Journal of Macromolecular Science, Part A

Monomer and Polymer Grafting on Nylon Film Using Cobalt-60 Radiation

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ABSTRACT

Rates of γ-ray-induced grafting on nylon 6 film were
compared for pentafluorostyrene (PFS) and trifluoroethyl-
methacrylate (TFEM). The logarithm of the measured
rate of PFS grafting on nylon 6, plotted against reciprocal
temperature, gave a straight-line Arrhenius plot between
23 and 80°C, the slope indicating an activation energy of
6.5 kcal/mole. The addition of methanol accelerated the
room temperature grafting of both PFS and TFEM on
nylon 6, the rate passing through a maximum at 40 and
30 vol% methanol, respectively. The grafting of PFS on
nylon 6 takes place most probably by a free radical mech-
anism, as indicated by the value of the energy of activa-
tion and by the fact that the reaction is not inhibited by
water.
Some work was done to extend the quantitative aspects of
the theory of cocross-linking, and certain analogies with
the theory of copolymerization were demonstrated.
Radiation-induced cocross-linking between a 5% solution
of polyvinyl alcohol and a nylon film surface was shown,
the initial rate of nylon weight gain due to grafted PVA
being 0.14%/hr.

INTRODUCTION

The objective of this project was to investigate radiation-induced grafting on polyamides, with emphasis on fluorine-containing vinyl monomers.

The principal experimental technique was to be the γ-ray irradiation of polyamide film samples immersed in suitable vinyl monomers. Some preliminary work was done to determine the effect of water on the grafting reaction, since grafting on polyamide is similar in some respects to grafting on polyvinyl alcohol, and it is known that water has an accelerating effect in grafting on polyvinyl alcohol.

For example, Sakurada [1] found in the radiation-induced grafting of styrene on polyvinyl alcohol film that a dosage of 2.7×10^6 R produced zero grafting when the film contained no water, but caused 444% grafting when the film contained 20% water. The addition of water to the monomer being grafted also accelerated grafting on polyvinyl alcohol as shown by Chapiro [2].

In the present study of water effects, nylon films containing water were prepared by storing film for several days in desiccators at controlled 57% relative humidity. The saturation water absorption amounted to about 4% by weight after 2 days storage. Figure 1 shows the water uptake curve for films stored at 57% relative humidity, as well as the mirror-image weight loss curve obtained by storing "wet" films in a dry desiccator over calcium chloride.

The technique of using nylon films of controlled water content introduces delicate film conditioning and moisture content control problems. Accordingly, the idea of using water was abandoned when it was found that addition of methanol to various monomers enabled grafting at a measurable rate on completely dry nylon films. This grafting technique was successful with pentafluorostyrene (PFS), trifluoroethyl methacrylate (TFEM), and vinyltrifluoroacetate (VTA). Most of the work on the present project has been done with PFS.

EXPERIMENTAL METHODS

The 0.5-Ci ^{60}Co source contained encapsulated cobalt in the form of a hollow cylinder. A similar source design was described previously by Daniels [3]. Each film sample measured about
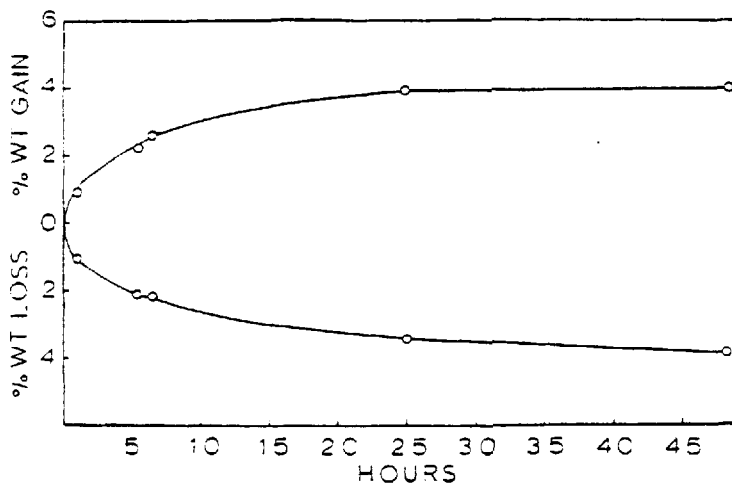
FIG. 1. Water uptake and loss vs time for 0.008 in. nylon 6 film stored at 57% R.H. and room temperature.

0.5 by 1.0 cm, and was placed in a section of a glass reaction tube measuring 2.5 cm in length and 0.7 cm in inside diameter. The film in each case was 0.008 in. nylon 6, dried completely by several days storage in a desiccator over calcium chloride. The glass reaction tube containing the film was always positioned at the same point in the center of the ^{60}Co source during each irradiation run. This method resulted in excellent consistency and reproducibility of grafting measurements. An exposure dose rate of 590 R/hr was determined by ferrous sulfate dosimetry [4].

The monomers used included 2,3,4,5,6-pentafluorostyrene, 2,2,2-trifluoroethyl methacrylate, and vinyltrifluoroacetate, obtained from PCR Inc. Each monomer 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 for several days prior to use. Just before each grafting run, oxygen was eliminated from the monomer by use of a high-vacuum system. The monomer was then carried through several successive cycles of freezing in a Dry-Ice trap, pumping down, and melting the monomer again. In the last cycle the monomer was transferred to the reaction tube which was surrounded by a Dry-Ice/acetone bath. The reaction tube with

its contents of film and monomer was sealed off from the system
while pumping on the system. The reaction tube was then placed
inside the ^{60}Co cylinder in a predetermined position.

After the irradiation of the reaction tube containing polymeric
film and monomer, the film was extracted by stirring in warm
acetone for 48 hr, then dried in air and weighed. This was done
to remove any homopolymer in or on the film, since it was shown
in a separate experiment that acetone was an excellent solvent
for the homopolymer of PFS. A correction for film weight loss
during extraction was made by running a blank (ungrafted) film
through the extraction and drying procedure. Unless otherwise
noted, all grafting runs were carried out at the temperature of
the irradiation room, $23 = 1^{\circ}C$.

