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John L. Garnett[a]; Robert S. Kenyon[a]; Ronald Levot[a]; Mervyn A. Long[a]; Nguyen T. Yen[a]
[a] Department of Chemistry, The University of New South Wales, Kensington, NSW, Australia

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Acid Enhancement Effects in the Radiation Grafting of Monomers to Polyethylene and the Use of These Copolymers for Enzyme Immobilization and Related Reactions

JOHN L. GARNETT, ROBERT S. KENYON, RONALD LEVOT, MERVYN A. LONG and NGUYEN T. YEN

Department of Chemistry
The University of New South Wales
Kensington, NSW, 2033, Australia

ABSTRACT

The use of mineral acid to enhance the radiation grafting of monomers to trunk polymers such as polyethylene is shown to be of value for the insolubilization of enzymes and the heterogenization of catalytically active homogeneous complexes. Two general methods are described showing how acid enhancement effects can be used in the immobilization reactions. In the first technique, styrene is grafted, and the resulting copolymer can be nitrated followed by subsequent chemical reactions to yield an appropriate substituent to which the attachment processes can occur. Alternatively, p-nitrostyrene can be grafted directly. In the latter method, the acid enhancement is shown to be valuable, since the monomer is deactivating in radiation grafting and any technique for improving yields is useful. The acid enhancement effect is also shown to be of value for grafting to polyethylene, since this backbone polymer is less susceptible to grafting than the other two trunk polymers studied, i. e., polypropylene and PVC. A novel mechanism for the acid effect is proposed. The grafting

of p-nitrostyrene is more satisfactory for the insolubilization reactions when compared with the alternative of styrene grafting followed by nitration.

INTRODUCTION

Radiation grafting to polymers is an attractive method of modifying these materials for use as insoluble supports for organic synthesis. Typical applications of these polymeric reagents are the immobilization of enzymes and the heterogenization of catalytically active homogeneous metal complexes. The polyolefins possess advantages [1, 2] for these insolubilization processes, especially when compared with crosslinked polystyrene derivatives which are a class of synthetic resins frequently used for this purpose.

The principle of the technique is to radiation graft to a backbone polymer, a monomer which contains an appropriate functional group to which the organic reagent may be covalently attached. A suitable monomer for this purpose is p-nitrostyrene, since, once copolymerized, this nitro group can subsequently be reduced to the amine from which a suitable derivative can be prepared for the attachment reaction. The essential disadvantage with p-nitrostyrene is that it grafts only very slowly with ionizing radiation.

An alternate method for introducing the nitro group in a radiation grafting process is to copolymerize styrene to the backbone polymer first, then nitrate the grafted styrene. This has a potential advantage for insolubilization reactions, in that styrene grafts much more efficiently than p-nitrostyrene. Thus significantly lower doses of ionizing radiation are required to achieve comparable styrene grafts. This property is especially important for backbone polymers that are radiation-sensitive. Thus for p-nitrostyrene (and even with styrene grafting reactions), any method for enhancing radiation copolymerization would be valuable for insolubilization reactions.

In previous work it has been found [3-7] that addition of mineral acid to a monomer solution enhances the radiation grafting of certain monomers to cellulose [3-5] and wool [6, 7]. Solvents such as the low molecular weight alcohols which swell these naturally occurring macromolecules favor the acid enhancement reaction. Mechanistically this acid enhancement reaction with cellulose and wool has been attributed to reactions such as depicted in Eq. (1), which produce an increase in radiolytic hydrogen atoms [5, 7]. Further work [8] has also demonstrated

$$H^+ + e^- \longrightarrow H^\cdot \qquad (1)$$

that the effect of acid on the stability of the intermediate charge-transfer complex in the grafting is important.

In a recent preliminary communication [9], analogous acid enhancement effects have been reported for the radiation grafting of styrene in methanol to the polyolefins. This reaction is significant, since methanol does not swell the polyolefins as it does wool and cellulose. The mechanism of the acid enhancement with the polyolefins is thus extremely interesting. It is the purpose of this paper to report further, more detailed studies of this acid effect for the grafting of styrene (predominantly) and p-nitrostyrene in solution to polyethylene. A comparison of the two techniques for insolubilization has also been performed, i. e., grafting of styrene followed by nitration versus direct copolymerization of p-nitrostyrene. Preliminary studies of the use of polyethylene versus polypropylene and PVC for these insolubilization reactions are also reported.

EXPERIMENTAL

Materials

Low-density polyethylene films of 0.01 mm thickness were supplied by Union Carbide. Styrene was donated by Monsanto (Aust.) Ltd., while all other monomers were purchased from Polysciences Inc. The grafting technique was a modification of that previously used with cellulose [5], wool [7], and polypropylene [10]. Monomers were purified by column chromatography on alumina, a procedure that has previously been satisfactory for radiation copolymerization [5, 7]. High purity methanol (acetone-free, ACS reagent, code 1212) was purchased from Allied Chemicals; the remaining alcohols, dimethylformamide, dimethyl sulfoxide, acetone, and dioxane were AR grade and used without further purification. These materials were satisfactory in earlier grafting reactions to cellulose [5].

