

# Radiation-Induced Grafting of Sulfonates on Polyethylene

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## Synopsis

Indirect methods for introducing sulfonate groups into polyethylene, using the preirradiation technique, were studied. One of the methods involved graft polymerization of 2,3-epoxypropyl acrylate into polyethylene followed by sulfonation of the epoxy ring with bisulfite. The hydroxy sulfonate thus obtained was unstable in an acid or base environment and hydrolyzed at the ester bond. The second method involved hydrophilization of the polyethylene by forming a pregraft of polyacrylic acid or polyvinyl alcohol, followed by preirradiation grafting with sodium styrene sulfonate or, less successfully, with sodium vinyl sulfonate. The sulfonates thus obtained were resistant to acids and bases. The acid capacity, water absorption, and water permeability of the grafted films were determined.

## INTRODUCTION

Radiation-induced grafting has been used frequently to impart new properties to given polymers.<sup>1</sup> Among the most important applications is the hydrophilization of highly hydrophobic polymers. Monomers such as acrylic acid (AA), *N*-vinyl pyrrolidone, acrylamide, and hydroxyethylmethacrylate have been grafted on many occasions.<sup>1,2</sup> Many studies have been published on the grafting of weak acids such as AA on polyethylene (PE) but very few on the grafting of strong acids such as those derived from sulfonic acid. Nevertheless, other methods for the grafting of sulfonic groups without using vinyl monomers have been used.<sup>3-5</sup> Sulfoxidation<sup>3,4</sup> and sulfochlorination<sup>3</sup> induced by gamma radiolysis as well as by photolysis are known. An indirect method for grafting a sulfonic group onto PE has been reported by Chen et al.<sup>6</sup> In their work styrene was radiolytically grafted on PE, and the benzene ring was chlorosulfonated and finally hydrolyzed to form the styrene sulfonic acid graft copolymer.<sup>6</sup> Indirect methods are used because of the very low yield obtained when vinyl monomers bearing sulfonic acid groups are grafted. In a recent publication,<sup>7</sup> the initial polymerization rate of vinylsulfonic acid was compared to that of acrylic acid using pulsed ESR technique. The results showed almost identical initial rate constants for the two monomers. It seems therefore that the polymerization rate does not represent an obstacle for the grafting of vinylsulfonic acid on PE. However, the highly ionized  $\text{SO}_3^-$  groups with their hydration sphere are incompatible with PE and cannot diffuse into the PE bulk, thus preventing the polymerization reaction. It seems therefore that limited diffusion is the only reason for the lack of graft copolymerization of vinyl sulfonic acid on PE.

In the present study attempts were made to introduce sulfonic groups into PE films radiolytically using the preirradiation technique.

## EXPERIMENTAL

### Materials

Vestolen 6042 high-density polyethylene film (100  $\mu\text{m}$  thickness) from Chemische Werke Huls AG was used as received. 2,3-Epoxypropyl acrylate (EPA), sodium vinyl sulfonate (SVS), *p*-sodium styrene sulfonate (SSS) from Polysciences and acrylic acid from Fluka were all CP grade and used without further purification. Vinyl acetate from Merck was distilled at atmospheric pressure before use. All inorganic materials were Baker-analyzed reagents.

### Graft Polymerization

Irradiation was carried out using a commercial High Voltage electron beam accelerator, model EPS-550-IND, supplying a maximum current of 20 mA at 250–520 MeV and a scan width of 43 cm. The HDPE samples were subjected to electron beam irradiation under air atmosphere by means of a conveyer traveling at a rate of 10 m/min. Most irradiations were carried out at a dose rate of  $\sim 3$  Mrad/pass. The films were then immersed in a nitrogen-saturated monomer solution which was bubbled with nitrogen for 30 min at room temperature to remove traces of oxygen and then held at 70°C for a certain period of time to permit the graft copolymerization reaction to take place. After grafting, the samples were washed thoroughly for 6–8 h to remove any traces of monomer absorbed on the film. Water–acetone mixture (1:1) was used for EPA, methanol was used for vinyl acetate, and warm water for AA and SSS. After washing, the films were dried in a vacuum oven at 50°C and weighed. The percent of grafting was calculated as  $100 \times (w_g - w_i)/w_i$ , where  $w_i$  and  $w_g$  represent the weights of the initial and grafted film, respectively.

Films grafted with polyvinyl acetate were hydrolyzed by refluxing in a 10% KOH in methanol solution for 4 h. Acrylic-acid-grafted PE were obtained using solutions containing 20–30% AA and 0.5–5-mM  $\text{FeSO}_4$  (except for sample 6 in Table I, where  $\text{FeSO}_4$  was excluded).