Percent grafting was computed from corrected film weight
(P_0) prior to grafting and weight after grafting (P_g) as

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

In several cases the weight of the swollen film (P_s) at the end of
the run was determined by quickly drying the film between filter
papers and weighing it in a weighing bottle. The percent swelling
uncorrected for grafting was calculated as

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

In the runs at higher temperature, the temperature was held
constant by means of a glass constant temperature jacket located
within the hollow cobalt source. The constant temperature jacket
was shaped like a hollow cylinder, and the reaction tube containing
film and monomer was positioned in the center of the constant
temperature jacket. Distilled water was pumped through the
jacket by a Haake Model FE circulator, with a temperature
control capability of $\pm0.005^{\circ}C$ indicated by the manufacturer.
Estimated temperature control within the reaction tube was
better than $\pm0.1^{\circ}C$, as shown by measurements made in the
center of the constant temperature jacket.

EFFECT OF TEMPERATURE

Figure 2 presents a plot of percent grafting vs time at room
temperature (23°C). Using the constant temperature jacket, graft-
ing runs were also made at 50, 65, and 80°C, with the results
shown in Fig. 3. A summary of the computed rates at different
temperatures is given in Table 1.
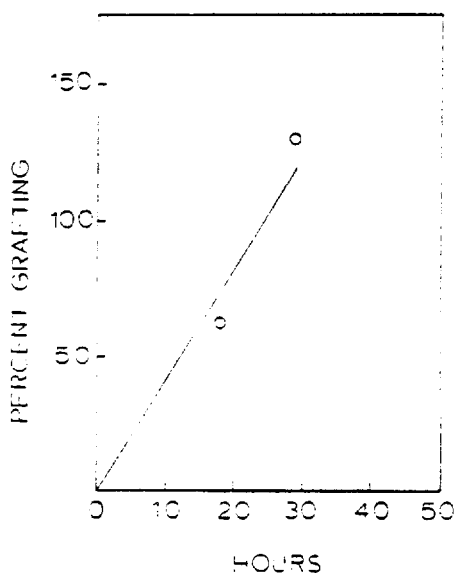
FIG. 2. Percent grafting vs time for PFS on 0.008 in. nylon 6
film at 23°C.

Figure 4 presents an Arrhenius plot of the logarithm of rate vs
the reciprocal of the absolute temperature. The resulting line was
quite straight, the slope of the line indicating an energy of activation
of 6.5 kcal/mole.

This value agrees well with the estimate of E for radiation-induced
polymerization computed by Chapiro [5]. who employed the equation,

$$E = 1/2 E_i + E_p - 1/2 E_t \tag{3}$$
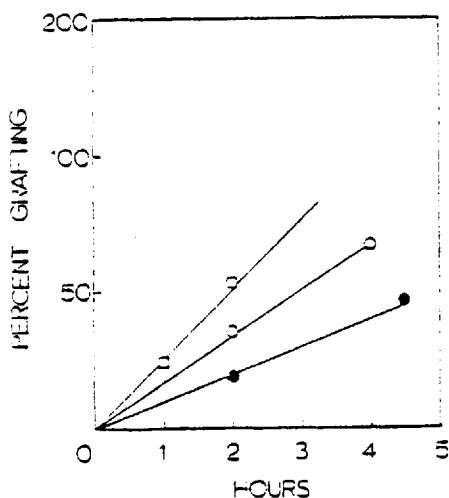
FIG. 3. Percent grafting vs time for PFS on 0.008 in. nylon 6 film at 50°C (●), 65°C (○), and 80°C (□).

TABLE 1. Rate of PFS Grafting on Polyamide Films at Various Temperatures

Temperature (°C)	$\bar{\tau}_c$, hr	Mole/kg/sec, $\times 10^5$	Log (mole/kg/sec $\times 10^5$)	$1/T$
23	4.07	5.83	0.766	0.00338
50	10.0	14.3	1.155	0.00309
65	16.7	23.9	1.378	0.00296
80	25.0	35.9	1.555	0.00283

where E is the overall activation energy, and E_i, E_p, and E_t are the partial activation energies for the initiation, propagation, and termination steps, respectively. He assumes that E_p is about 7 kcal/mole, E_t about 2 kcal/mole, and E_i is zero for radiation initiation, giving

$$E = 0 + 7 - 1 = 6 \text{ kcal/mole} \tag{4}$$

FIG. 4. Logarithm of grafting rate vs 1/T for PFS on 0.008 in. nylon 6 film.

which agrees closely with the above experimental value of 6.5 kcal/mole for the PFS polyamide grafting reaction.

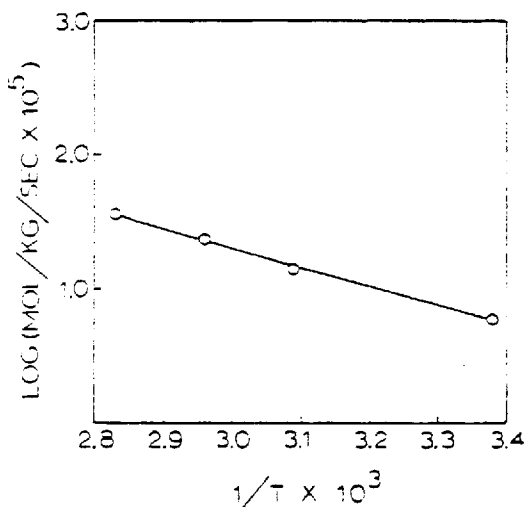The unusual features about this behavior are the following: 1) the straight line plot of log rate vs reciprocal temperature, and 2) the agreement of the value of E with the "textbook" value. The reason this is unusual is that many monomer/film grafting reactions do not exhibit normal or conventional kinetics, primarily because of the limiting and complicating effects of the slowness of monomer diffusion within the film. For example, in the radiation-induced grafting of styrene on 0.035 mm polyethylene films, Hoffman [6] observed the highest rate at 20°C, but with a higher rate at 70°C than at 40°C, presumably due to the complicating effects of diffusion. Also, in the radiolytic grafting of styrene on polymethylpentene film [7], a zero energy of activation was observed, possibly because of the complicating effects of diffusion.