Irradiation Procedure

Grafting experiments were performed in Pyrex tubes, solvent being added first, followed by acid or a concentrated solution of acid in the solvent, then monomer to a total volume of 20 ml. Polyethylene strips (25 mm × 37.5 mm) were then fully immersed in the monomer solutions. Only homogeneous solutions were used for grafting. This is important, especially with acid additives, since there is a limit of acid concentration before phase separation occurs. Irradiations of the lightly stoppered tubes containing the reagents were carried out in cobalt-60 or spent fuel element facilities at the Australian Atomic Energy Commission. At the completion of the irradiation, the grafted polymer film was quickly removed from the monomer solution, and soaked for two days in benzene to remove homopolymer. This film was then washed with methanol and dried at 60°C to constant weight.

The grafting yield was the percent increase in weight of the original film. The degree of homopolymerization was determined by the following modification of the Kline procedure [11]. After irradiation, the grafting solution was poured into methanol (200 ml) to precipitate homopolymer. The sample tube was then rinsed with methanol (50 ml). Any homopolymer which adhered to the polymer film and to the tube was dissolved carefully in dioxane (20 ml) and the dioxane solution added to the methanol in a beaker, together with the benzene washings from the extraction of the original film. The beaker was heated on a steam bath with frequent stirring until all polystyrene coagulated. The mixture was cooled, filtered through a tared sintered glass crucible, washed three times with methanol (100 ml), and the crucible dried to constant weight at 60°C. The percentage homopolymer was calculated from the weight of homopolymer divided by the weight of monomer in solution. The grafting efficiency was the weight of graft divided by the weight of homopolymer plus the weight of graft.

For the immobilization of the enzyme and the heterogenization of the catalytically active complexes, both low-density and high-density polyethylene powders were used. Some experiments were also carried out with polypropylene powder (from Shell) containing no additive and PVC powder (from ICI). For the polyethylene and polypropylene work, powders (5 g) of these materials were irradiated in air as a suspension in p-nitrostyrene (30% v/v) in N,N-dimethylformamide (6 ml) at 2×10^5 rad/hr to a total dose of 3×10^6 rad. For the PVC run, methanol was used as solvent. After irradiation, homopolymer was removed, and the nitro group reduced to the amine in which form it was suitable for the heterogenization of the catalytically active complexes. Diazotization of the amino derivative and subsequent reaction yielded the chloro compound which was also used for heterogenization. Conversion of the amino derivative to the isothiocyanate material [1, 2] then permitted the covalent attachment of the enzyme, trypsin, by suspending the copolymer in a solution of trypsin in a bicarbonate buffer (pH = 9.6, 25 ml). The weight of protein bound to the polymer was determined by acid hydrolysis of the polymer-enzyme conjugate. The esterase activity of trypsin in the conjugate was determined using N-α-benzoyl-L-arginine ethyl ester, while the proteolytic activity was evaluated with N,N-dimethylhemoglobin [1, 2].

RESULTS

Grafting to polyethylene films is facile in the presence of the normal alcohols up to heptanol (Table 1) with a maximum occurring at approximately 30-40% styrene concentration. The results are thus similar to those obtained previously by Odian and co-workers [12] with methanol, the only solvent used by these earlier authors. The

TABLE 1. Acid Effect in Grafting Styrene to Polyethylene by Using Alcohol and Hydrocarbon Solvents[a]

	Graft (%)										
	In CH_3OH		In n-C_3H_7OH		In n-$C_6H_{13}OH$		In n-$C_7H_{15}OH$		In n-$C_{10}H_{21}OH$		In n-C_6H_{14}, no H_2SO_4
Styrene (% v/v)	No H_2SO_4	0.2 M H_2SO_4	No H_2SO_4	0.2 M H_2SO_4	No H_2SO_4	0.2 M H_2SO_4	No H_2SO_4	0.2 M H_2SO_4	No H_2SO_4	0.2 M H_2SO_4	
10	5	18	14	19	13	12	12	17			0
20	57	63	44	63	43	51	71	82			0
30	75	130	92	121	84	116	119	163	45	32	0
40	79	100	108	105	91	130	125	170	49	55	0
50	68	75	76	84	76	83	101	142			2
60	60	83	64	69	64	74	68	123			4
70	56	66	56	83	51	92	68	119			8
80	52	-	48	-	43	-	43	-			10
90	46	-	43	-	56	-	40	-			

[a]Total radiation dose was 0.2×10^6 rad at 0.040×10^6 rad/hr.