### Membrane Capacity and Permeability

Membrane capacity was determined by immersing a weighed sample of the basic form of the grafted film in 0.1 N HCl, stirring overnight, and back titrating with 0.1 N NaOH. The same procedure was repeated by immersing in base and titrating with acid. Water permeability (pervaporation) was measured at 32°C and 50% RH according to ASTM E96-66 (Procedure BW, inverted water method).

## RESULTS AND DISCUSSION

### Sulfonation via Epoxy Groups

All our attempts to induce direct graft polymerization of either SVS or SSS onto HDPE films failed. As a result, an indirect approach was used where epoxy groups were grafted first, and the epoxide was then sulfonated with bisulfite.<sup>8</sup> The degree of grafting of epoxypropyl acrylate (EPA) on PE as a function of dose

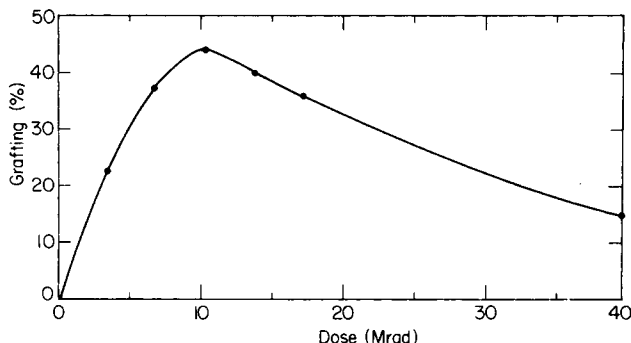
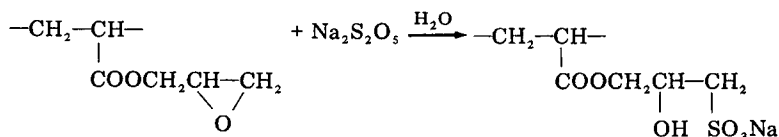


Fig. 1. Grafting yield of 2,3-epoxypropyl acrylate (EPA) on HDPE as a function of dose, obtained by preirradiation and immersion in 30% EPA in 3:4 water:acetone deoxygenated solution at 70°C for 10 minutes.

in water-acetone solution is given in Figure 1. As seen in the figure, the grafting yield reaches a maximum at about 10 Mrad and decreases continuously at higher doses. This decrease in grafting is explained by the fact that irradiation of PE also leads to crosslinking; at relatively high doses the crosslinking density increases, probably causing a decrease in the diffusion of the monomer into the PE, which slows down the propagation reaction. The effect of reaction time on the grafting yield of EPA is given in Figure 2. Figure 3 represents the dimensional changes of the film with the grafting yield.

For the sulfonation reaction, samples of 91% EPA-grafted PE films were refluxed in a 40% aqueous  $\text{Na}_2\text{S}_2\text{O}_5$  solution for 8 h:



A weight gain of 10.7% was observed, compared to a possible theoretical gain

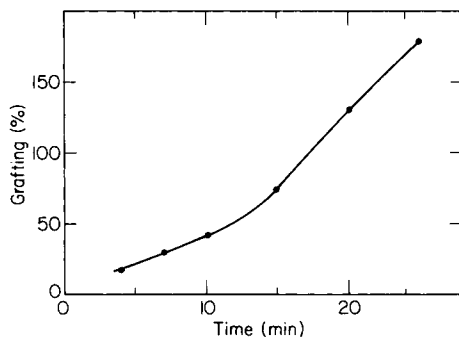


Fig. 2. Grafting yield by preirradiation (10 Mrad) of 2,3-epoxypropyl acrylate (EPA) on HDPE as a function of reaction time in deoxygenated solutions containing 3:3:4 EPA:water:acetone at 70°C.

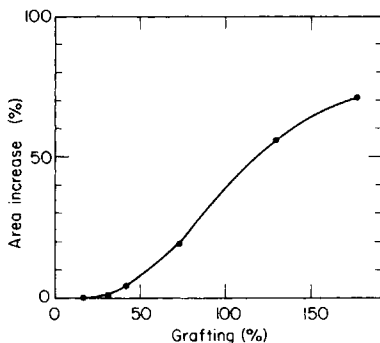


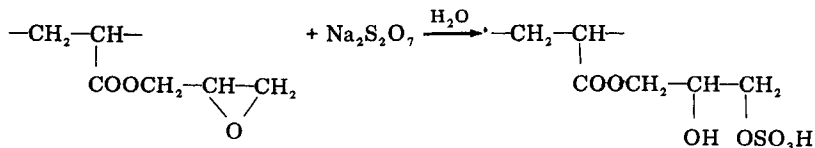
Fig. 3. Percent area increase of HDPE as a function of percent grafting of 2,3-epoxypropyl acrylate (EPA).

