Polymer/Solvent Interaction in the Radiation-Induced Grafting of Vinyl Monomers on Polymeric Films

J. E. Wilson[a]

[a] Physical Science Department, Bishop College, Dallas, Texas

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J. E. WILSON

Physical Science Department
Bishop College
Dallas, Texas 75241

ABSTRACT

More evidence has been obtained concerning rate effects in
the radiation-induced grafting of vinyl monomers on polymeric
films resulting from plasticization of the film by the grafting
solution, the plasticizing efficiency of the solution being
indicated by its Hildebrand solubility parameter. Two types
of solvent acceleration mechanisms are defined and illustrated
by the styrene/nylon and styrene/polyethylene systems in
terms of grafting rate measurements for selected grafting
solution compositions. The grafting mechanisms are elucidated
by the construction of three-component phase diagrams for the
polymer/solvent (1)/solvent (2) grafting systems using
equations based on the Flory-Huggins theory of polymer/
solvent interaction.

INTRODUCTION

The accelerating effect of selected solvents on the rate of radiation-induced grafting for various monomer/polymer pairs has been known for a long time, but no adequate theory has been available to explain the effect. Many of the published rates were described as "anomalous." A new theoretical approach to the rate of radiation-induced grafting has been developed recently [1, 2], which stresses rate dependence on film plasticity and assesses the plasticizing efficiency of the grafting solution in terms of its Hildebrand solubility parameter, δ.

The new theory may be discussed in terms of the following conventional equation for the rate of free radical polymerization [3]:

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

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 the average monomer concentration within the film. Assuming that R_i is constant because it depends on (constant) 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 monomer concentration and 2) changes in k_t due to variations in the internal plasticity of the film.

An increase in $[M]$ can take place when a solvent is added which increases the 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. According to the theory of plasticizer action stated by Immergut and Mark [4], the plasticizing efficiency of the grafting solution depends on the values of δ_p and δ_s, the Hildebrand solubility parameters for the polymer and grafting solution, respectively. The details of the theory have been discussed previously in connection with other grafting rate studies [1, 2]. In brief, in order to select an effective plasticizer (or solvent), one tries to make the enthalpy of solution, ΔH, as small as possible by minimizing $|\delta_p - \delta_s|$, because ΔH is proportional to $(\delta_p - \delta_s)^2$ according to Hildebrand [5]. 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, efficient

plasticization results from minimizing $|\delta_p - \delta_s|$, but a higher grafting rate is produced by maximizing $|\delta_p - \delta_s|$. Work with δ values is facilitated by the fact that lists of such values for many solvents and plastics have been compiled by Hildebrand [5], Immergut [4], and others [6, 7].

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 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. The complicated shape of such rate vs concentration curves is probably due to the simultaneous variation of [M] and k_t in Eq. (1).

The virtue of the δ value theory is that it enables one to hold internal film plasticity constant by using a series of grafting solutions of constant δ value, which in turn holds k_t constant and allows one to assess the effect of other variables such as monomer concentration [2]. For example, in the grafting of pentafluorostyrene (PFS) on nylon film employing carefully selected grafting solutions designed to hold the δ value constant, it was found [2] that grafting rate vs monomer concentration in the grafting solution gave a linear plot, suggesting first-order rate dependence on [M] as shown in Eq. (1). A similar series of runs at constant δ value was made for the styrene/nylon system, and a linear plot of rate vs monomer concentration in the solution was again obtained [2]. These results confirmed the usefulness of the δ value theory in grafting rate studies, and led to an expanded investigation into related areas.

While the work of Hildebrand applied to solutions in general, the early theoretical work of Flory [8] and Huggins [9] concerned solutions of polymers. In brief, Flory and Huggins independently developed thermodynamic equations for polymer solutions based on a suggestion of K. H. Meyer [10] that the flexible nature of a polymer chain allows it to assume many more configurations in solution than would be the case for a compact molecule of the same molecular weight. By assigning to the solvent a quasi-lattice structure, and arranging on this lattice a randomly coiled polymer chain, Flory and Huggins were able to calculate the partial molal entropy of dilution by statistical mechanical methods. The partial molal heat of solution was based in a semiempirical manner on a Hildebrand-van Laar-Scatchard term [5]. The derived expressions for the various thermodynamic quantities contained a parameter, χ, which is generally referred to as the Flory polymer/solvent interaction parameter.

Hildebrand [5] and Krigbaum [11] have stated the relationship between Hildebrand's δ value and Flory's χ value. Krigbaum [11]

has derived equations based on Flory's χ value which can be used to clarify polymer/solvent interactions relating to grafting rates. For example, when nylon film is immersed in styrene/methanol solution for grafting, the styrene/methanol volume ratio in the external solution is generally quite different from the styrene/methanol ratio within the film. Krigbaum's equations enable the theoretical calculation of the styrene/methanol ratio within the film from the styrene/methanol ratio in the grafting solution external to the film [11]. Since the grafting reaction actually takes place within the film, such information is helpful in the interpretation of grafting rate as a function of grafting solution composition. Krigbaum's equations can also be used to construct ternary composition diagrams for polymer/solvent (1)/solvent (2) grafting systems as described below.

EXPERIMENTAL TECHNIQUE

The design of the ^{60}Co source and the technique of placing successive film samples in the identical position in the source have been described previously [12]. Precise positioning of the film sample permits reproducible rate measurements to be obtained. An exposure dose rate at the film capsule location of 477 R/hr was measured by ferrous sulfate dosimetry [13].

Film samples of 0.01 to 0.02 g in weight were used in the individual runs. The polyethylene film samples were of 0.93 density and 0.012 in. thickness, and were supplied by Consolidated Thermoplastics of Woonsocket, Rhode Island. The other film employed was a nylon film of 0.0080 in. thickness from Nylonic Engineering of Herts, England. All nylon film samples were dried in a desiccator before use to prevent any possible change in rate caused by a variation in water content.

The styrene monomer from Eastman was washed three times with 10% aqueous sodium hydroxide, then three times with distilled water, dried with anhydrous calcium sulfate, distilled at reduced pressure, and stored over anhydrous calcium sulfate at refrigerator temperature prior to use.

The following solvents of reagent grade were used in this work: benzene, methanol, ethanol, methyl ethyl ketone, acetone, cyclohexanol, and acetonitrile. Each solvent was stored in its bottle over anhydrous calcium sulfate for several days before use, and always used from the same bottle. This technique was essential to obtain reproducible grafting rates, since a very slight change in water content of the grafting solution may cause an appreciable change in grafting rate.

Just before making a grafting run, the grafting solution was freed of oxygen by freeze-thaw cycling in a vacuum system as

discussed earlier [12]. The reaction capsule containing film and deoxygenated grafting solution was frozen down and sealed from the vacuum line while pumping, then placed in the ^{60}Co source in the selected position.