TABLE 2. Acid Effect in Grafting Styrene to Polyethylene by Using Miscellaneous Solvents[a]

	Graft (%)								
	In DMF		In DMSO		In acetone		In 1,4-dioxane		In $CHCl_3$,
Styrene (% v/v)	No H_2SO_4	0.2 M H_2SO_4	No H_2SO_4	0.2 M H_2SO_4	No H_2SO_4	0.2 M H_2SO_4	No H_2SO_4	0.2 M H_2SO_4	no H_2SO_4
10	5	16	11	24	1	4	1	7	0
20	29	44	14	41	6	18	9	16	0
30	48	73	18	60	12	30	35	35	0
40	57	89	33	83	20	55	29	75	2
50	61	91	41	115	28	50	50	93	4
60	71	104	82	104	39	44	55	89	7
70	64	105	85	101	36	40	44	61	10
80	63	-	87	-	43	-	59	-	16
90	51	-	82	-	33	-	41	-	29

[a]Total dose of 0.2×10^6 rad at 0.04×10^6 rad/hr.

TABLE 3. Effect of Acid on Homopolymerization during Radiation Grafting of Styrene in Methanol to Polyethylene[a]

Styrene (% v/v)	Grafting yield (%)		Homopolymerization (%)		Grafting efficiency (%)	
	No H_2SO_4	0.1 M H_2SO_4	No H_2SO_4	0.1 M H_2SO_4	No H_2SO_4	0.1 M H_2SO_4
20	13	44	0.6	1.3	30	45
40	80	109	1.6	1.5	40	45
60	65	75	1.4	1.7	26	27
70	-	73	-	1.7	-	22
80	52	-	1.6	-	16	-

[a]Total dose of 0.2×10^6 rad at 0.032×10^6 rad/hr.

grafting yields at 30-40% styrene in n-decanol are relatively poor, indicating that there is a limiting chain length of the alcohols beyond which the gel accelerating effect is inoperative. DMF and DMSO are efficient solvents for this radiation grafting; however the Trommsdorff peak occurs at 60-80% in these materials (Table 2). Acetone and 1,4-dioxane increase the grafting continuously with increasing monomer concentration (Table 2) whereas chloroform (Table 2) and hexane (Table 1) retard copolymerization such that no grafting is observed at concentrations of styrene below 40%. The homopolymerization of styrene which accompanies grafting to polyethylene also increases with higher styrene concentration. In general, the effect of solvents in the radiation grafting of styrene is similar for both polyethylene and polypropylene [9, 10, 13].

The effect of 0.2 M H_2SO_4 in the styrene grafting solutions is shown in Tables 1-3. The solvents chosen to demonstrate the effect must be sufficiently polar to keep 0.2 M H_2SO_4 in homogeneous phase in solutions up to 70% monomer concentration. All grafting conditions reported for the acid effects are identical to those which were used in the absence of acid. The data show that the inclusion of 0.2 M H_2SO_4 improves the yields in all solvents. In the alcohols, the gel effect is still observed at 30-40% styrene; however a higher percentage acid enhancement in yield is found at 50-70% monomer with the higher alcohols than occurs in the lower molecular weight materials. The Trommsdorff peak in DMF and DMSO in acid still occurs at about 60% monomer. With acetone and dioxane, significant acid enhancement at the gel peak is observed, particularly with the latter solvent at 50-60% monomer. Unfortunately, in the presence of acid, homopolymerization is also increased; thus the grafting efficiency is only slightly improved by the presence of acid.

The effect of acid structure on the radiation induced grafting of

TABLE 4. Effect of Various Acids in Grafting Styrene in Methanol to Polyethylene[a]

Styrene (% v/v)	Graft (%)				
	No acid	In HCOOH[b]	In HCl[b]	In H_2SO_4[b]	In HNO_3[b]
20	17	26	31	36	55
30	34	47	65	94	110
40	52	46	53	118	127
50	42	32	36	108	109
60	34	26	28	98	100

[a]Total dose of 0.2×10^6 rad at 0.08×10^6 rad/hr.
[b]0.1 N acid.

styrene in methanol to polyethylene film is shown in Table 4. Formic acid shows a small but significant enhancement at the lowest monomer concentrations. Hydrochloric acid raises the yield further, while sulfuric and nitric acids give an enhancement of over 300% in some solutions. The gel peak remains at 40% monomer; thus inclusion of acid markedly increases the intensity of this peak.

Because sulfuric acid was one of the best acids for the enhancement effect, further studies with this acid were carried out. These included level of acidity (Table 5) and dose-rate effect (Table 6). In the study of the influence of sulfuric acid concentration on the styrene grafting in DMF (Table 5), there is a continuous improvement in yield with increasing acidity at any concentration of styrene. Concentrations of styrene in DMF are possible up to 90% with 10^{-4} to 10^{-2} M H_2SO_4, up to 75% with 10^{-1} M H_2SO_4, and up to 45% with 5×10^{-1} M H_2SO_4 before phase separation occurs. A maximum grafting yield still is observed at around 60-80% styrene in DMF at concentrations of H_2SO_4 from 10^{-4} to 10^{-1} M, but shifts to the highest possible concentration of styrene at 5×10^{-1} M (i. e., 45%).