of 38.7% for full sulfonation. In addition to the ring opening, the esteric group most probably was partially hydrolyzed, resulting in the formation of acrylic acid groups. Such a process causes a decrease in the sample weight, which compensates for some of the weight increase resulting from sulfonation. The occurrence of hydrolysis was verified by the acid capacity of the treated film. The overall acid capacity was found to be 2.5 meq/g compared to the 0.93 meq/g expected, assuming that the 10.7% weight increase resulted only from sulfonation. Using the above weight increase and acid capacity, we found that the separate acid capacities of the sulfonic and carboxylic groups were  $\sim 1.4$  meq/g for the  $\text{SO}_3\text{Na}$  groups and  $\sim 1.1$  meq/g for the  $\text{COONa}$  groups.

The water absorption measured after equilibration for 3 h at room temperature was 6.6% from acid solution and 45.7% from base. Samples dried at  $50^\circ\text{C}$  in a vacuum oven were brittle, but became elastic after absorbing moisture from the air.

### Sulfation of the Epoxy Groups

Similarly to the sulfonation procedure, EPA-grafted PE films were reacted with  $\text{Na}_2\text{S}_2\text{O}_7$  by refluxing for 8 h in a 40% pyrosulfate solution in 2:1 water: acetone. The increase in weight was 11%, and the acid capacity was 2.1 meq/g. The increase in weight clearly indicates that sulfation of the epoxy ring took place:



As in the case of the sulfonation reaction under similar conditions, some hydrolysis took place, resulting in the formation of acrylic acid groups. From the weight increase and the total acid capacity, we calculated the separate capacity of  $\text{SO}_4\text{H}$  as 1.1 meq/g and that of  $\text{COOH}$  as 1.0 meq/g.

Both the sulfonated and sulfated films showed instability towards dilute acids

and bases. On repeated immersions of the films in 0.1 N acid and 0.1 N base at room temperature, a systematic decrease of weight was observed, accompanied by an increase in the acid capacity. This is explained by hydrolysis of the carboxylate esteric group with the formation of acrylic acid graft. A blank experiment where EPA-grafted PE film was immersed in acid and base under the same conditions did not result in any weight changes or formation of acidic groups. It seems therefore that the sulfonate and sulfate groups induce instability in the carboxylate esteric bond, leading to hydrolysis in fairly mild conditions.

### Sulfonation on Polyvinyl Alcohol and Polyacrylic-Acid-Grafted PE

As mentioned before, sulfonates cannot be directly grafted on PE because these compounds are incompatible with PE. We therefore attempted to induce grafting of sulfonate groups by improving the compatibility by hydrophylyzation of the PE with either polyvinyl alcohol (PVA) or polyacrylic acid (PAA).

Vestolen films, preirradiated in air at a dose of 5.3 Mrad, were reacted with polyvinyl acetate at 80°C for 2 h. The grafting yield thus obtained was 175%. The grafted films were hydrolyzed in 10% KOH solution, yielding a weight increase of 89% PVA grafted on PE, which served as the basis for additional grafting with sulfonates. This hydrophylyzed film was preirradiated again (10.4 Mrad) and grafted with SSS at 70°C for different periods of time. The results of SSS grafting for two types of pretreated films, one containing 89% PVA graft and the other containing 38% PAA graft are given in Figure 4.

In all grafting experiments with SSS it was found that saturating the monomer solution with sodium acetate doubled the grafting yield (the pH was not effected by this addition). A similar effect was found previously in homopolymerization of SVS.<sup>9</sup> The influence of acetate salts on the rate of polymerization has been rationalized<sup>9</sup> by partial neutralization of the growing sulfonate chain via ion pair formation so that the SVS ions can approach the growing chain more readily.

As one would expect, the extent of SSS grafting depends on the hydrophylic nature of the pregrafted film, and therefore, to a certain degree, it will be proportional to the percent of PVA or PAA in the PE film. Figure 5 demonstrates

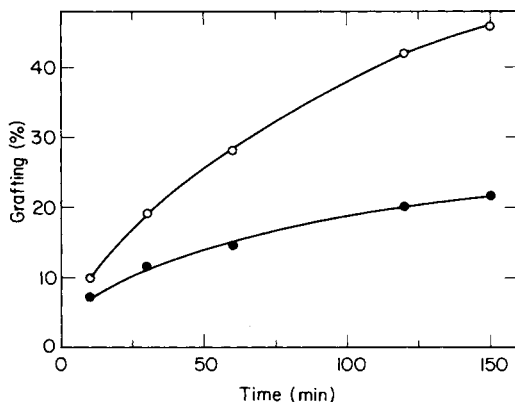


Fig. 4. Grafting yields of sodium styrene sulfonate (SSS) as a function of time on 38% polyacrylic acid (PAA)-grafted PE (●) and on 89% polyvinyl alcohol (PVA)-grafted PE (○), obtained by preirradiation (10 Mrad) and immersion in deoxygenated 11% SSS in 8% sodium acetate aqueous solution at 70°C.