The straight line plot of log rate vs 1/T, taken in combination with the value of E, would appear to indicate that the radiolytic grafting of PFS on polyamide films follows "normal" free radical polymerization kinetics. The methanol appears to enable the PFS to penetrate into the film so rapidly that slowness of monomer

diffusion does not control or limit the grafting reaction in any way. Another indication of the free radical nature of the grafting reaction is the fact that water does not inhibit the reaction. Small quantities of water are very effective in the inhibition of anionic or cationic polymerization.

EFFECT OF ADDED METHANOL

The addition of methanol to PFS or TFEM accelerated the radiolytic grafting of these monomers on nylon film. Grafting vs time curves for PFS/methanol volume ratios of 80, 20 and 60/40 are presented in Fig. 5, and for the 40, 60 ratio in Fig. 6. Figure 7 shows grafting rates in moles/kg, sec plotted against vol% methanol, and the computed rates are summarized in Table 2.
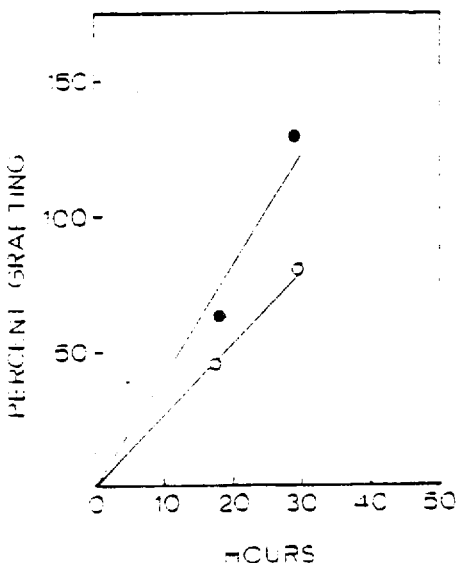

FIG. 5. Percent grafting vs time on 0.008 in. nylon 6 film at 23°C for PFS/methanol volume ratios of 30, 20 (○) and 60, 40 (•).
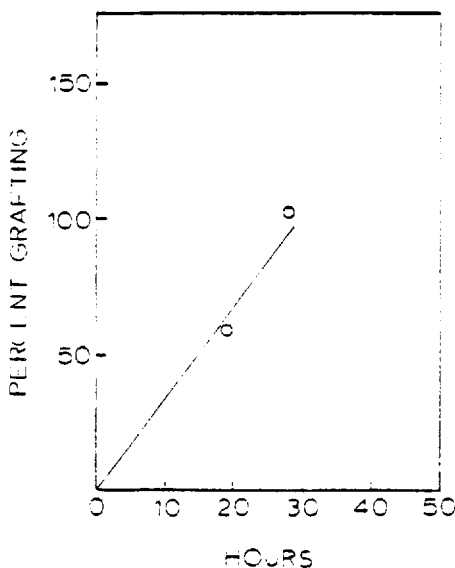
FIG. 6. Percent grafting vs time on 0.008 in. nylon 6 film at
23°C for PFS/methanol ratio of 40/60.

Examination of Fig. 7 indicates a maximum grafting rate for PFS/
nylon at about 40 vol% methanol. The point at 0% methanol is very
important, and shows that zero grafting takes place in the absence
of methanol, apparently because the PFS cannot penetrate the film
and reach the active radical sites.

Similar results were obtained in TFEM/polyamide grafting
studies. Grafting vs time curves for TFEM/methanol volume
ratios of 70/30 and 60/40 are presented in Fig. 8, and for the
80/20 ratio in Fig. 9. Figure 10 exhibits grafting rates in moles/
kg/sec vs vol% methanol, and the computed rates are given in
Table 3. It is evident that the grafting rate passes through a
maximum at about 30 vol% methanol. Again, the point at the
origin in Fig. 10 indicates that the grafting rate is zero when
methanol is absent. The curve in Fig. 9 shows autoacceleration
following the initial linear rate, an effect not uncommon for
methacrylate monomers. The rate computed from Fig. 9
involved only the initial portion of the curve.
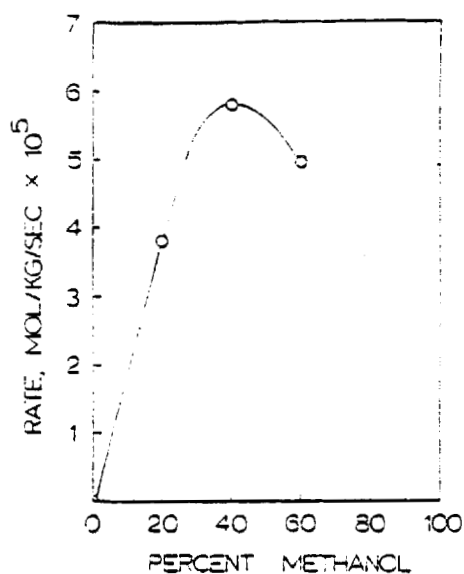
FIG. 7. Rate of grafting of PFS on 0.008 in. nylon 6 vs vol%
methanol.

TABLE 2. Rate of PFS Grafting on Polyamide Films at Various
Methanol Concentrations

Vol% methanol	Rate (%/hr)	Rate (mole/kg, sec × 10^5)
0	0	0
20	2.67	3.83
40	4.07	5.83
60	3.46	4.95

The accelerating effect of methanol on grafting rate in the above
examples can only result from an acceleration of the initiation step,
an acceleration of the propagation step, or a slowing down of the
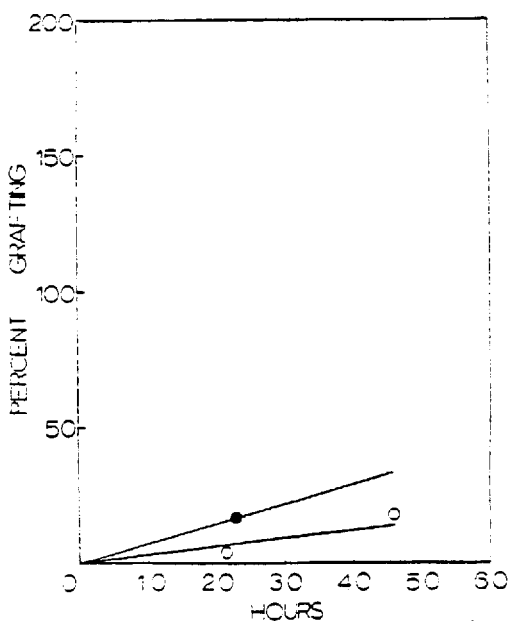
FIG. 8. Percent grafting vs time on 0.008 in. nylon 6 at 23°C for TFEM/methanol volume ratios of 60/40 (○) and 70/30 (●).

termination step. The following are three possible ways in which such effects could be produced:

1. Acceleration of initiation through some type of energy transfer from methanol to polyamide, or through some reaction mechanism involving interaction of methanol radiolysis products with polyamide.