The dose-rate effect (Table 6) is particularly significant. Thus, without acid, at monomer concentrations less than 50% in methanol, there is a continuous decrease in copolymerization yield with increasing dose-rate from 1.17 to 5.46×10^5 rad/hr. However, at higher monomer concentrations there is a decrease in graft to 2.79×10^5 rad/hr, but at 5.46×10^5 rad/hr the yield is doubled although, in absolute terms, the yield is still low. Addition of acid leads to yields which are virtually independent of dose-rate at 50-70% monomer concentration. However, the important feature of the results is that at the maximum, the difference in grafting yield between acid and the corresponding non-acid solutions increases with increasing dose-rate.

TABLE 5. Effect of Sulfuric Acid Concentration on Grafting of Styrene in DMF to Polyethylene[a]

	Graft (%)					
Styrene (% v/v)	No H_2SO_4	10^{-4} M H_2SO_4	10^{-3} M H_2SO_4	10^{-2} M H_2SO_4	10^{-1} M H_2SO_4	5×10^{-1} M H_2SO_4
10						27
15						38
20		14	15	15		75
25						85
30		31	31	38		124
35						135
40	50	50	56	65	82	149
45					92	146
50	75	74	79	88	100	
55					108	
60	86	88	88	103	120	
65					120	
70	88	89	94	101	123	
75					123	
80	87	93	94	103		
90	82	82	86	89		

[a]Total dose of 0.5×10^6 rad at 0.08×10^6 rad/hr.

Further, the addition of acid induces a Trommsdorff peak especially at the highest dose rate whereas previously, acid enhanced the intensity of the gel peak which was already present.

These acid enhancement effects discussed for styrene grafting can be extrapolated to the copolymerization of other monomers [8, 9]. Preliminary studies [14] show that the enhancement can also be achieved with p-nitrostyrene which is an extremely useful monomer for enzyme insolubilization (Table 7) and heterogenization of catalytically active homogeneous complexes (Table 8). In the former system, the data in Table 7 show that polypropylene and PVC powders graft p-nitrostyrene more efficiently than does polyethylene. However the last trunk polymer is satisfactory and, with

TABLE 6. Effect of Dose Rate on Grafting of Styrene in Methanol to Polyethylene in Presence of Acid[a]

	Graft (%) at various dose rates							
	117 krad/hr		186 krad/hr		279 krad/hr		546 krad/hr	
Styrene (% v/v)	No H_2SO_4	0.1 N H_2SO_4	No H_2SO_4	0.1 N H_2SO_4	No H_2SO_4	0.1 N H_2SO_4	No H_2SO_4	0.1 N H_2SO_4
20	11	16	7	12	4	7	2	26
30	20	110	12	50	7	36	2	21
40	25	128	12	69	7	116	2	42
50	22	117	10	109	5	113	2	113
60	21	105	9	104	5	103	18	100
70	19	106	9	106	5	105	17	89
80	16		8		5		17	

[a]Total dose of 0.2×10^6 rad.

TABLE 7. Reactivity of p-Nitrostyrene-Grafted Polymers in Trypsin Immobilization[a]

Backbone polymer	p-Nitrostyrene graft (%)	Protein bound (mg/g)	Esterase activity
Low-density polyethylene	4	b	c
High-density polyethylene	3	b	c
Polypropylene[d]	30	6.9	31[e]
PVC[f]	15	25	e

[a]Total dose 3×10^6 rad at 2×10^5 rad/hr.
[b]Protein bound but quantitative reproducibility of determination low.
[c]Finite esterase activity but not determined quantitatively.
[d]Unstabilized polypropylene powder used.
[e]Relative to an equal weight of soluble trypsin (100%); protease activity 13%.
[f]PVC insoluble during grafting.

acid enhancement, is suitable for the insolubilization reactions. The same conclusions apply to the heterogenization process (Table 8). Although these data only use polypropylene, preliminary studies [14] show that polyethylene is satisfactory for this purpose.

DISCUSSION

Effect of Solvent in Grafting

Solvent effects are extremely important in radiation grafting to polyethylene (Tables 1 and 2) since, not only is the efficiency of the copolymerization affected, but also the possible appearance of a Trommsdorff peak can give high yields for comparable radiation doses. Methanol has been one of the most frequently used solvents in this reaction particularly since this solvent appreciably accelerates grafting. The research groups of Odian [12] and Silverman [15] have attributed the accelerating effect of methanol in styrene grafting to polyethylene to the physical changes in the system caused by methanol. These authors did not consider possible contributions from the radiation chemistry of the grafting reaction. Little attention has also been directed to the effect of other solvents in this grafting system, although the effect of a large number of solvents, including methanol, has been studied for analogous grafting to cellulose [5]