After each run the styrene-grafted film sample was extracted by stirring in warm benzene for 2 days. The purpose of the extraction was to remove homopolymeric styrene formed within the film. Along with each extraction of a grafted film, 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, $23 \pm 1°$C. Percent grafting was computed from the original film weight (P_0) before grafting, and the weight after grafting and drying to comstant weight (P_g) by the use of

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

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

$$\text{percent swelling} = \left[\frac{P_s - P_0}{P_0}\right] \times 100 \tag{3}$$

Saturation swelling measurements on nylon and polyethylene films immersed in styrene/methanol at various selected ratios provided the data used in constructing ternary composition diagrams. Each film was immersed for about 24 hr in the desired styrene/methanol composition, blotted dry with filter paper, and weighed in a closed weighing bottle. The blotting and weighing operation was repeated several times at 0.5 hr intervals to obtain an average weight of the swollen film, P_s, from which the weight percent swelling was computed by the use of Eq. (3).

RESULTS AND DISCUSSION

Grafting Rates for Styrene/Polyethylene Using a Variety of Solvents

In previous work [2] on radiation-induced grafting it was shown that the rate is proportional to the monomer concentration in the grafting solution for certain monomer/polymer systems, providing the δ value of the grafting solution is held constant. In that work, however, the number of grafting solvents employed was rather limited. In the present work on styrene/polyethylene, one of the objectives was to use a variety of solvents of different chemical types while holding the δ value of the solvent mixture constant, and to observe whether the rate remains proportional to the monomer concentration under such a broad range of conditions.

A series of runs of approximately 24-hr duration was made with the results shown in Table 1. While a variety of solvent combinations is shown, the composition of the grafting solution was carefully controlled in all cases to have a δ value of 10.4 as computed by a method described previously [1, 2]. For each solution composition the approximate rate of grafting was obtained by dividing the percent of grafting by the length of the run in hours, with the results shown in the right-hand column of Table 1. The

TABLE 1. Grafting of Styrene on Polyethylene: Solution Solubility Parameter of 10.4 in All Cases[a]

Run no.	Grafting solution composition	Grafting (%)	Run Length (hr)	Rate (% hr)
1D	27/20/53 styrene/benzene/cyclohexanol	8.8	22.5	0.39
2D	38/20/42 styrene/benzene/acetonitrile	6.9	28.3	0.24
3D	43/37/20 styrene/benzene/methanol	12.9	20.3	0.64
4D	70/12/18 styrene/acetone/methanol	33.3	22.9	1.45
5D	50/31/19 styrene/MEK/methanol	24.1	20.4	1.18
6D	40/41/19 styrene/MEK/methanol	15.8	21.0	0.75
7D	53/27/20 styrene/benzene/methanol	25.5	20.9	1.22

[a]Solubility parameters used: methanol, 14.3; styrene, 9.2; benzene, 9.2; methyl ethyl ketone, 9.3; acetone, 10.0; cyclohexanol, 11.4; acetonitrile, 11.8.

types of solvents evaluated included alcohols (methanol and cyclo-hexanol), ketones (acetone and methyl ethyl ketone), an aromatic (benzene), and a nitrile (acetonitrile).

Several concentrations of styrene were used in the runs listed in Table 1. Since the δ value of all of the grafting solutions is the same, the simple theory described earlier [1, 2] would indicated that grafting rate plotted vs styrene concentration should give a straight line. Such a plot is shown in Fig. 1, and all of the points except one do fall reasonably close to a straight line. The only data point that falls significantly off the line is the point for the grafting solution con-taining acetonitrile. It is noteworthy that the solubility of polystyrene in acetonitrile is only 0.056 g/100 g [14], resulting in the formation of a considerable amount of insoluble polystyrene in the acetonitrile solution during the grafting run. It has been observed by the writer on several occasions that the formation of insoluble material in the grafting capsule renders the rate unpredictable and unreproducible.

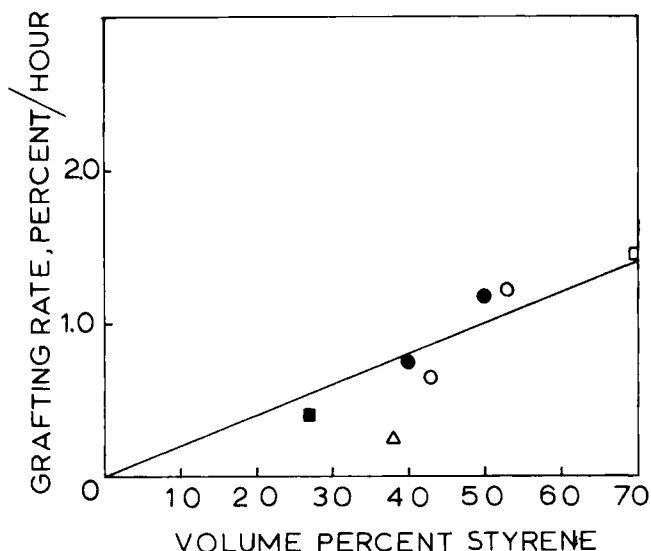All of the solvents used in Fig. 1, whose data points fall near the

FIG. 1.   Grafting rates for styrene on 0.012 in. polyethylene film vs vol % styrene in the grafting solution at constant δ value of 10.4.   Other constituents of grafting solutions: (o) benzene/methanol, (●) MEK/methanol, (□) acetone/methanol, (■) benzene/cyclohexanol, and (△) benzene/acetonitrile.

line, have been described in the literature [14, 15] as excellent
solvents for polystyrene. One other run, not indicated in Table 1
or Fig. 1, in which the grafting solution consisted of an 80/20 volume
ratio of styrene/nitromethane, resulted in almost no grafting at all.
In this case again, the solubility of polymerized chains of styrene in
nitro-alkanes is known to be very low [14]. The tentative conclusion
to be drawn from Fig. 1 appears to be that the grafting rate in this
system at constant δ value is approximately proportional to styrene
concentration in the grafting solution for a variety of chemical types
of solvent, providing the polymeric chains produced by grafting are
soluble in the grafting solution.

It is of interest to compare Runs 3D and 7D using benzene (open
circles, Fig. 1) with Runs 5D and 6D using MEK (filled circles,
Fig. 1). Benzene and MEK have closely similar δ values, namely
9.2 and 9.3, respectively. Many writers have cited the "protective
effect" of benzene in radiation chemistry, by which is meant the
tendency of benzene to absorb radiation and lessen possible absorp-
tion and reaction by other molecules [16]. In this case, however,
comparison of the rates for the benzene runs (3D and 7D) with those
for the MEK runs (5D and 6D) shows little or no retarding effect
attributable to the benzene. This does not prove the nonexistence of
the protective effect, but does indicate that monomer concentration
and film plasticity are probably more important in the determina-
tion of grafting rates.

Mechanism of Solvent Acceleration in the Styrene/Nylon System

One objective of this work was to determine experimental differ-
ences observable in the rate behavior patterns for two different
types of solvent acceleration. In Type (1), illustrated by styrene/
nylon, a solvent such as methanol must be added to the styrene to
aid penetration into the nylon, or no grafting will take place. In
Type (2), illustrated by styrene/polyethylene, the monomer readily
penetrates the polymer, but when a solvent of quite different δ value
is added to the monomer the magnitude of $|\delta_s - \delta_p|$ is increased,
causing a decrease in k_t and an acceleration of grafting.