2. A Trommsdorf or gel effect caused by methanol, involving a slowing down of termination (recombination of growing chain radicals).

3. An acceleration of propagation, brought about by the action of methanol in expediting the penetration of monomer into the polymer film, thus bringing monomer into contact with the active radical sites.

Each of these hypotheses will be discussed in turn.
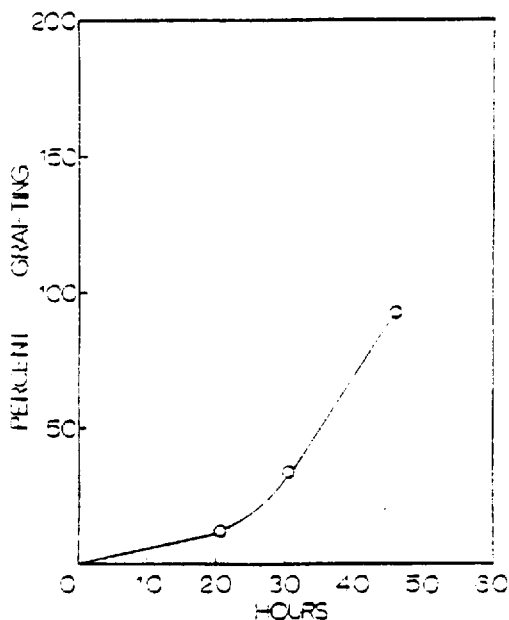
FIG. 9.   Percent grafting vs time on 0.008 in. nylon 6 at 23°C
for TFEM, methanol volume ratio of 80, 20.

Energy Transfer from Solvent to Polymer

   This is a possibility that has been discussed in a general theo-
retical way by Chapiro [8], involving influence of the rate of
initiation by an added substance, either by energy transfer or by
radiolysis of the added substance to generate active radicals
which are capable of abstracting hydrogens from the polymer.
The radiolysis of methanol is known to produce ·CH_2OH and CH_3O·
radicals [9, 10], which would perhaps abstract hydrogens from
the polymer molecules. However, there is no definite evidence
for this effect in the present case, while there is evidence for
the third hypothesis given below.

Trommsdorf Effect

   A Trommsdorf or gel effect would be conceivable for growing
styrene chains in the presence of methanol, because the polar
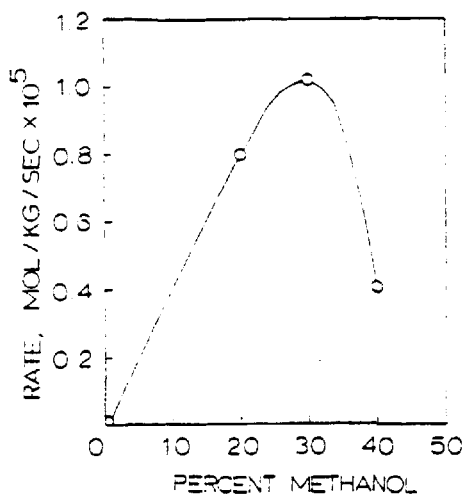
FIG. 10. Rate of grafting of TFEM on 0.008 in. nylon 6 vs vol% methanol.

TABLE 3. Rate of TFEM Grafting on Polyamide Films at Various Methanol Concentrations

Vol% methanol	Rate (%/hr)	Rate (mole/kg/sec × 10^5)
0	0	0
20	0.56	0.80
30	0.71	1.02
40	0.29	0.41

methanol (a nonsolvent for polystyrene) might tend to immobilize or curl up the growing nonpolar styrene chains and slow down termination by radical combination. In the present work, however, the growing chains of PFS and TFEM are somewhat polar in nature, since the homopolymers of both were shown to be insoluble in benzene and soluble in acetone. Hence, the polar methanol is

unlikely to produce a Trommsdorf slowing of the combination of PFS radicals or TFEM radicals.

Film Penetration Assisted by Methanol

The zero rate of grafting at zero methanol concentration is a strong argument that methanol enables the penetration of PFS (or TFEM) monomer to the radical sites within the polyamide film. In a sense, this effect would tend to accelerate propagation by making monomer available to radical sites capable of initiating polymerization. This accelerating effect would dominate up to 30 or 40 vol% methanol. Above that concentration, two other effects would become important which would cause the grafting rate to decrease: Monomer concentration is decreasing, which would tend to decrease the grafting rate. Also, the increasing methanol concentration spreads the nylon chains apart and allows more freedom of movement of radical chains, thus causing faster termination and slowing the overall grafting rate.

The action of methanol may be similar to that of water, which is also known to accelerate the small grafting of various monomers on polyamides [11]. In such cases the rate is also extremely slow or zero in the complete absence of water.

Further evidence for Hypothesis 3 is provided by the relation between grafting and swelling in the PFS/polyamide system. Figure 11 presents a plot of percent film swelling vs percent grafting for most of the runs employing PFS discussed above. It can be seen that the swelling increases as the grafting increases. This probably only means that a graft copolymer containing a higher percentage of PFS is capable of absorbing a higher percentage of PFS monomer, resulting in greater swelling. If the best straight line were to be drawn through the points, it would intersect the swelling axis at approximately 20%. This would imply that the polyamide film took up about 20% methanol before the PFS molecules could penetrate the film and reach the radical sites which initiate polymerization.