TABLE 8. Hydrogenation of Cyclohexene on p-Nitrostyrene-Grafted Polypropylene

Polymer[a]	Metal on surface (%)	Temp (°C)	Hydrogenation (%)[c]
p-NST/PP/$RhCl_3$	0.01	50	0
p-AST/PP/$RhCl_3$	0.43	50	100
p-NST/PP/$RhH(CO)(Ph_3P)_3$	0.04	50	100
p-AST/PP/$RhH(CO)(Ph_3P)_3$	0.12	50	100
p-CIST/PP/$RhCl(CO)(Ph_3P)_2$		50	36
p-CIST/PP/$RhCl(CO)(Ph_3P)_2$		120	100

[a]p-NST = p-nitrostyrene; p-AST = p-aminostyrene; p-CIST = p-chlorostyrene; PP = polypropylene.
[b]Hydrogenation temperature (4 days).
[c]Approach to equilibrium.

and wool [7]. The wetting and swelling behavior of these solvents, as well as their radiation chemistry, were all considered to be important for grafting to these backbone polymers since such solvents permitted access of monomer to the cellulose sites even though the monomer itself did not wet or swell the trunk polymer. Thus only hydrophilic solvents, particularly methanol and ethanol, were useful for grafting styrene and related monomers to cellulose and wool, whereas butanol was not. By contrast, for grafting to polyethylene, especially with styrene, swelling and wetting effects of solvents are not necessary, since this backbone polymer is extensively swollen by the monomer.

The Gel Effect

One of the important observations in the grafting of styrene to polyethylene is the appearance of a maximum at a particular monomer concentration. Odian and co-workers [12] have suggested that the presence of this peak, especially in methanol, is a Trommsdorff-type effect and occurs because this solvent is a precipitant of polystyrene. While the grafted polystyrene chains are precipitated, they become immobilized or curled up. Thus further collisions with the precipitated polystyrene are inhibited; hence, the termination rate is reduced while there is essentially no reduction in the initiation rate, and rate of grafting is thus increased. It is emphasized that

the termination rate in the grafting of undiluted styrene is already very hindered because of the high viscosity of the grafting medium (mainly amorphous polyethylene, according to these authors), but the hindrance is further increased in the presence of methanol, due to the precipitating effect. Thus, the Trommsdorff effect which already exists in the system is enhanced by the presence of methanol. This mechanism of the accelerating effect of methanol in the grafting of styrene to polyethylene is also applicable to all alcohols due to their similar precipitating effect on polystyrene. Thus, Chapiro [16] observed that, in the polymerization of styrene in different alcohols by radiation, the polymer is precipitated into powder particles at high dilution (e. g., at 90 mole % methanol, 85 mole % n-propanol, 80 mole % n-butanol, or 60 mole % n-octanol, all these being 70% alcohol by volume). In the present work, these concentrations of alcohols were also found to give maximum grafting yields.

DMSO is also a nonsolvent for polystyrene, although only a marginal Trommsdorff effect was obtained with this solvent. The observed accelerating effect of DMF with a maximum value at 60% styrene cannot be explained by the previous theories, because DMF dissolves polystyrene. When a solvent has a good solubility for polystyrene, the grafted chains are not immobilized so that the termination rate is not decreased and there will be no accelerating effect. Instead, the grafting rate will decrease with dilution of styrene by the solvent as the rate is now directly proportional to the monomer concentration [17]. This is the case with 1,4-dioxane, which is a good solvent for polystyrene. However, the data show a marginal gel peak at 80% monomer. Acetone is only a weak solvent for polystyrene, but again a marginal Trommsdorff effect is observed at 80% monomer. Hexane does not dissolve polystyrene but does not accelerate grafting, probably because it does not precipitate polystyrene grafted chains in the presence of styrene.

In general, the Trommsdorff-type effect proposed by Odian and co-workers [12] can be used to explain most of the observed results in all solvents used, with the limitations discussed in the preceding paragraph. However, the Odian model also fails to explain satisfactorily grafting data obtained in preliminary studies [8] with additional solvents other than those reported in this paper.

Machi, Kamel, and Silverman [15] did not agree with the above mechanism of the Trommsdorff effect. These authors analyzed mixtures of styrene and methanol which were absorbed in polyethylene films prior to grafting. They found that the methanol fraction in the mixture was very low ($\leq$ 4%), and was not enough to precipitate the polystyrene grafted chains. Therefore, they proposed a new mechanism for the Trommsdorff effect based on the concentration of the occluded styrene in polyethylene and the viscosity of the amorphous region of polyethylene which is swollen by styrene. In terms of this mechanism, methanol reduces the concentration of the occluded styrene in polyethylene; hence, the swelling of polyethylene decreases, and the viscosity of the grafting medium increases. At low styrene

concentrations, the initiation rate and the propagation rate are low and increase with increasing styrene concentration, while the termination rate is also low because of the high viscosity of the medium. At high styrene concentrations, the propagation rate tends to increase, but the termination rate also increases due to the decreased viscosity of the swollen polymer. Therefore, there is an optimum styrene concentration at which the grafting rate is a maximum. The mechanism proposed by Machi, Kamel, and Silverman [15] can be used to successfully explain the accelerating effect of the alcohols, DMF and DMSO as these solvents do not swell polyethylene. According to this mechanism, when a solvent swells a polymer the grafting rate should decrease continuously with the dilution of the monomer by the solvent, because there is no Trommsdorff effect. However, the mechanism cannot account for the acetone results which showed no accelerating effect despite the fact that the solvent does not swell polyethylene. Further preliminary studies [8] with additional solvents in this system also indicate that this second model is not completely satisfactory for explaining all aspects of the solvent effect in the grafting. Thus both Odian and Silverman mechanisms are deficient in certain respects.