Table 2 shows a series of grafting solution compositions that
was employed in grafting styrene on nylon. The composition of all
of the solutions was planned to yield a δ value of 9.6. For example,
the following computation applies to the 90/10 styrene/ethanol
composition (Run 4N):

$$CED = (0.9)(9.2)^2 + (0.1)(12.7)^2 = 92.3 \qquad (4)$$

$$\delta = (92.3)^{1/2} = 9.6 \qquad (5)$$

TABLE 2. Styrene/Nylon Runs: Solution Solubility Parameter of 9.6 in All Cases[a]

Run no.	Styrene (vol%)	Benzene (vol%)	Ethanol (vol%)	Solution E (vol%)	Run length (hr)	Grafting (%)
1N	30	60	10	0	25.0	16.4
2N	50	40	10	0	21.0	34.1
3N	70	20	10	0	21.3	43.5
4N	90	0	10	0	21.8	57.3
5N	30	60	0	10	21.7	8.4
6N	50	40	0	10	22.2	14.5
7N	70	20	0	10	22.4	23.3
8N	90	0	0	10	20.7	28.6

[a]Solubility parameters used: methanol, 14 3; styrene, 9.2; benzene, 9.2; ethanol, 12.7. Solution E contained 36/64 volume ratio of benzene/methanol, having a solubility parameter of 12.7 (equal to ethanol).

where CED indicates cohesive energy density. In Runs 2N through 4N, a change in the percentage of styrene does not change the overall δ value, because the total percentage of styrene plus benzene is held constant at 90%. Benzene has the same δ value, 9.2, as styrene.

In Runs 5N through 8N, the 10% of ethanol is replaced by 10% of Solution E. Solution E consists of a 36/64 volume ratio of benzene/methanol having a δ value of 12.7 (equal to ethanol). According to the simple view of the δ value theory, grafting rates for all solutions in Table 2 should produce a straight line when plotted against volume percent styrene monomer in the grafting solution. Figure 2 shows that such is not the case, but that two straight line plots are produced, the upper line with open circles corresponding to a constant 10% ethanol content, and the lower line with filled circles corresponding to 10% Solution E. Computation of the slope of the upper curve for ethanol indicates

$$rate = (0.0291)(vol\% \text{ styrene}) \tag{6}$$

and from the lower curve for compositions containing Solution E,
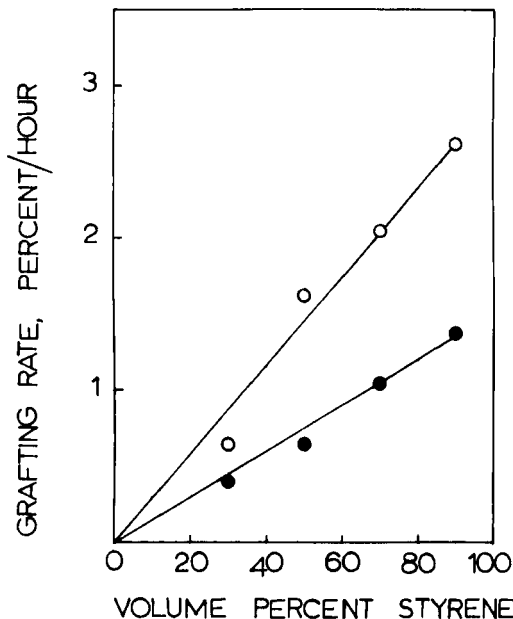
$$rate = (0.0145)(vol\% \text{ styrene}) \tag{7}$$

FIG. 2. Grafting on 0.008 in. nylon film using styrene/benzene
solutions at constant δ value of 9.6: (o) contains 10% ethanol,
(•) contains 10% Solution E.

Both linear curves suggest rates first order in monomer concentration
in accord with Eq. (1), providing the concentration of styrene in the
film is proportional to its concentration in the grafting solution. All
rates in Fig. 2 were computed from the percent grafting and run
duration figures listed in Table 2. Each run was about 1 day in
length, shown by previous experience to give an apparent grafting
rate closely approximating the initial grafting rate, which is the
only valid rate pertaining to nylon film of unchanged (ungrafted)
composition [2].

   The wide gap between the upper and lower lines in Fig. 2 can
probably not be attributed to the benzene protective effect, because
points on the lower curve correspond to only 3.6% more benzene
in each case than points on the upper curve (Table 2). The
simplest explanation is that the 6.4% methanol of the lower curve is
not as effective in promoting sytrene penetration of the nylon as
the 10% ethanol employed in the grafting solution of the upper curve.
It is concluded that the equivalence of the δ value for the upper
and lower curves does not assure equivalence of styrene concentra-
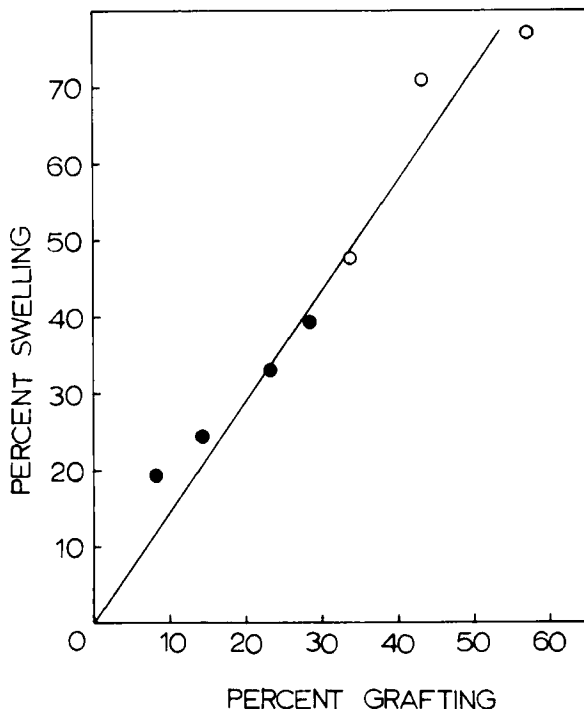tion in the film for the two cases. This is the type of situation

FIG. 3. Swelling vs grafting plot for styrene/nylon runs of
Table 2: (o) 10% ethanol in grafting solution, and (●) 10% Solution
E in grafting solution.

where the δ value theory cannot be relied upon to predict accurately
the relative solubilities of styrene in the film, a fact that is dis-
cussed more fully below in the section on polymer/solvent interaction.