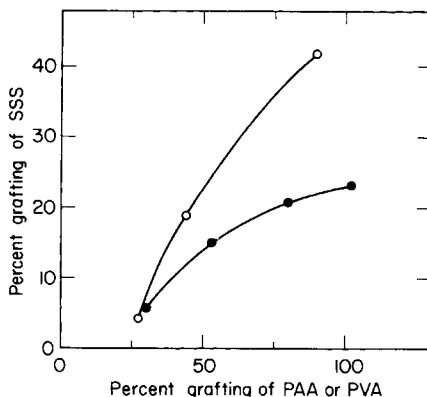


Fig. 5. Grafting yields of sodium styrene sulfonate (SSS) on pregrafted PE as a function of percent of polyacrylic acid (PAA) (●), and polyvinyl alcohol (PVA) (○), pregrafted on PE. All experimental conditions are the same as those given in Figure 4.

this dependence. As seen in the figure, PVA is more efficient than PAA in promoting SSS grafting. Although we have no experimental evidence, it is reasonable to assume that part of the SSS grafting takes place on the pregrafted PVA or PAA backbone.

Experiments with SVS on PVA- and PAA-grafted PE films were only partially successful. Low grafting yields (1.5–2%) were obtained with 20% SVS solution saturated with sodium acetate. No graft at all was observed on PE alone. Mutual irradiation experiments were also conducted for the grafting of SVS using a  $^{60}\text{Co}$  source with the intention of increasing the grafting yield. No improvement was obtained with the pretreated film containing PVA, but with a PAA-grafted PE film a graft of 5% SVS was obtained within 48 h of irradiation at a total dose of 2.4 Mrad.

The acid capacity, water absorption, and water permeability of some of the films were measured and the results are summarized in Table I. For comparison purposes, Nafion 125 is also included in the table. From the table one can see that the water permeability of the films grafted with acrylic acid only increased with an increasing percent of grafting (compare lines 2 and 3). When the acrylic acid was transformed to the sodium salt, the permeability in some cases increased by about an order of magnitude, but its dependence on the percentage of grafting was much less pronounced compared to the acid form (lines 2s and 3s).

The effect of additional grafting of SSS to AA graft on the water permeability was found to depend on the acidity of the grafted films. In the basic form, the effect of adding SSS to a grafted sodium acrylate PE film on the water permeability seems to be similar to that obtained by increasing the sodium acrylate content (compare line 4s to 2s and 3s). On the other hand, when the grafts were in the acid form, the change in permeability caused by the additional styrene sulfonic acid (SSA) grafting was relatively more pronounced (compare lines 2 and 3 to 4 and 5). The reason for this behavior seems to be that the ionic character of the graft is the most important factor in determining the degree of water permeability. Acrylic acid, having a low degree of ionization, should impart smaller permeability to a membrane as compared to its salts. On the other hand, sulfonic acid, with a relatively high degree of ionization should impart similar permeability to a membrane when either in the acid or salt state.

TABLE I  
Water Permeability, Acid Capacity, and Water Absorption of PE Films Grafted with Different Monomers

No.	Film composition (% graft on HDPE)	Form <sup>a</sup>	Permeability <sup>b</sup>		Capacity (meq/g)	Water absorption <sup>c</sup> (%)	
			g/m <sup>2</sup> ·h	g·mm/m <sup>2</sup> ·h		Solution	Air <sup>d</sup>
1	Blank	—	0.6	0.06	0		
2	PAA (30%)	A	8	0.8	3.0	7.7	2.8
3	PAA (61%)	A	53	6.5	4.3	18	4.6
2s	PAA (30%)	S	260	26		36	11
3s	PAA (61%)	S	296	36		73	18
4	PAA (30%) + SSS (16%)	A	57	6	2.9	14	4
5	PAA (61%) + SSS (36%)	A	322	44	4.5	32	7
4s	PAA (30%) + SSS (16%)	S	300	31		38	14
5s	PAA (61%) + SSS (36%)	S	470	64		77	24
6	PAA (102%) + SSS (49%)	S	0.6	0.06	6.1	83	26
7	PVA (89%)	—	99	14	0	39	2.8
8	PVA (89%) + SSS (10%)	A	190	23	0.3	26	3.8
9	PVA (89%) + SSS (19%)	A	224	29	0.8	32	3.0
10	PVA (89%) + SSS (42%)	A	257	35	1.4	46	5.7
11	PVA (89%) + SSS (81%)	A	308	45	2.1	77	15
8s	PVA (89%) + SSS (10%)	S	286	35		28	7.3
9s	PVA (89%) + SSS (19%)	S	335	43		33	8.7
10s	PVA (89%) + SSS (42%)	S	387	53		43	11
11s	PVA (89%) + SSS (81%)	S	527	76		62	12
12	Nafion	A	342	43		10	
12s	Nafion	S	336	44	1.0	13	2.3