The Radiation Chemistry Effect

The fact that the radiolysis products of solvent (particularly) and monomer may influence the grafting process should also be considered in any complete mechanistic scheme. It is acknowledged that initiation of a grafting site on polyethylene by γ-radiation is usually by carbon-hydrogen bond scission as in Eq. (2).

$$PH \xrightarrow{\gamma} P^{\cdot} + H^{\cdot} \tag{2}$$

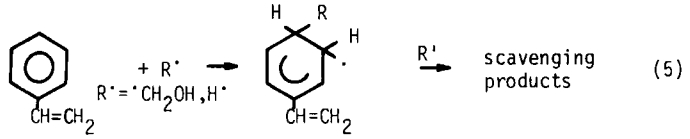
Hydrogen abstraction reactions by free radicals, usually $H^{\cdot}$, derived from the radiolysis of the appropriate solvent, also lead to grafting sites, i. e., Eqs. (3) and (4), where $S^{\cdot}$ is solvent radical.

$$PH + H^{\cdot} \longrightarrow P^{\cdot} + H_2 \tag{3}$$

$$PH + S^{\cdot} \longrightarrow P^{\cdot} + HS \tag{4}$$

The importance of the reaction of nonpolymeric radicals with trunk polymer to form grafting sites has been discussed previously. In particular, reactions (3) and (4) have been used to explain the effect of different solvents on the grafting of styrene to cellulose [5], wool [7], and in very preliminary studies, the polyolefins [9] based

on the G(H) of solvents. In this earlier work [18], styrene in the styrene-methanol system was considered to be a radical scavenger in the same way that benzene is in the radiolysis of benzene-methanol solutions [19]. Radical scavenging was presumed to occur preferentially on the benzene ring of styrene by addition reactions [Eq. (5)] and also by radical attack on the double bond in the side chain.



(5)

I

Thus, for the grafting of styrene to cellulose, a mechanism for the accelerating effect of methanol was suggested based on the relative numbers of styrene molecules and methanol radicals. At low concentrations of styrene, styrene will essentially scavenge methanol radicals while at high concentrations of styrene, the styrene will scavenge other styrene radicals. Thus, homopolymerization is preferred to grafting in both cases. However, in the middle range of styrene concentrations, a compromise is attained where there is sufficient styrene to scavenge all methanol radicals, yet a slight excess of styrene is still available for grafting by the charge-transfer mechanism proposed by Dilli and Garnett [18].

Recent studies [8] on the radiolysis of binary mixtures of benzene-methanol and pyridine-methanol suggest that hydrogen atoms play a predominant role in product formation, especially since small additions (5%) of benzene and pyridine significantly reduce the $G(H_2)$ yield from methanol by scavenging H atoms. Above 5% additive the $G(H_2)$ is further reduced but at a slower rate. By analogy, in the styrene-methanol grafting solution for the present polyethylene copolymerization, although G(H) is reduced by the presence of scavenger styrene, there remains a sufficient concentration of H atoms compared with other radicals to explain the accelerating effect of methanol by abstracting hydrogen from the backbone polymer to give additional grafting sites [Eq. (3)]. Thus the enhancement of the initiation rate by methanol decreases with increasing styrene concentration. Simultaneously, the propagation rate increases with increasing styrene [17]. Between these two extremes, there is a concentration of styrene where grafting is maximized.

A similar explanation for accelerative effects observed in grafting with other solvents can be advanced. Thus the higher straight chain alcohols [20] give radicals with yields similar to methanol, especially G(H). As the carbon chain length of the alcohols increases, the radical products tend to include smaller amounts of those characteristic

of the alcohol group, and more of those resulting from the bond-breaking of the hydrocarbon chain, the grafting yield then dropping when the chain length reaches a certain limit. With respect to DMSO and DMF, G(H) in the two solvents are lower [21, 22] than in the alcohols and a lower graft is observed. No significant accelerating effect was found with acetone consistent with the low G(H) from this solvent reported by Holroyd [20]. It thus appears that solvents with high G(H) do participate in accelerated grafting and the radiolysis pathway is a contributing mechanism to the overall copolymerization reaction.