Figure 3 presents a plot of percent swelling vs percent grafting
for the runs of Table 2. A linear plot is obtained with a slope of
1.44, indicating

$$(\% \text{ swelling}) = (1.44)(\% \text{ grafting}) \tag{8}$$

All points in Fig. 3 fall near the same straight line, whether the
grafting solution contains ethanol (open circles) or Solution E (filled
circles). At first sight this evidence might appear to imply that
ethanol and Solution E are equally effective in inducing styrene
absorption by the film, but actually the "percent swelling" gives no
indication of the percent styrene in the sorbed liquid, which may

differ in a complex way from that present in the external solution as shown below by the application of the theories of Flory and Krigbaum. In addition, the large percent swelling values in Fig. 3 must represent mostly liquid absorbed by grafted styrene chains within the film, since much smaller percent swelling values are characteristic of ungrafted nylon film (see Fig. 7).

Mechanism of Solvent Acceleration in the Styrene/Polyethylene System

Table 3 summarizes a series of grafting solution compositions that were employed in grafting sytrene on polyethylene. Again, the δ value was held constant at 9.6 for all of the solutions by properly selecting the compositions. In two of the runs (2P and 4P) the grafting solution contained 10% ethanol, while in the other two runs (1P and 3P) the grafting solution contained 10% Solution E. Figure 4 presents the corresponding plot of grafting rate vs volume percent styrene, and in this case all of the points fall on the same straight line (within experimental error):

$$\text{rate} = (0.0156)(\text{vol\% styrene}) \tag{9}$$

Hence, for this particular grafting system, the constancy of the δ value, whether the added solvent is ethanol or Solution E, is apparently sufficient to assure that all points in Fig. 4 fall on the same straight line. All of the points on the line have the same value of $|\delta_p - \delta_s|$, where δ_p is the solubility parameter for the polymer, and δ_s is the

TABLE 3. Styrene/Polyethylene Runs: Solution Solubility Parameter of 9.6 in All Cases[a]

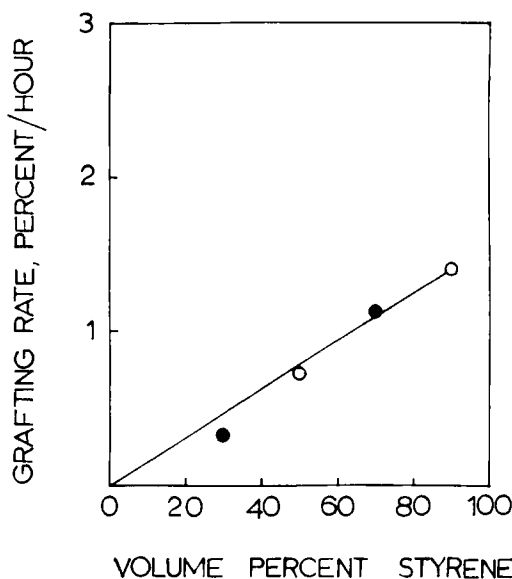| Run no.	Styrene (vol%)	Benzene (vol%)	Ethanol (vol%)	Solution E (vol%)	Run length (hr)	Grafting (%)
1P	30	60	0	10	21.3	6.9
2P	50	40	10	0	21.3	15.5
3P	70	20	0	10	23.9	27.1
4P	90	0	10	0	21.0	29.4

[a]Same solubility parameters used as in Table 1.

FIG. 4. Grafting on 0.012 in. polyethylene film using styrene/
benzene solutions at constant δ value of 9.6: (○) contains 10%
ethanol, and (●) contains 10% Solution E. Not comparable to Figs. 1
and 5 due to change in source position.

solubility parameter of the grafting solution. For this type of graft-
ing mechanism (Type 2), the grafting rate equals some constant times
monomer concentration, the magnitude of the constant apparently
depending only on the size of $|\delta_p - \delta_s|$, and being more or less in-
dependent of the chemical nature of the added solvent(s). This
postulate is in agreement with the conclusion already drawn from
Fig. 1.

A quite different method for demonstrating the equivalence of
grafting solutions of the same $|\delta_p - \delta_s|$ value would be a grafting
study on a series of grafting solutions of different δ value. For ex-
ample, it is well known that the addition of increasing amounts of
methanol or ethanol to a styrene/polyethylene grafting system
produces a plot of rate vs percent styrene which passes through a
maximum at a certain styrene/alcohol volume ratio. The grafting
solution compositions for such a series of runs are shown in Table
4, with Runs 8P and 6P employing 10 and 30 vol% ethanol in the
styrene, respectively. Runs 7P and 5P employ 20 and 40 vol%
Solution E in the styrene. If ethanol and Solution E are equivalent

TABLE 4. Styrene/Polyethylene Runs: Variable Solubility Parameter

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

in their accelerating effect on the grafting rate, all grafting rates for Table 4 compositions should fall on the same smooth curve of rate vs percent styrene, which should pass through a maximum at a certain styrene concentration in the usual way.

Such a plot is shown in Fig. 5, and it is seen that all of the points fall on the same smooth curve whether the solvent added to the styrene is ethanol or Solution E. In fact, as far as grafting rate is concerned, ethanol and Solution E appear to be identical and inter-changeable. Hence in this case of the Type 2 mechanism, for this particular monomer/polymer pair, the equal δ values of ethanol and Solution E are a sufficient condition to assure that these two additives have identical accelerating effects on the grafting rate. Based on the evidence now available, it would be premature to pre-dict that equal δ values for added solvents indicate identical acceler-ating effects whenever the Type 2 mechanism applies. However, the carrying out of a similar series of runs on other monomer/polymer pairs should lead to interesting comparisons that might shed light on the characteristics of the grafting kinetics in each case.

Figure 6 shows a plot of swelling vs grafting for the runs sum-marized in Tables 3 and 4. Again a linear plot results, all points falling near the line regardless of whether the additive is ethanol or Solution E. The equation for the line is

$$(\% \text{ swelling}) = (1.70)(\% \text{ grafting}) \tag{10}$$

The slope of 1.70 is about equal to the corresponding slope of 1.67 obtained in earlier work on styrene/polyethylene grafting [1], even though several grafting compositions including styrene/acetone were employed in the earlier work.
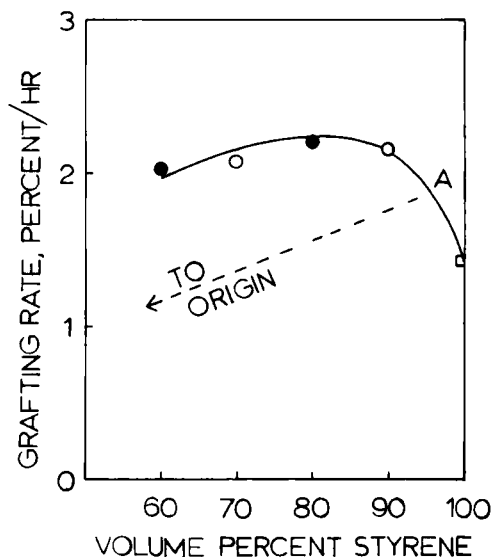
FIG. 5. Grafting of styrene solutions on 0.012 in. polyethylene film with variable δ value: (o) contains ethanol, (●) contains Solution E, and (□) pure styrene. Not comparable to Figs. 1 and 4 due to change in source position.