<sup>a</sup> A: acid, S: sodium salt.

<sup>b</sup> Measured under controlled conditions at 32°C and 50% RH.

<sup>c</sup> Measured as percent of the dehydrated polymer.

<sup>d</sup> At 20–22°C and 60–70% RH.

Sample 6 in Table I is an example of a film which is not permeable to water in spite of the fact that it has a high percentage of grafting of both AA and SSS. This unusual behavior was found to originate from inhomogeneous distribution of the graft in the direction of the film thickness. Microscopic observations of dyed microtome cuts<sup>10</sup> showed that all samples presented in the table except sample 6 had been homogeneously grafted. Sample 6 had a nongrafted layer in the middle part of the film.

In samples 8–11s SSS was grafted on PVA-pregrafted PE. It can be seen that increasing the percentage of SSA or SSS from 10% to 81% caused only a moderate increase in the water permeability. When the sulfonic acid was transformed to the sodium salt, an increase in the permeability of the order of only 50% was observed, compared to a 1-order-of-magnitude increase in the case of grafted AA. Similar trends in water absorption, depending on the nature of the grafted monomer and its acid state, were observed (see Table I).

## SUMMARY

Direct graft polymerization of monomers bearing sulfonate groups on PE was not feasible because of the lack of intimate interaction between the highly hydrophylic monomers and the hydrophobic polymer carrying the radical sites. Indirect sulfonation was obtained by two different methods. The first involves

graft polymerization of EPA followed by thermal reaction of the epoxy ring with sodium bisulfite. The resulting hydroxy sulfonate graft was unstable and hydrolyzed under mild acid or base conditions. The second method was by hydrophylation of the PE by first introducing either PVA or PAA to the PE, and then grafting with SSS (or SVS). SSS gave much higher grafting yields than SVS. Thus the use of the latter was impractical. Since SVS is very reactive in its homopolymerization reaction,<sup>7,9</sup> the difference in the grafting yields reflects the fact that the SSS is more compatible with the modified PE.

The water absorption of the modified PE increased markedly with an increased percent of grafting of each of the monomers used. With the AA graft a three- to fourfold increase in the water absorption took place when the acid was transformed to the sodium salt. This effect was not observed with the sulfonates, where the water absorption was high in both acid and salt forms.

### References

1. See, for example, A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Interscience, Academic, London, 1962.
2. B. D. Ratner and A. S. Hoffman, *J. Appl. Polym. Sci.*, **18**, 3183 (1974).
3. K. Konishi, K. Yamaguchi, and M. Tekehishi, *J. Appl. Polym. Sci.*, **15**, 257 (1971) and references therein.
4. R. V. Dzhagatspanyan, V. I. Zetkin, and E. N. Zykova, U.S.S.R. Pat. 135,639 (1961).
5. R. Mesalem, C. Forgacs, J. Michael, and O. Kedem, *J. Appl. Polym. Sci.*, **31**, 383 (1977).
6. W. K. W. Chen, R. B. Mesrobian, D. S. Ballantine, D. J. Metz, and A. Glines, *J. Polym. Sci.*, **23**, 903 (1957).
7. D. Behar, R. W. Fessenden, and J. P. Hornak, *J. Radiat. Phys. Chem.*, to appear.
8. See, for example, R. T. E. Schenk and S. Kaizerman, *J. Amer. Chem. Soc.*, **75**, 1636 (1953) and references therein.
9. D. S. Breslow and A. Kutner, *J. Polym. Sci.*, **27**, 295 (1958).
10. Grafted films were dyed with 2% aqueous solution of rhodamine B at 50°C for 4 h followed by washing for a few hours with water at 60°C. Dyed strips of about 5 × 20 mm were imbedded in paraffin and sliced with a microtome for microscopic observation.

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