Acid Enhancement Effect in Grafting

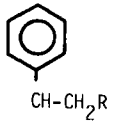
The significance of the preceding discussion of the role of hydrogen atoms in radiation grafting becomes more evident when acid is utilized as an additive. Acid, at the levels used, should not markedly affect the precipitation of the polystyrene grafted chains or the swelling of the polyethylene. Thus the effect of acid would appear to be due predominantly to a radiation chemistry phenomenon consistent with the observation by Baxendale and Mellows [23] that addition of acid to methanol increases $G(H_2)$ appreciably. The precursors of the additional hydrogen were suggested to be hydrogen atoms from thermalized electron capture reactions of the type depicted in Eq. (6). Acid enhancement in the radiation

$$CH_3OH_2^+ + e \longrightarrow CH_3OH^* + H \qquad (6)$$

grafting of styrene in methanol to cellulose [5] and wool [7] has previously been proposed as being predominantly due to such reactions. A similar explanation has also been advanced for analogous acid effects found in very preliminary studies by the present authors for radiation grafting to the polyolefins [9].

Such radiolytic H atom formation appears to be of importance in the current acid enhancement grafting work. However further work [8] has shown that the mechanism of the acid effect is more complicated. Thus the role of intermediate radicals (I, II, III) formed

II



III

by styrene scavenging reactions (either addition, I, or substitution, II) of the solvent fragments is significant. At low styrene concentrations in methanol, these intermediates (MR·) will predominantly react with other available solvent radicals by addition or disproportionation processes. The probability of MR· reacting with another styrene molecule in this region is low and hence homopolymerization is low in this region, as is the grafting (Table 3). At high styrene concentrations, MR· will react mainly with other available styrene molecules to give homopolymer, consistent with the observed increasing homopolymer formation with increasing styrene concentration in methanol (Table 3). Homopolymerization decreases again in undiluted styrene because of lack of solvent radicals as initiators.

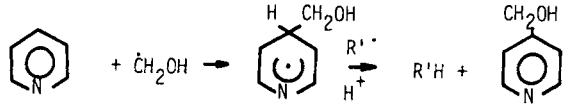
Between these two extremes, the probability of MR· abstracting a hydrogen atom from the adjacent polymer chain to give a polymer radical [Eq. (7)] is high, and as discussed previously [18] grafting can thus be induced in the "cage" [Eq. (8)]. Therefore, the grafting yield is a maximum in the medium range of styrene concentrations.

$$PH + MR^{\cdot} \longrightarrow P^{\cdot} + MRH \qquad (7)$$

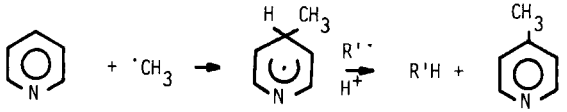
$$P^{\cdot} + MRH \longrightarrow [P^{\cdot} \longrightarrow MRH] \longrightarrow PMRH^{\cdot} \qquad (8)$$

This mechanism, involving reaction of styrene-solvent radicals MR· is supported by the fact that the yields of the predominant scavenging products in the radiolysis of benzene-methanol, like cyclohexadiene-methanol or anisole [19], or, in the radiolysis of the pyridine-methanol, like pyridylmethanol or methylpyridine [8], always displayed maximum values at approximately 20-30% aromatic in methanol, the same region where the Trommsdorff peak appears for the present grafting of styrene in methanol to polyethylene.

For the purposes of this discussion, styrene and pyridine are structurally somewhat analogous, since the aromatic ring of styrene is complemented by the electron rich $-CH=CH_2$ group, while pyridine has the nitrogen lone pair. Acid effects observed in the pyridine-methanol system can thus be extrapolated to styrene-methanol. In preliminary studies [8] it has been shown that the yields of gaseous products H_2, CH_4 from methanol, which were already reduced considerably when pyridine was added, did not change further with the addition of acid. More importantly, the quantities of scavenging products, i. e., pyridylmethanol and methylpyridine, were increased appreciably and, in place of pyridylethanol, some unidentified acid-induced products were formed. The mechanism whereby acid increases the yield of scavenging products has not been completely clarified [8], especially the role of the anion. However, a plausible interpretation is that acid enhances the disproportionation of the aromatic-methanol radicals [Eqs. (9) and (10)] to give more scavenging products due to the greater migration of electrons from the ring to a more positive environment, thus facilitating the severance of the C–H bond in the disproportionation reactions.



(9)



(10)

The effect of acid in the styrene-methanol grafting system may well be similar. Thus it is proposed that acid facilitates the hydrogen abstraction reaction from an adjacent polymer molecule by styrene-methanol radicals MR· to give more grafting sites [Eq. (11)].

$$PH + MR\cdot \xrightarrow{H^+} P\cdot + MRH \qquad (11)$$

The styrene-methanol radicals MR· can also simultaneously react more efficiently with monomer in the presence of acid to give higher homopolymer yields, consistent with the present observations especially at low monomer concentrations. At high styrene concentrations, the acid effect on homopolymer yield is marginal, probably because homopolymer is already significant without additive.