Further analysis of Fig. 5 is of some interest. At any point on the curve, such as Point A, it should be possible to hold δ_s constant and make a sequence of rate measurements that would fall on the dotted line from A to the origin, in accordance with the demonstrated linear dependence of rate on monomer concentration. Such linear dependence for the styrene/polyethylene system is shown in Fig. 4, and was observed earlier [2] for the styrene/nylon and pentafluoro-styrene/nylon systems. It is reasonable to assume that Point A could be located anywhere on the curve of Fig. 5, and a straight line to the origin be constructed for rate vs monomer concentration. It has been shown repeatedly that such straight lines to the origin can be constructed by regulating the grafting solution composition so as to hold the δ value of the solution constant, while allowing monomer concentration to vary [2]. The equation for all rates measured along the dotted line from A to the origin is

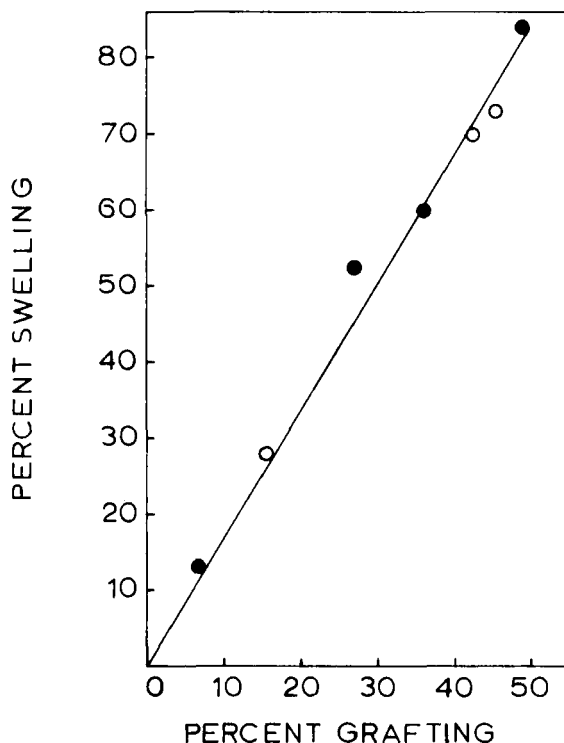rate = slope × volume fraction styrene   (11)

FIG. 6. Swelling vs grafting for styrene/polyethylene runs of Tables 3 and 4: (o) contains ethanol, and (●) contains Solution E.

For the Point A shown in Fig. 5, the magnitude of the slope is 2.00, which would increase as A moves up the curve, and decrease as A moves down the curve.

It is concluded that for this example of the Type (2) mechanism, constancy of δ_s appears to be a reliable indication of the constancy of k_t. That is, when δ_s is identical for two grafting solutions, k_t would appear to be identical for the two solutions regardless of their chemical compositions. Caution should be exercised in extrapolating this conclusion to other monomer/polymer pairs until further examples of such behavior have been confirmed.

Monomer/Polymer Solubility Diagrams

Grafting on Nylon Films

If an analytical expression is available for the free energy of mixing as a function of concentration, it is theoretically possible to derive

the complete solubility and phase relationships for a polymer and two
liquids [17]. Unfortunately, the mathematics are sometimes so
cumbersome as to render the results virtually useless. Krigbaum
[11] has shown how the results may be simplified when the polymer
is entirely confined to one phase. Such a treatment would apply to a
polymeric film immersed in a grafting solution of two nonsolvents,
such as nylon immersed in a styrene/methanol solution. Krigbaum
derived the equations

$$\ln R = \phi_3 \left[L\chi_{23} - \chi_{13} - \chi_{12} + 2\chi_{12} \left(\epsilon/\phi_3 + v_2 \right) \right] + (L + 1) \ln(1 - \phi_3 - \epsilon/v_2)$$
(12)

$$(1 - \phi_3 + \epsilon/v_1)/(1 - \phi_3 - \epsilon/v_2) = (\phi_1/\phi_2)/(v_1/v_2) = R$$
(13)

where the symbols have the following definitions for the styrene (1)/
methanol (2)/nylon (3) system:

χ_{ij} = Flory interaction parameters.

ϕ_3 = volume fraction of polymer in swollen film.

L   = V_1/V_2 = 115.7/40.7 = molar volume ratio for styrene/
       methanol.

v_1/v_2 = styrene/methanol volume ratio in external solution.

ϕ_1/ϕ_2 = styrene/methanol ratio in the polymer phase.

R   = composition ratio.

The weight percent swelling data needed for the computation were ob-
tained by immersing nylon film samples in solutions having various
styrene/methanol ratios, with the results plotted in Fig. 7. The nylon
showed a saturation weight increase of 11.5% in pure methanol, and
no absorption when immersed in styrene only. The latter fact accounts
for the lack of grafting in the absence of methanol.
    In order to employ Eq. (12), it was necessary to obtain approximate
values of the three χ_{ij} parameters. The χ_{23} value for methanol/nylon
was estimated with the aid of a graph of log ϕ_3 vs χ constructed by
Hildebrand [5] for the case of a single solvent absorbed by polymer.
The 11.5% methanol absorbed by nylon indicates log ϕ_3 = -0.066,
which corresponds to a value of χ_{23} = 1.43 as read from Hildebrand's
graph. The densities of styrene, methanol, and nylon are 0.907,
0.792, and 1.14, respectively.
    The χ_{13} for styrene/nylon was computed by means of an equation
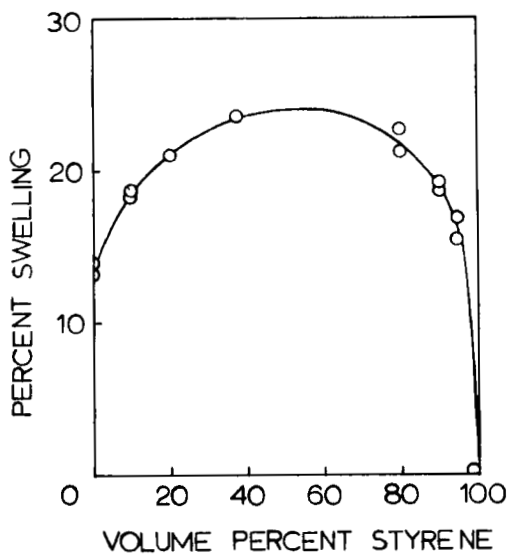due to Krigbaum [11]:

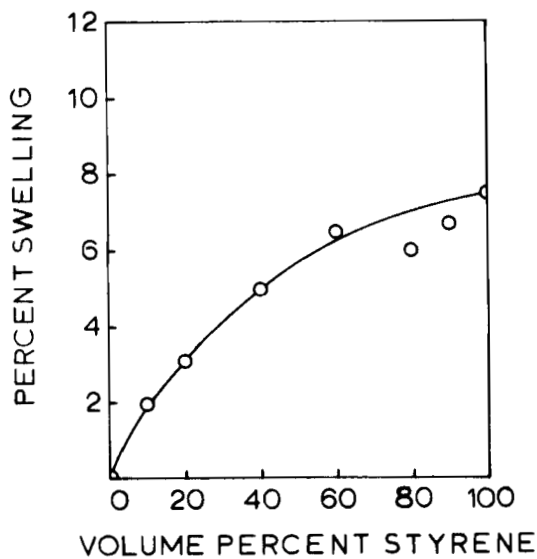FIG. 7. Saturation weight percent swelling of nylon film in styrene/methanol solutions.

