regions. It has also generally been deduced that the liquid monomer is absorbed mainly or entirely in the amorphous regions of the film. This complicates the picture because it is necessary to consider not only the distribution of each grafting solution component between the solution and the film, but also the distribution of each component between the amorphous and crystalline regions of the film.

In general, the fact that both crystalline and amorphous regions exist in the film probably leads to an intensification of the effects discussed in the interpretation of Table 2. For example, if a liquid component Q is absorbed mainly in the amorphous region at 2.0% on total film weight, and if the film is two-thirds crystalline, then the actual concentration of component Q in the amorphous region is approximately 6.0% by weight. Hence the saturation absorption weight percent figures shown in Table 2 on the basis of total film weight might be magnified greatly if they were recomputed as percent by weight of the amorphous region. Further discussion of the effect of the crystalline/amorphous distribution is beyond the scope of this article. Again, the effect of this factor was minimized by using films of the same crystalline content in all comparative studies.

Another complication results from the fact that the composition of the original film changes as the grafting reaction proceeds. For example, when PFS is grafted on polyethylene, the absorption characteristics of the film change as the content of grafted PFS increases. Figure 11 presents saturation absorption studies on PE films having various percentages of grafted PFS in solutions of PFS/methanol at a 60/40 volume ratio and in PFS/acetone at a 60/40 volume ratio. The percent absorbed PFS/methanol is slightly greater than for PFS/acetone in ungrafted PE and continues to remain greater as the percent of grafted PFS increases. Figure 12 presents a plot of saturation absorption of PFS/methanol (60/40) and PFS/acetone/methanol (60/30/10) in nylon film as a function of percent grafted PFS. The PFS/methanol (60/40) starts off with a higher percentage saturation absorption in pure nylon but does not increase much as the percent grafted PFS increases.

One cause of the difficulties in the interpretation of Table 2 is the imprecise character of the δ values, which may vary somewhat depending upon the method of computation or measurement employed in their determination. While some of the δ values used in Table 2 may be open to question, the general approach is probably

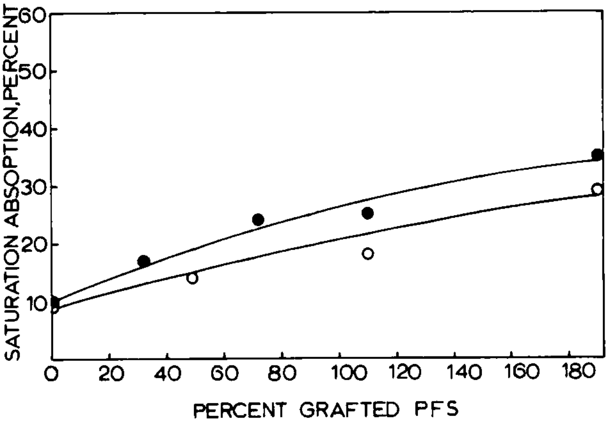

FIG. 11. Percent saturation absorption for 0.012 in. PE film vs percent grafted PFS; (●) in PFS/methanol, 60/40; and (○) in PFS/acetone, 60/40.

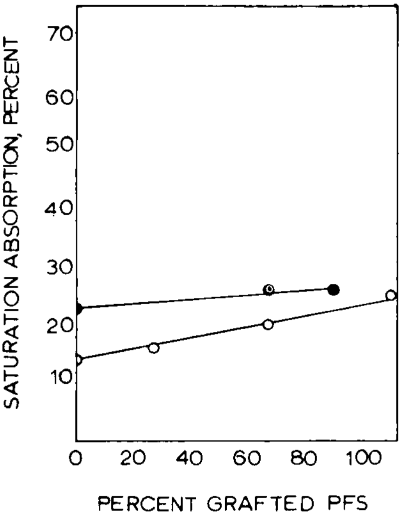

FIG. 12. Percent saturation absorption for 0.008 in. nylon film vs percent grafted PFS; (●) in PFS/methanol, 60/40; and (○) in PFS/acetone/methanol, 60/30/10.

correct because the magnitude of [M] and k_t must influence the grafting rate as indicated in Eq. (3). The present theory offers some prospect for the development of quantitative expressions for grafting rate that would at least give self-consistent results for the grafting of a specific monomer plus various solvents on a particular polymer. It would be desirable to have a more quantitative way of expressing plasticizer efficiency which would relate directly to the effectiveness of the plasticizer in facilitating the motion of polymer chains so as to expedite movement and combination of polymeric free radicals.

In spite of the many complicating factors, two simple rules have been found to hold true for many systems involving radiation-induced grafting of monomers on polymeric films:

1. A plot of percent swelling vs percent grafting is linear, with all points falling on the same line even when various amounts of different solvents are added to the grafting solution (Figs. 2, 4, 6, and 8).
2. A plot of percent grafting vs time is linear for several hours at the radiation intensity employed in the present studies (Figs. 1, 3, 5, and 7).