POLYMER GRAFTING ON NYLON

The above discussion has dealt only with the radiation-induced grafting of monomers on nylon. It is also possible to graft
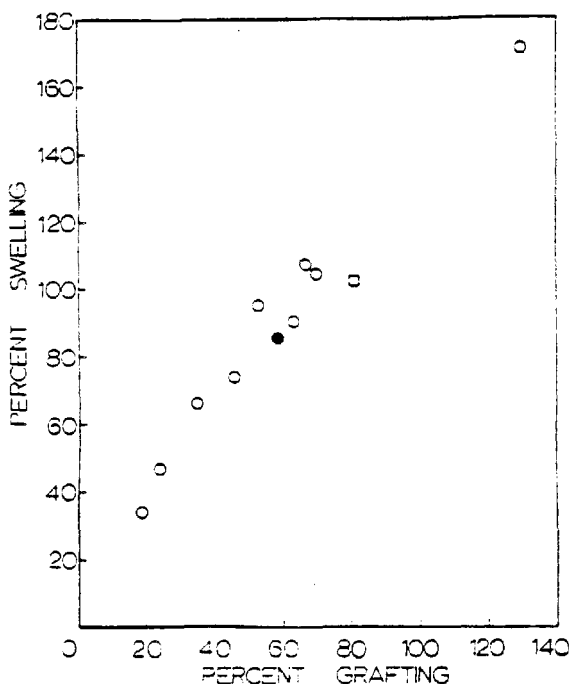
FIG. 11. Percent swelling vs percent grafting for PFS on
0.008 in. nylon 6 film at 23°C for 20% methanol (□), 40% methanol
(○), and 60% methanol (●).

polymers on nylon. In spite of the evident theoretical and practical
importance of the subject, little research has been done on polymer/
polymer grafting. Most of the work to date has been done by
Henglein [12], who has referred to the chemical linking of Polymer A
to Polymer B by the term "cocross-linking."

    Henglein produced cocross-linking by dissolving Polymer A and
Polymer B in a common solvent, followed by the irradiation of their
common solution. His studies of this process were extensive [13],
and he developed the following theoretical points.

    1. When two polymers, A and B, are irradiated in homogeneous
solution, two types of free macroradicals can potentially be formed.
Combination of the two different macroradicals corresponds to the
formation of a cross-link between A and B (cocross-linking).

2. If the rate constants for combination of the appropriate macroradicals are indicated by k_{aa}, k_{ab}, and k_{bb}, cocross-linking will be favored when $k_{ab} > k_{aa}$ and $k_{ab} > k_{bb}$, but will not be favored when $k_{aa} > k_{ab}$ and $k_{bb} > k_{ab}$.

3. Even if Macroradical A does not combine with Macroradical B, cross-linked chains of A can become physically entangled with chains of B, forming what Henglein calls a "mixed network." He refers to a network of A and B formed by chemical linking of A and B as a "conetwork."

4. At low degrees of cross-linking, cocross-linking will be indicated by the appearance in the solution of polymer molecules of the type that normally result from the radiation-induced grafting of one monomer on the other, such as,
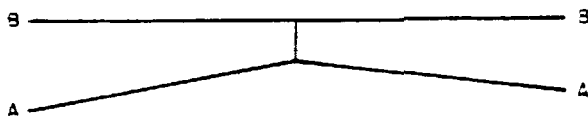
5. Cocross-linking will also be indicated by the dependence of the rate of cross-linking on polymer concentration. In each solvent there is a "critical concentration" for A, and also for B, below which scission predominates and gelation cannot be induced no matter how large the radiation dose may be. However, if cocross-linking occurs, both A and B can be present at less than critical concentration and yet gel formation takes place, showing that both A and B are involved in forming the total network (gelation).

In addition to the above characteristics of cocross-linking, a sixth concept due to Chapiro should be mentioned.

6. Chapiro postulated that cocross-linking would be expected to take place if both A and B are of the cross-linking type. If B is of the cross-linking type and A is of the scission type, one would expect the formation of grafted structures such as

If neither A nor B is of the cross-linking type, the yield of cocross-linking would be expected to be very low. However, no experimental check of these postulates for a large number of A, B polymer pairs has been made.

The principles of cocross-linking in solution are perhaps best illustrated by Henglein's work [12] on polyvinylpyrrolidone (PVP) and polyacrylamide (PAM). Separate water solutions of the two polymers were first irradiated by γ rays from ^{60}Co at an exposure dose rate of about 7×10^4 R/hr. The effects of radiation were studied at several different concentrations of each polymer. As polymer concentration decreases, more solvent radicals and fewer macroradicals will be formed. However, the simultaneous scission of the main chain by direct action of the radiation will still take place with unchanged efficiency according to Henglein [13]. The result is that the p/q ratio (density of scission to density of cross-linking) will increase as polymer concentration decreases. Hence, a critical concentration should exist below which gelation is not possible (p/q > 2), no matter how large the dose. Henglein [13] estimated the critical concentration in organic solvents to be about 10% by weight.

Water is a much more efficient solvent for the cross-linking of a polymer, and the critical concentration in water is about 1% by weight. The data are generally presented as a plot of the gel dose vs polymer concentration, which passes through a minimum slightly above the critical concentration. The addition of solvent to a polymer first leads to a decrease in gel dose, since the mobility of the macroradicals in recombining is increased as viscosity falls. This effect is counterbalanced and surpassed as concentration drops further, due to the decrease in inter-molecular cross-linking and the increase in p/q.

Henglein's work on a water solution of PVP alone showed a critical concentration of 0.28 wt%, while the corresponding critical concentration for PAM alone was 0.25 wt%. Hence, a solution containing 0.27% PVP and 0.24% PAM should not gel on irradiation unless cocross-linking between the two polymers takes place. As a matter of fact, a solution containing 0.20% PVP and 0.12% PAM did exhibit gelation on irradiation, indicating clearly that cocross-linking was taking place between PVP and PAM.

The concepts of Henglein form the basis for a qualitative but not quantitative theory of cocross-linking. The writer has been working recently to extend the quantitative aspects of the theory of cocross-linking. In regard to the quantitative viewpoint, it is worth noting that the effect of viscosity on the rate of macroradical

combination has often been overlooked. In most theoretical dis-
cussions of the irradiation of polymers, it has generally been
assumed that the ratio of scission rate to cross-linking rate (p, q)
remains constant during irradiation up to and including the process
of gelation [14-16]. In fairness it should be noted that the assump-
tion of constant p/q appears to be specifically stated only in dis-
cussions of solid polymer irradiation. However, there is much
research dealing with the irradiation of polymer solutions in
which the idea of p/q constancy is either used or implied, and
certainly nothing is said about the variation of p, q as the irradia-
tion proceeds and the viscosity of the solution changes.