FIG. 8. Saturation weight percent swelling of polyethylene films in styrene/methanol solutions.

$$\chi_{ij} = \left(\frac{V_i}{RT}\right)(\delta_i - \delta_j)^2 \qquad (14)$$

where V_i is the molar volume of the first component (115.7 cc for styrene in the present case), R is the gas constant, T is the absolute temperature, and δ_i and δ_j are the Hildebrand parameters, namely, 9.2 and 13.6 for styrene and nylon, respectively. Substitution of the numerical values in Eq. (14) yields a χ_{13} value of 3.77 for styrene/nylon. A value of $\chi_{12} = 1.00$ is taken for styrene/methanol, by analogy with the same value taken for the chemically similar benzene/isopropanol system by Scott [18]. The values of χ_{13}, χ_{23} $> \frac{1}{2}$ is a necessary and sufficient condition for the nylon to be insoluble in both styrene and methanol [17]. The fact that $\chi_{12} < 2$ indicates that styrene and methanol are mutually soluble.

By substitution of the numerical values in Eqs. (12) and (13) it is now possible to calculate liquid volume ratios, ϕ_1/ϕ_2, within the film corresponding to liquid volume ratios, v_1/v_2, external to the film. The computation is started by choosing some external styrene/methanol ratio such as 80/20, and selecting a corresponding arbitrary value for R that is believed to be in the right range. An initial estimate of ϕ_3 is obtained by assuming an 80/20 styrene/methanol ratio in the film, at the proper weight percent absorption read from the smoothed curve in Fig. 7. The arbitrary value of R is substituted in Eq. (13) to yield a value of ϵ, which is then substituted in Eq. (12) to yield a second value of R.

Another value of R that is intermediate between the first and second R is selected, and Eqs. (12) and (13) are again used in the same way. By successive trials in this way of improved estimates of R, a value of R is finally found which gives an ϵ value leading to no change in R when substituted in Eq. (12), indicating that this R value satisfies Eqs. (12) and (13) simultaneously. Calling this solution the "first estimate" of R, an improved internal ratio of ϕ_1/ϕ_2 is computed from Eq. (13), from which an improved "second estimate" of ϕ_3 is calculated. From the second estimate of ϕ_3, a second estimate of R is computed by the process of iteration described above. The whole procedure is continued until an estimate of ϕ_3 is reached that shows no change from the previous estimate. Usually the third estimate of ϕ_3 is found to be no different from the second estimate. Results of several calculations of R and ϕ_3 at various v_1/v_2 ratios are listed in Table 5, which also gives the corresponding values of $\phi_1/(\phi_1 + \phi_2)$.

Krigbaum [11] has rearranged Eq. (12) in the form

$$(1/\phi_3)[\ln R + (1 - L)\ln(1 - \phi_3 - \epsilon/v_2)] = (L\chi_{23} - \chi_{13} - \chi_{12}) +$$

$$2\chi_{12}(\epsilon/\phi_3 + v_2) \qquad (15)$$

TABLE 5. Composition Data for Solubility Diagram of Styrene/Methanol/Nylon System

v_1/v_2	Wt% absorbed	ϕ_3	R	$\dfrac{\phi_1}{\phi_1 + \phi_2}$	Left-hand side of Eq. (15)	$\epsilon/\phi_3 + v_2$
100/0	0	0.836	-	1.000	-	-
80/20	21.7	0.773	0.246	0.496	-0.475	0.110
60/40	23.9	0.750	0.225	0.252	-0.111	0.284
40/60	23.6	0.750	0.198	0.117	0.290	0.506
20/80	21.0	0.770	0.172	0.041	0.793	0.753
0/100	13.6	0.836	-	0	-	-

Referring to the left-hand side of Eq. (15) as L.H.S., a plot of L.H.S. against $(\epsilon/\phi_3 + v_2)$ should be represented by a straight line, the slope and intercept of which are functions of the interaction parameters characterizing the system

$$\text{slope} = 2\chi_{12} \tag{16}$$

$$\text{intercept} = L\chi_{23} - \chi_{13} - \chi_{12} \tag{17}$$

Figure 9 shows a plot of L.H.S. vs $(\epsilon/\phi_3 + v_2)$ for the styrene/methanol/nylon system, and the slope and intercept values are -0.70 and 2.00, respectively, as predicted by Eqs. (16) and (17). The fact that the data yield a straight line plot in Fig. 9 confirms neither the correctness of Eqs. (12) and (13) nor the absolute accuracy of the R and ϕ_3 values in Table 5, but it does indicate that no arithmetical errors were made in computing R and ϕ_3 values by the use of Eqs. (12) and (13).

   The data from Table 5 can be used to construct a solubility diagram for this ternary system in the shape of an equilateral triangle, a technique employed previously by Flory [19], Tompa [17], and others. Generally each of the three components is placed at one vertex of the equilateral triangle. Figure 11 represents a modified form of the technique, with only the 100% nylon vertex shown and arrows pointing to the 100% styrene and 100% methanol vertices. This method magnifies the solubility curve, which would appear quite small if the complete triangle were drawn. The disadvantage of the method is that it is not possible to show the tie lines running from points on the curve to the corresponding external solution composition points on the styrene/methanol side of the triangle
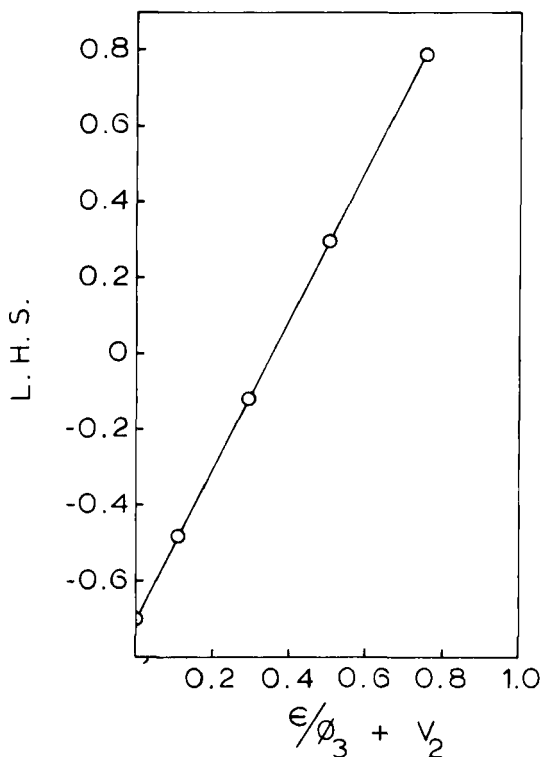
FIG. 9. Krigbaum plot of Eq. (15) for nylon film saturated with styrene/methanol solutions; data from Table 5.