Reflection on the theory outlined above indicates that it should be possible to obtain very high grafting rates by providing a low but adequate monomer concentration in the polymeric film, while at the same time arranging for the monomer to be highly incompatible with the film. For example, water [11] has a very large solubility parameter ($\delta = 23.4$) and is readily absorbed by nylon film. Hence a nylon film containing water would be very incompatible with PFS because of the latter's very small solubility parameter ($\delta = 6.7$). To assure the presence of water in the film, a grafting formulation of PFS/methanol/water at a volume ratio of 60/39.2/0.8 was employed. Irradiation of the nylon film immersed in this formulation for 46 hr grafted 671% PFS on the film when the same irradiation intensity and experimental techniques were employed as in the previous runs. Auxiliary runs showed that essentially the same results were obtained when the nylon film was first allowed to absorb water, followed by immersion in PFS/methanol and irradiation. Perhaps the best theoretical interpretation of the phenomenon is to assume that a PFS solution of low δ value penetrates a nylon/water moiety of very high δ value.

The same method could be used to produce rapid grafting on nylon by styrene and other monomers having relatively low δ values. This reasoning is in line with literature reports that water accelerates the grafting of styrene and other vinyl monomers on nylon [18] and polyvinyl alcohol [19, 20].

CONCLUSIONS

1. In the radiation-induced grafting from PFS/methanol solution on nylon film, the addition of acetone retards the reaction.
2. In the grafting of PFS on polyethylene film, the addition of methanol retards the reaction while the addition of acetone causes an acceleration.
3. In grafting on nylon film from styrene/methanol solution, the addition of acetone retards the reaction.
4. In grafting styrene on polyethylene film, the addition of methanol accelerates the reaction but added acetone has little effect on the rate of grafting.
5. Small amounts of water greatly accelerate the grafting of PFS on nylon film (from PFS/methanol solution).
6. The above effects can be interpreted in terms of how changes in the grafting solution affect $[M]$ and k_t in the fundamental equation for the free radical polymerization rate.
7. In each of the four monomer/polymer systems studied, a plot of percent swelling vs percent grafting is linear, with all points falling on the same line regardless of the amount of methanol and/or acetone added.
8. The effect of k_t on grafting rate has been assessed in terms of the plasticizing efficiency of the grafting solution, as determined by the difference in δ values of the polymer film and grafting solution.
9. The grafting of minor amounts of PFS on nylon film greatly reduces its rate of water vapor absorption in a humid atmosphere and considerably improves the clarity of the film.

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REFERENCES

[1] J. E. Wilson, J. Chem. Phys., 22, 333 (1954).
[2] J. E. Wilson, J. Macromol Sci.—Chem., A5, 777 (1971).
[3] J. E. Wilson, Ibid., A6, 391 (1972).
[4] J. E. Wilson, Ibid., A7, 845 (1973).
[5] J. Weiss, A. O. Allen and H. A. Schwarz, Proceedings of the International Conference on Peaceful Uses of Atomic Energy, Vol. 14, United Nations, New York, 1956, p. 179.

[6] T. Takamatsu, J. Polym Sci., A-1, 4, 197 (1966).
[7] S. Machi, I. Kamel and J. Silverman, Ibid., A-1, 8, 3329 (1970).
[8] S. Benson and A. North, J. Amer. Chem. Soc., 81, 1339 (1959).
[9] M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, Ibid., 73, 1700 (1951).
[10] Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 15, 2nd ed., Wiley, New York, 1963, p. 727.
[11] E. H. Immergut and H. F. Mark, in "Plasticization and Plasticizer Processes," Advan. Chem. Ser., 48, (1965).
[12] J. H. Hildebrand and R. L. Scott, The Solubility of Nonelectrolytes, Reinhold, New York, 1950.
[13] J. H. Hildebrand and D. R. F. Cochran, J. Amer. Chem. Soc., 71, 22 (1949).
[14] R. L. Scott, Ibid., 70, 4092 (1948).
[15] R. B. Richards, Trans. Faraday Soc., 42, 10, 20 (1946).
[16] A. K. Doolittle, Technology of Solvents and Plasticizers, Wiley, New York, 1954.
[17] H. Matsuo, K. Iino, and M. Kondo, J. Appl. Polym. Sci., 7, 1833 (1963).
[18] Y. Shinohara, Ibid., 1, 251 (1959).
[19] I. Sakurada, T. Okada, and E. Kugo, Isotopes and Radiat., 2, 296, 306, 316 (1959).
[20] A. Chapiro and V. Stannett, Int. J. Appl. Radiat. Isotopes, 8, 164 (1960).

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