Although nitric and sulfuric acids enhanced the grafting yield more significantly than hydrochloric, the presence of all three strong acids led to an appreciable increase in copolymerization at certain monomer concentrations. There thus appears to be a predominant common mechanism for this acid effect, i. e., acid facilitates hydrogen abstraction from trunk polymer molecules by styrene-solvent intermediates. Such an explanation is also consistent with Silverman's observations [15] concerning the small amounts of methanol which were found in swollen polymer. Once the polyethylene is swollen by the monomer, a dynamic equilibrium could be established such that intermediates MR· could diffuse to trunk polymer sites and graft.

The acid enhancement effect, especially at high dose rates, is obviously of preparative importance. However mechanistically the concept is complicated. Radiolytically produced hydrogen atoms are obviously present in the system and affect the grafting rate. However the more recent scavenging experiments suggest that the acid effect on the subsequent reaction of the MR· species is the predominant pathway.

Application of the Acid Effect in Reagent Immobilization

The data (Tables 7 and 8) show that p-nitrostyrene is extremely useful as a grafted monomer for immobilizing enzymes and

heterogenizing catalytically active homogeneous metal complexes. The fact that, in preliminary studies, acid enhanced grafting has been observed is particularly important for the present polyethylene work. This monomer is slow to graft, particularly to polyethylene (Table 7), so any method of enhancement is valuable for the studies. The enhancement is extremely useful for attachment to those trunk polymers which are radiation-sensitive, since the lower the total dose required for grafting the better the physical properties of the final copolymer. Also, acid in the grafting medium does not appear to affect the reactivities of the insolubilized reagents whether the backbone polymer is polyethylene (Table 7) or polypropylene (Tables 7 and 8). Finally, recent work [14] has shown that grafting of styrene followed by nitration gives a different type of copolymer from that obtained by direct grafting of p-nitrostyrene. Certain of the advantages of using the latter technique have previously been discussed [1, 2]. However these later results [14] show that if the nitro groups from the former grafting process are reduced and then diazotized, subsequent internal coupling tends to reduce the effectiveness of this method for insolubilization. No such competing process is found with the analogous diazo derivative from the p-nitrostyrene graft. This observation is significant, since the diazo derivative is an important intermediate for the preparation of copolymers containing specific substituents such as Cl, CNS, etc. The direct p-nitrostyrene grafting procedure is thus better than the alternative of grafting styrene followed by nitration and is to be preferred for the immobilization reactions.

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REFERENCES

[1] J. L. Garnett, R. S. Kenyon, and M. J. Liddy, Chem. Commun., 1974, 735.
[2] M. J. Liddy, J. L. Garnett, and R. S. Kenyon, J. Polym. Sci. Polym. Symp. Ed., 49, 109 (1975).
[3] S. Dilli, J. L. Garnett, and D. H. Phuoc, J. Polym. Sci. Polym. Letters Ed., 11, 711 (1973).
[4] J. L. Garnett, D. H. Phuoc, P. L. Airey, and D. F. Sangster, Austral. J. Chem., 29, 1459 (1976).
[5] J. L. Garnett, Cellulose Chemistry and Technology (ACS Symp. Series, 48), 334 (1977).
[6] J. L. Garnett and R. S. Kenyon, J. Polym. Sci. Polym. Letters Ed., 15, 421 (1977).

[7] J. L. Garnett and J. D. Leeder, Textile Paper Chemistry and Technology (ACS Symp. Series, 49), 197 (1977).
[8] G. Fletcher, J. L. Garnett, and N. T. Yen, unpublished data.
[9] J. L. Garnett and N. T. Yen, J. Polym. Sci. Polym. Letters Ed., 12, 225 (1974).
[10] J. L. Garnett and N. T. Yen, Austral. J. Chem., 32, 585 (1979).
[11] G. M. Kline, Analytical Chemistry of Polymers, Part 1, Interscience, New York, 1966.
[12] G. Odian and A. Rabie, J. Radiat. Phys. Chem., 9, 495 (1977).
[13] J. L. Garnett, J. Radiat. Phys. Chem., 14, 79 (1979).
[14] C. H. Ang, J. L. Garnett, and R. Levot, in press.
[15] S. Machi, I. Kamel, and J. Silverman, J. Polym. Sci. A-1, 8, 3329 (1970).
[16] A. Chapiro, Radiation Chemistry of Polymeric Systems, Interscience, New York-London, 1962.
[17] G. Odian, M. Sobel, A. Rossi, and R. Klein, J. Polym. Sci., 55, 663 (1961).
[18] S. Dilli and J. L. Garnett, J. Polym. Sci. A-1, 4, 2323 (1966).
[19] A. Ekstrom and J. L. Garnett, J. Phys. Chem., 70, 324 (1966).
[20] R. A. Holroyd, in Fundamental Processes in Radiation Chemistry, P. Ausloos, Ed., Interscience, New York, 1968.
[21] I. Flagiu and V. Stannett, J. Macromol. Sci.–Chem., A7, 1677 (1973).
[22] N. Colebourne, E. Collinson, and F. S. Dainton, Trans. Faraday Soc., 59, 866 (1963).
[23] J. H. Baxendale and F. W. Mellows, J. Am. Chem. Soc., 83, 4720 (1961).