(corresponding to 0 vol% nylon). Some compensation for the lack has been made by arrows indicating points on the curve where the tie lines would terminate that lead from external solution styrene/ methanol ratios of 60/40, 80/20, etc.

While Fig. 11 discloses many details of interest, perhaps the most interesting is the fact that a very small internal methanol concentration corresponds to a relatively large internal styrene concentration. For example, at the point on the curve indicated by the arrow corresponding to a 95/5 styrene/methanol ratio in the external grafting solution, an internal concentration of about 3 vol% methanol and about 14 vol% styrene in the film is indicated. This confirms the earlier hypothesis that methanol produces its acceler- ating effect in this type of system by greatly increasing [M] in Eq. (1).
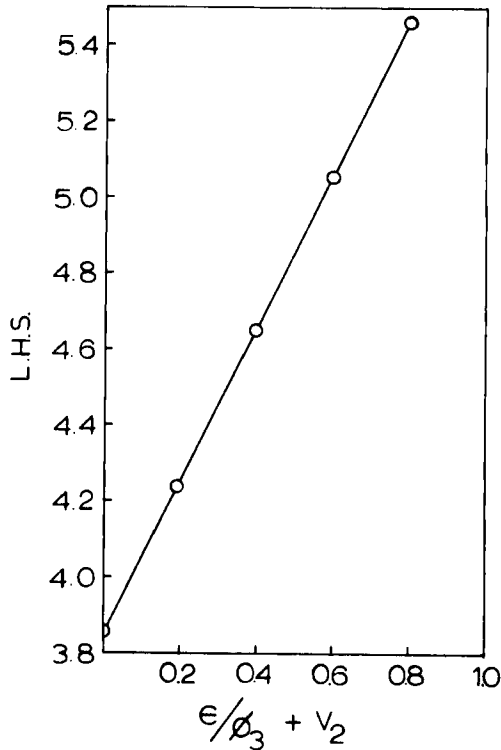
FIG. 10. Krigbaum plot of Eq. (15) for polyethylene film saturated with styrene/methanol solutions; data from Table 6.

It can reasonably be assumed that the point on the curve at the 95/5 arrow would probably represent the internal methanol concentration corresponding to any external solution having a total of styrene plus benzene amounting to 95 vol%. This follows from the fact that styrene and benzene have the same δ value and are very similar in chemical composition. Thus the point at the 95/5 arrow would also correspond to an external solution containing a 47.5/47.5/5 volume ratio of styrene/benzene/methanol. The internal composition corresponding to the latter external solution would probably be a volume ratio of about 7/7/3 of styrene/benzene/methanol. This assumption is in line with earlier kinetics studies on this same system showing that the grafting rate drops to half its value when half of the styrene in the grafting solution is replaced by benzene, while holding the percent methanol constant [2].
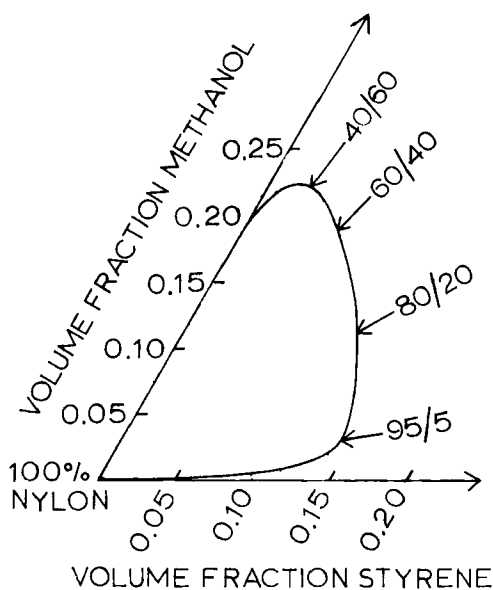
FIG. 11. Solubility diagram for styrene/methanol/nylon system computed from Eq. (12) and Fig. 7.

It is recognized that Eqs. (12) and (13) based on the Flory-Huggins theory can only predict phase relationships in a semiquantitative way. At the same time, such equations can be relied upon to reveal all the characteristic features of the phase behavior of polymer solutions [17]. In the present work the possible errors in Fig. 11 are limited to some extent because the theoretical results are made to conform to the experimental facts summarized in Fig. 7. It would probably be difficult to reproduce one particular point on the Fig. 11 solubility curve (such as the point corresponding to 10% Solution E in the external solution) by replacing methanol with an equivalent amount of ethanol on the basis of its δ value. This difficulty probably accounts for the different effects on grafting rate in Fig. 2 produced by 10% Solution E as compared to 10% ethanol.

It is notable that Fig. 11 indicates a minimum nylon content (maximum volume swelling) on the solubility curve at a 17/83 ratio of styrene/methanol. These solvents have δ values of 9.2 for styrene and 14.3 for methanol, which bracket the 13.6 value for nylon. According to the simple Hildebrand theory [5], the maximum swelling of a polymer takes place in a liquid having the same δ value as the polymer, and there is no difficulty in interpretation as long as

one discusses a liquid having a single component. When the liquid in question consists of two components, the internal (absorbed) liquid and external liquid generally have different component ratios, and hence have different δ values. It would appear logical that the absorbed liquid composition determines the degree of swelling of the polymer, and it is of interest to compute the δ value of the absorbed liquid in the nylon at the point of maximum swelling indicated in Fig. 11 corresponding to 17 vol% styrene and 83 vol% methanol:

$$CED = (0.17)(9.2)^2 + (0.83)(14.3)^2 = 185.4$$

$$\delta = (185.4)^{1/2} = 13.6$$

which is the δ value for nylon. Such precise agreement is probably fortuitous in view of the approximate character of the δ value theory.

Grafting on Polyethylene Films

The technique described above was also used to construct a triangular solubility diagram for styrene/methanol/polyethylene. The required weight percent swelling data were obtained by immersing polyethylene film samples in solutions having various styrene/methanol ratios. The percent swelling vs composition plot is shown in Fig. 8. The graph indicates that polyethylene absorbs 7.47% by weight of pure styrene, but will not absorb any pure methanol.

The χ_{ij} parameters were obtained as described previously.

The χ_{12} value of 1.00 for styrene/methanol was again employed. A value of χ_{13} of 1.70 for styrene/polyethylene was read from the Hildebrand [5] graph, corresponding to 7.47% by weight absorption of styrene in polyethylene.

Equation (14) was used to compute a χ_{23} value of 2.31 for methanol/polyethylene, employing $V_i = 40.7$ cc for methanol.

The computations of R and ϕ_3 were carried out by the technique already described, and selected examples of the resulting data are shown in Table 6. A Krigbaum plot of L.H.S. vs $(\epsilon/\phi_3 + v_2)$ is shown in Fig. 10. The slope of the line again is $2\chi_{12} = 2.00$, and the intercept is

$$L\chi_{23} - \chi_{13} - \chi_{12} = 3.86$$

The solubility diagram for polyethylene film is presented in Fig. 12. Again, arrows on the solubility curve indicate the termination points for tie lines coming from external solutions having styrene/methanol ratios of 20/80, 40/60, etc.