While the change in viscosity would probably not affect the rate
of scission (p), it would certainly affect the rate of cross-linking
(q), which involves the rate of combination of macroradicals
moving in a viscous medium. A large amount of evidence is
now available for the strong effect of viscosity on the rate of
macroradical combination. To cite a few examples, Benson [17]
showed that the radical combination (chain termination) rate con-
stant for various monomers decreased as the viscosity increased.
Matheson [13] found that k_p k_t increases as percent conversion
(and viscosity) of styrene increases, indicating a decrease in k_t
since k_p is assumed unchanged. In the radiolytic grafting of sty-
rene on polyvinyl chloride, Takamatsu [19] found that an increase
in styrene concentration from 2.0 to 5.2 mole/liter decreased the
viscosity of the PVC and increased the termination rate (macro-
radical combination) by a factor of about 300. Many other examples
of the effect of viscosity on macroradical combination rate exist in
the literature.

In this connection the work of Henglein [12] on the irradiation
of solutions containing PVP and PAM is of particular interest.
In the irradiation of an aqueous solution of 0.20% PVP and 0.07%
PAM, there was first a considerable increase in viscosity, after
which the measured viscosity went through a rather sharp maximum
and then dropped markedly. In order to explain this result, there
must be at least two processes or mechanisms involved, one of
which tends to increase the viscosity while the other tends to
decrease the viscosity. Without attempting to go into details of
the reactions involved, assume for the moment that macroradical
combination (cross-linking) is related to viscosity increase while
chain scission results in viscosity decrease. In order to explain
the observed effect, the relative importance of scission and

cross-linking would have to change during the course of the irradia-
tion in such a way that cross-linking becomes of progressively less
relative importance: in other words, in such a way that the p/q
ratio becomes continuously larger as the irradiation proceeds.
The value of p/q can increase either as a result of p becoming
larger or of q becoming smaller. However, there is no reason
to believe that the rate of chain scission (p) increases as the
viscosity increases. On the other hand, there is every reason to
think that the rate of radical combination (q) decreases with
increasing viscosity, simply because the rate of radical diffusion
through the medium must decrease as viscosity increases.

Hence, a method of estimating the change in radical combina-
tion rate as viscosity changes is needed. One method that has
been fairly successful in estimating the effect of viscosity on
diffusion-controlled reactions is the use of the Smoluchowski
[20] equation, which states

$$k = \frac{4 \pi N_0}{1000} (r_1 + r_2)(D_1 + D_2) \text{ mole}^{-1} \text{ liter sec}^{-1} \tag{5}$$

where N_0 is Avogadro's number, and the r's and D's are the radii
and diffusion coefficients of the reacting macroradicals, respectively.

The radii of the PVP and PAM molecules can be estimated by
assuming molecules of approximately spherical shape of volume
approximately $4/3 \pi r^3$, using Henglein's [12] average molecular
weight of 10^6 for both molecules, and density figures of 1.20 and
1.092 g/cc for PVP [21] and PAM [22], respectively. The results
indicate radii of 6.91×10^{-7} cm for PVP and 7.13×10^{-7} cm for PAM.

Figure 12 presents viscosity vs irradiation time in the initial
portion of the curve (Henglein's Fig. 1c, Ref. 12), where Henglein's
values for relative viscosity have been converted to centipoise.
For each viscosity the diffusion coefficients for PVP and PAM
molecules can be estimated from a combination of Stoke's and
Fick's laws, yielding

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

where R is the gas constant, T is the absolute temperature, N_0 is
Avogadro's number, η is viscosity in poise, and r is the molecular
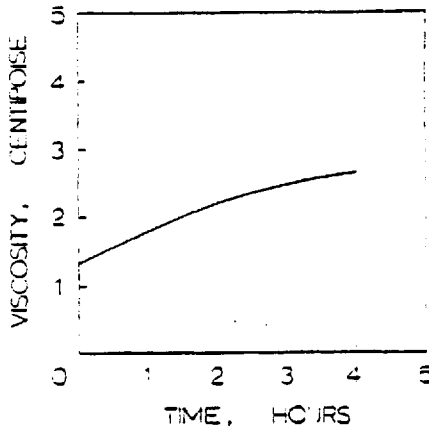
FIG. 12. Radiation-induced viscosity increase of aqueous solution of 0.20% PVP and 0.07% PAM, computed from the data of Henglein [12].

radius. Substitution of the estimated radius for PVP and the known constants yields

$$D_{PVP} = \frac{3.16 \times 10^{-9}}{\eta} \tag{7}$$

and for PAM

$$D_{PAM} = \frac{3.07 \times 10^{-9}}{\eta} \tag{8}$$

Substitution of the computed D and r values in Eq. (5) gives

$$k = \frac{4\pi N_0}{1000} (6.91 \times 10^{-7} + 7.13 \times 10^{-7})(D_1 + D_2)$$

$$= (1.057 \times 10^{16}) \left(\frac{6.23 \times 10^{-9}}{\eta} \right)$$

$$= \frac{6.60 \times 10^{-7}}{\eta} \tag{9}$$

the latter form showing clearly the inverse relationship between rate constant and viscosity. The rate constants for PAM and PVP radical combination have been computed for the viscosity values in Fig. 12 using Eq. (9), and the results are presented in Fig. 13. This much of a decrease in cross-linking rate might be enough to reverse the trend toward gelation, and thus account for Henglein's observed viscosity behavior outlined above. Any comprehensive theory of cocross-linking must explain the remarkable rise then fall of solution viscosity observed by Henglein.
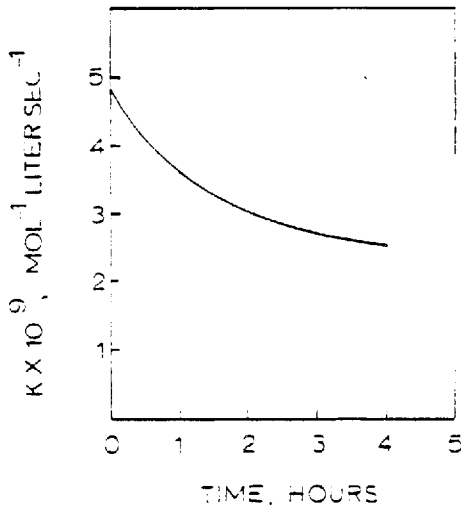
FIG. 13. Rates of PVP and PAM macroradical combination for the viscosity values of Fig. 12, computed from the Smoluchowski [20] equation.

It is possible to draw further theoretical conclusions by considering the individual cross-linking steps involved in gelation. Let A· and B· represent the specific macroradicals from polymers A and B, respectively, that undergo cross-linking during irradiation. Then the fundamental cross-linking reactions (radical combinations) with the corresponding rate constants can be written:

$$A\cdot + A\cdot \xrightarrow{\quad k_{aa} \quad} A{-}A \qquad (10)$$

$$B\cdot + B\cdot \xrightarrow{k_{bb}} B-B \tag{11}$$

$$A\cdot + B\cdot \xrightarrow{k_{ab}} A-B \tag{12}$$

$$B\cdot + A\cdot \xrightarrow{k_{ab}} B-A \tag{13}$$

This reaction sequence bears a superficial resemblance to the sequence outlined in copolymerization theory by Mayo [23] and others, but with two important differences: 1) These equations refer to radical/radical reactions in each step, while the copolymerization steps involve monomer/radical reactions in each case. 2) While the steady-state assumption is necessary in copolymerization theory and constant radical concentrations are assumed, in the present sequence the following equation results immediately because of the equivalence of Eqs. (12) and (13) without the need for any steady-state assumption and without any assumption of constancy of radical concentrations:

$$\frac{d[A\cdot]}{d[B\cdot]} = \frac{k_{aa}[A\cdot]^2 + k_{ab}[A\cdot][B\cdot]}{k_{bb}[B\cdot]^2 + k_{ab}[A\cdot][B\cdot]} \tag{14}$$

where $d[A\cdot]/d[B\cdot]$ indicates the instantaneous composition of insoluble gel being formed in terms of the relative amounts of the macroradicals $A\cdot$ and $B\cdot$ that it contains. The instantaneous gel composition will change as the irradiation proceeds, if one type of radical is entering the gel more rapidly than the other type.

Equation (14) is more difficult to handle experimentally than the corresponding one for copolymerization, because Eq. (14) refers to radical concentrations while the analagous one for copolymerization refers to monomer concentrations which are easily computed from the monomer feed.

The ratio $d[A\cdot]/d[B\cdot]$ can be determined for the initial gel formed by carrying out a chemical analysis of the gel and assuming that average molecular weights of macroradicals $A\cdot$ and $B\cdot$ are the same as the initial average molecular weights (measured) for Polymer A and Polymer B.

Certain limiting forms of Eq. (14) can be derived. If k_{ab} is negligibly small, indicating negligible tendency for A and B to cross-link, then Eq. (14) reduces to

$$\frac{d[A\cdot]}{d[B\cdot]} = \frac{k_{aa}[A\cdot]^2}{k_{bb}[B\cdot]^2} \tag{15}$$

If k_{ab} is much larger than either k_{aa} or k_{ab}, then

$$\frac{d[A\cdot]}{d[B\cdot]} = \frac{k_{ab}[A\cdot][B\cdot]}{k_{ab}[A\cdot][B\cdot]} = 1 \tag{16}$$

If the concentration of radicals A· and B· were measurable, Eq. (15) would permit direct calculation of the k_{aa}/k_{bb} ratio. Such a calculation would assume that $[A\cdot]$ and $[B\cdot]$ would approach quickly to constant and measurable values. The available experimental evidence, however, indicates that radical concentrations during polymer irradiation may become constant, increase continuously, pass through a maximum, or behave in other ways. To cite a few examples, Bodily [24] found in the γ-ray irradiation of polyethylene that the allyl and dienyl free radical concentrations grow with increasing rates as the irradiation proceeds. In the irradiation of polyvinyl chloride film immersed in styrene, Takamatsu [19] concluded that the concentration of free PVC radicals attains an equilibrium value very quickly after irradiation starts. Baugh [25] showed that the concentration of free radicals in cellulose continues to increase with irradiation time. Ohnishi [26] found that free radical concentration in the irradiation of polyethylene glycol first increases, then goes through a maximum, and finally decreases. Incidentally, any changes in $[A\cdot]$ and $[B\cdot]$ would provide another reason why the cross-link formation rate and the p/q ratio would not remain constant during the irradiation of a solution of Polymers A and B.

In concept it is possible to determine free radical concentrations by ESR spectroscopy or by various chemical methods. Often the methods are nonselective and measure total radical

concentration, with no way of knowing the concentration of the specific radical(s) involved in cross-linking.

Making the simplest assumption, that the cross-linking radicals quickly reach a measurable, constant concentration, consider the conclusions that can be drawn from Eq. (14). Setting

$$r_a = k_{aa}/k_{ab} \tag{17}$$

$$r_b = k_{bb}/k_{ab} \tag{18}$$

allows Eq. (14) to be rewritten as

$$\frac{d[A\cdot]}{d[B\cdot]} = \frac{r_a[A\cdot]^2 + [A\cdot][B\cdot]}{r_b[B\cdot]^2 + [A\cdot][B\cdot]} \tag{19}$$

Also, assuming that radical concentrations can be determined, and setting

$$r_m = [A\cdot]/[B\cdot] \tag{20}$$

permits Eq. (19) to be expressed as

$$r_b = r_m \left[\frac{d[B\cdot]}{d[A\cdot]} (1 + r_m r_a) - 1 \right] \tag{21}$$

which represents a straight line plot of r_b vs r_a. For each starting ratio of Polymer A to Polymer B, a different value of r_m and a different straight line should result. The intersection of two or more such lines should give the value of r_b, and the value of r_a would be determined in a similar manner. There is an evident resemblance of Eq. (21) to the corresponding equation for r_1 and r_2 in copolymerization theory.