TABLE 6. Composition Data for Solubility Diagram of Styrene/Methanol/Polyethylene System

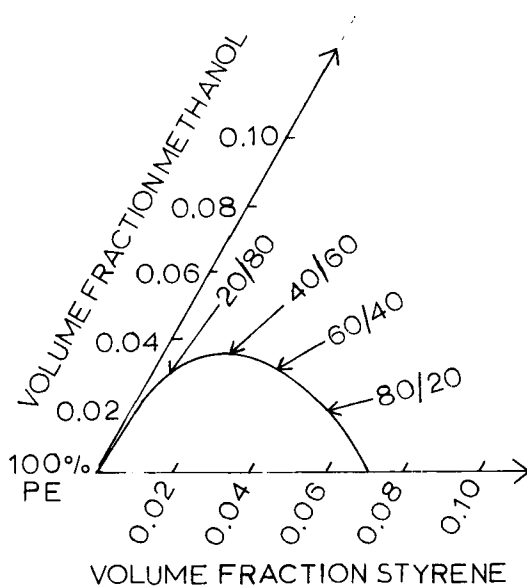| v_1/v_2	wt% absorbed	ϕ_3	R	$\dfrac{\phi_1}{\phi_1 + \phi_2}$	Left–hand side of Eq. (15)	$\epsilon/\phi_3 + v_2$
100/0	7.47	0.929	-	1.000	-	-
80/20	7.00	0.930	0.675	0.730	4.24	0.195
60/40	6.25	0.937	0.701	0.513	4.65	0.394
40/60	5.00	0.947	0.693	0.316	5.06	0.595
20/80	3.10	0.965	0.496	0.111	5.46	0.797
0/100	0	1.000	-	0	-	-

FIG. 12. Solubility diagram for styrene/methanol/polyethylene system computed from Eq. (12) and Fig. 8.

The amount of methanol added to the grafting solution affects graft-
ing rate in two ways: 1) by affecting monomer concentration within
the film, that is, by affecting the location of the point on the solubility
curve in Fig. 12 that corresponds to the grafting system, and 2) by
affecting the magnitude of $|\delta_s - \delta_p|$ and thus altering film

plasticity and k_t. With regard to the effect on [M], a study of the

styrene end of the solubility curve in Fig. 12 shows that a doubling of
the internal concentration from 10 to 20 vol% corresponds to a decrease
of only about 11% in the internal styrene concentration from 90 to 80
vol%. Hence the magnitude of [M] within the film is relatively
insensitive to changes in methanol concentration (either internal or
external). As for the second effect on $|\delta_s - \delta_p|$, the addition of

methanol would produce a gradual change in plasticity and k_t, rather

than a sudden or marked change. Hence, in this type of mechanism,
the change in rate should be somewhat insensitive to minor changes
in methanol content, whether caused by an error in the amount of
methanol added or by an imprecise attempt to replace methanol by
an equivalent amount of ethanol. These concepts may account for the
fact that the effects of ethanol and Solution E (containing methanol)
are experimentally indistinguishable in Figs. 4 and 5. It is evident
that this interpretation might not hold true for some other polymer/
liquid (1)/liquid (2) system because the effects observed will depend
upon the characteristics of the specific solubility curve that pertains
to the particular system, and the shape of such solubility curves can
obviously vary widely.

Caution should be used in comparing the data of Fig. 12 with
other published data. For example, Silverman [20] investigated the
absorption of styrene/methanol solutions by polyethylene films and
found a maximum of only 3.8 vol% methanol in the absorbed solution
at 90 vol% methanol externally. It is worth noting that the swelling
properties of polyethylene vary with its density, molecular weight,
degree of cross-linking, and other characteristics. The polyethylene
used by Silverman absorbed 14.8% styrene, about twice the
absorption observed with the polyethylene samples employed in
the present work. The higher solubility of styrene in polyethylene
would correspond to a much lower value of χ_{13}, which would correlate
with much higher styrene/methanol ratios in the absorbed solution
in line with Silverman's observations. The relatively low uptake of
methanol by Silverman's samples is also in accord with his observa-
tion of maximum grafting rate at 70% methanol in the styrene,
compared to a maximum rate at only 12% methanol in the styrene
observed in the present work (Fig. 5).

An examination of Figs. 11 and 12 leads to the question of what
would happen if the two liquids in the external solution were both
monomers. In qualitative terms, both monomers would penetrate

into the film and form copolymer chains grafted onto the film. The rate of such grafting would be influenced by the δ value of the solution of the two monomers, and by the magnitude of $|\delta_s - \delta_p|$ in the fashion already discussed. It is also possible that a further very interesting phenomenon may be observed. Consider the copolymerization of styrene with some polar monomer (PM) as it takes place within a polyethylene film. Due to statistical fluctuations, some of the growing chains will contain a higher percentage of PM units than others. Such growing chains reach a considerable size and may occupy a considerable volume of space (on a molecular scale of size).

Within the domain occupied by a PM-rich chain the effect may be similar to that of adding a polar solvent which increases $|\delta_s - \delta_p|$, reduces k_t, and increases the overall rate of copolymerization. Hence PM-rich chains might actually grow faster than chains containing lesser amounts of PM. This would tend to produce a higher PM content in the resulting copolymer than would be predicted by the conventional Lewis-Mayo copolymerization equation. As an alternative mechanism or model, perhaps only the PM units near the growing end of the chain would have an appreciable effect on $|\delta_s - \delta_p|$ and k_t. The net effect would still be an unexpectedly high PM content in the resulting copolymer.

A search of the literature has revealed one set of grafting data that provides the necessary comparisons to shed some light on this phenomenon. Odian [21] used radiation activation to graft mixtures of styrene with various polar monomers on polyethylene film. The M_1/M_2 monomer pairs studied included styrene/methyl acrylate (MA), styrene/acrylonitrile (AN), and styrene/4-vinyl pyridine (4VP). The actual analysis of the initial copolymer, dM_2/dM_1, was compared with that predicted by the Lewis-Mayo equation for the three systems. At a monomer loading of about 70 vol% M_2 in all three cases, it was found that the dM_2/dM_1 ratio exceeded the predicted value for 4VP, AN, and MA by about 166, 114, and 30%, respectively (the last figure being the average result for 60 and 80 vol% loadings of MA). The increases are in the same order as the δ values, which are 11.0, 10.5, and 9.5 for 4VP, AN, and MA, respectively. This result does not prove the above hypothesis, but it does suggest that further studies along this line would be of interest. A complete analysis of the phenomenon would be rendered more complex by the fact that the $[M_1]/[M_2]$ ratio within the film would generally differ from the $[M_1]/[M_2]$ loading in the solution external to the film, as indicated by Eq. (12).

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