Some experimental work was done on the cocross-linking of polyvinyl alcohol (PVA) and polyamide, but not by the technique

discussed above. Rather, the 0.008-in. nylon 6 film was immersed in a 5.0-wt% solution of PVA in a 50/50 volume ratio of methanol, water. This total assembly was irradiated for a measured time in a 400-Ci ^{60}Co source, designed in the form of a vertical hollow cylinder, into which the sample was mechanically lowered by a small elevator. The solution and PVA sample were contained in a stoppered test tube with no attempt to exclude air.

After irradiation, each nylon film sample (of about 0.1 g) was stirred in warm distilled water for 24 hr, blotted dry, and then dried in a desiccator over calcium chloride. A blank or control sample of 0.008 in. nylon film was taken through the same procedure, except that irradiation was omitted. The percentage weight loss of the blank was subtracted from the original weight of each film sample subjected to irradiation and grafting. The percent grafting of PVA on nylon film vs time is presented in Fig. 14, the slope indicating an initial grafting rate of 0.14 wt%/hr.

The grafting of PVA molecules onto nylon film is not surprising since Miller [27] previously observed the grafting of a thin layer of PVA onto the surface of polyethylene film when the latter was irradiated while in contact with a solution of PVA. Matsumoto [28]
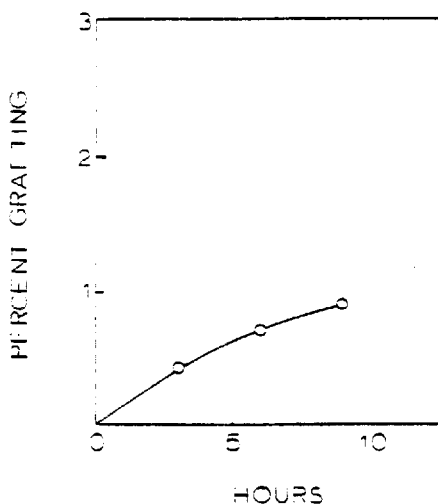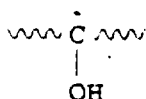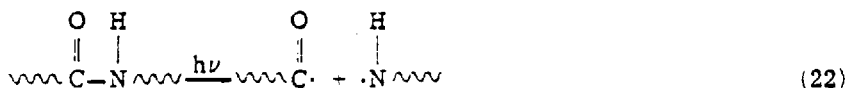

FIG. 14. Percent grafting vs time of PVA from 5.0% solution onto 0.008 in. nylon 6 film at room temperature, using a 400-Ci ^{60}Co source.
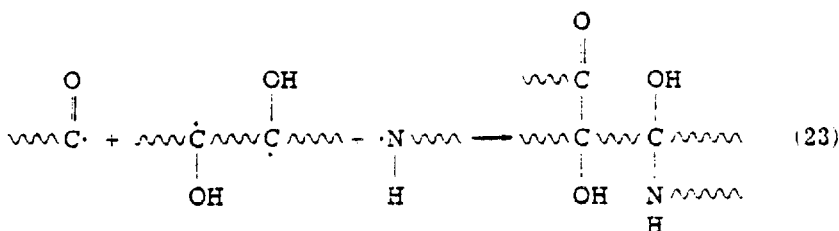
has presented evidence for the formation of the following radical in irradiated PVA,

$$\sim\!\!\sim\!\!\sim \overset{\displaystyle \cdot}{C} \sim\!\!\sim\!\!\sim$$
$$\underset{\displaystyle OH}{|}$$

Jellinek [29] has noted that the C−N bond is the weakest one in the nylon molecule (about 53 kcal, mole), and that it is ruptured during photolysis by near-UV light.

$$\sim\!\!\sim \overset{\overset{\displaystyle O}{\|}}{C} - \overset{\overset{\displaystyle H}{|}}{N} \sim\!\!\sim \overset{h\nu}{\longrightarrow} \sim\!\!\sim \overset{\overset{\displaystyle O}{\|}}{C}\cdot \; + \; \cdot \overset{\overset{\displaystyle H}{|}}{N} \sim\!\!\sim \tag{22}$$

a scission that may also be induced by γ radiation. Attack by the two radicals from Eq. (22) could then take place at points not far distant from each other on the PVA chain,

$$\sim\!\!\sim \overset{\overset{\displaystyle O}{\|}}{C}\cdot \; + \; \sim\!\!\sim \overset{\displaystyle \cdot}{\underset{\underset{\displaystyle OH}{|}}{C}} \sim\!\!\sim \overset{\displaystyle \cdot}{\underset{\underset{\displaystyle H}{|}}{C}} \sim\!\!\sim \; - \; \cdot \overset{\displaystyle }{\underset{|}{N}} \sim\!\!\sim \; \longrightarrow \; \sim\!\!\sim \overset{\overset{\overset{\displaystyle O}{\|}}{C}}{\underset{\underset{\displaystyle OH}{|}}{C}} \sim\!\!\sim \overset{\displaystyle C}{\underset{\underset{\underset{\displaystyle H}{N \sim\!\!\sim}}{|}}{|}} \tag{23}$$

The general type of process shown in Eq. (23) has been called "end-linking" and is essentially similar to cross-linking in its net results.

Equation (23) is only intended to show one possible mechanism for nylon linkage to PVA. Many other cross-linking mechanisms can readily be postulated. At present there is no definite evidence for the nature of the cross-linking mechanism.

A simple estimate shows quickly that a monomolecular layer of PVA molecules on a nylon surface would not provide the magnitude of weight gain shown in Fig. 14. A possible explanation is that one layer of PVA grafts onto the nylon surface, and then successive layers graft onto the PVA itself. Another possibility is that some of

the smaller PVA molecules penetrate the nylon film surface during its immersion in the methanol/water solution.

These results suggest questions as to the effect of solvent type on the rate of surface grafting of PVA on nylon, the effect of PVA molecular weight, and the ease of bonding other polymers to nylon film by a similar technique. These are questions of considerable interest, and more research is needed on this subject.

The advantage of this technique over monomer grafting is that the grafting polymer (unlike monomer) cannot penetrate far into the nylon, and this may be very desirable in cases where only surface modification is being sought. In view of the fact that chemical bonding appears to be taking place between the two polymers, this technique may be of practical interest in cases where improved bonding of a polymeric coating to a polymer substrate is being sought.

ACKNOWLEDGMENTS

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