

# Functionalization of Crosslinked Polystyrene by Radiation-Induced Grafting

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## SYNOPSIS

$\gamma$ -ray irradiated beads of poly(styrene-divinylbenzene) (PS-DVB) have been graft copolymerized with polyacrylic acid. Preirradiated PS-DVB beads were refluxed with acrylic acid in water, benzene, or toluene. Percentage of grafting was studied under various reaction parameters like total dose, reaction time, and molar concentration. Effects of reaction media, temperature of reaction, and presence of Mohr salt on the percentage of grafting were also studied. From the swelling property of PS-DVB beads in DMF and dichloromethane, it appeared that no appreciable cross-linking had occurred in the process of grafting. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Crosslinked polystyrene, poly(styrene-divinylbenzene), was the first successful support for solid-phase peptide synthesis used by Merrifield.<sup>1,2</sup> The polymer was prepared by free radical suspension polymerization of a mixture of styrene and divinylbenzene in the form of small beads and consisted of an amorphous gel with a random network of sparsely cross-linked chains. The degree of crosslinking determined the extent of swelling, the effective pore size, and the physical stability of beads. Two percent cross-linked polymer beads have been found to be ideally suited supports. These are easily manipulated and readily separated from solvents and reagents by filtration and washing. Merrifield and Littau<sup>3</sup> showed that with this kind of support, the chemical reactions were not limited to the outer surface of the beads but occur throughout the gel matrix. The high resorption of solvent by the dried beads ensures adequate diffusion of reagents to the interior, thus providing a large effective surface for the reactions. Swelling is negligible in very polar solvents like water and methanol or in very non-polar ones like hexane and is greatest in chlorinated and aromatic solvents, dioxane, and dimethylformamide (DMF). It

has been found that the degree of swelling is an important parameter for characterizing various resin preparations and for detecting unexpected cross-linking that may have occurred during their preparation or derivatization.<sup>4</sup> The beads are mechanically strong, chemically inert, and insoluble in all common solvents. All these properties make the cross-linked polystyrene beads the most suitable polymer for use as a support for reagents, substrates, catalysts, and enzymes.

Functionalization of PS-DVB is done chemically. Pendant benzene rings easily undergo substitution, and the functional groups so introduced are amenable to further chemical transformation. Alternatively, functional groups are introduced into PS-DVB by free radical-initiated grafting of selected homopolymers. Both chemical methods and high-energy radiations are available for the generation of free radicals. However, not many reports have been cited on grafting onto PS-DVB.

Poly-*N*-vinyl *t*-butyl carbamate has been grafted onto macroporous PS-DVB through chemical initiation with limited success.<sup>5</sup> Relatively high grafting was obtained in extensive studies carried out in the laboratory of A. Guyot.<sup>6,7</sup> Guyot and colleagues used PS-DVB with a high surface area and large pore volume and graft copolymerized various monomers in their experiments under carefully selected conditions. It was concluded that grafting occurs through copolymerization at the residual double

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bonds of PS-DVB. Accessibility to the grafted functional groups was very good.

The properties of fibrous sulfonic cation exchangers based on DVB propylene-styrene graft copolymers were studied by Soldatov<sup>8</sup> as a function of their compositions. Soldatov<sup>9</sup> studied the physico-mechanical properties of strongly acidic and strongly alkaline ion-exchange fibers and non-woven fabrics based on polypropylene modified with DVB-styrene graft copolymer. Shunkevich et al.<sup>10</sup> studied quantitative characteristics of graft copolymerization of polystyrene and a copolymer of styrene and DVB to polypropylene fibers. Structure of oriented fibers of polypropylene grafted with styrene-DVB copolymer was studied by Soldatov et al.<sup>11</sup> by 9–71% radiochemical grafting.

Battaerd and Tregear grafted polystyrene onto poly(trifluorochloroethylene) through  $\gamma$ -radiation.<sup>12</sup> The polystyrene chains firmly bound to the inert fluorocarbon core were then chloromethylated, and the polymer was used for peptide synthesis in the same way as the Merrifield resin.<sup>13–17</sup> The results of grafting of acrylic acid onto preirradiated poly(styrene-divinylbenzene) have been presented in the present manuscript.

A detailed study of the effects of changing the various reaction parameters on grafting has been made. Grafting of polyacrylic acid introduces the elements of glutaric acid into PS-DVB, which offers sites for chemical transformation for designing some interesting polymeric reagents. Work on these aspects is in progress.

## EXPERIMENTAL

Beaded poly(styrene-2% divinylbenzene), 200–400 mesh, was received from Fluka. Freshly distilled acrylic acid was used as a monomer. Benzene and toluene used were of reagent grade. The resin was irradiated in air from a 2100 Ci cobalt-60 gamma radiation source installed in Gamma Chamber-900, supplied by BARC, Bombay, India.

## GENERAL PROCEDURE

Poly(styrene-divinylbenzene) was irradiated in air in a gamma chamber at a constant dose rate (0.80 MR/h) for preset periods of time. A predetermined amount of acrylic acid and benzene was added to the irradiated PS-DVB beads (100 mg). The reaction mixture was refluxed in an oil bath at 90°C for 3 h. A similar experiment was done at 125°C using

toluene as the reaction medium. Homopolymer, poly(acrylic acid), formed during the reaction was removed by thoroughly washing with warm water on a weighed sintered crucible. The crucible was dried at 50°C to a constant weight. Percentage of grafting was calculated from the increase in the initial weight of the PS-DVB powder in the following way:

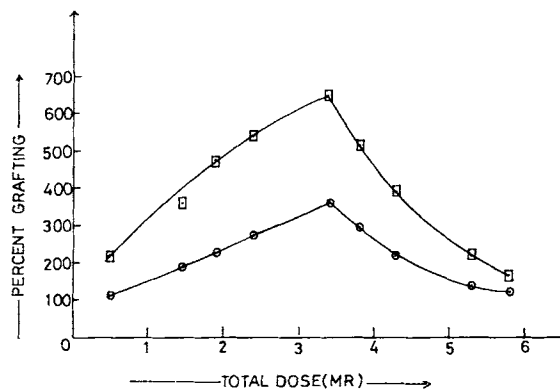
$$\text{Percentage of grafting} = \frac{W_1 - W_0}{W_0} \times 100$$

where  $W_1$  = weight of grafted PS-DVB powder after complete removal of the homopolymer, and  $W_0$  = weight of original PS-DVB powder.

Percentage of grafting was determined as a function of total dose, reaction time, and molar concentration of acrylic acid. Effect of media, temperature, and presence of Mohr salt and alcohols in the reaction solvent were also studied. Changes in swelling property of PS-DVB beads in selected solvents were studied to gain an idea of any unintentional cross-linking in the process of grafting.

## EFFECT OF TOTAL DOSE ON GRAFTING IN BENZENE AND TOLUENE AS THE REACTION MEDIA

Irradiation of PS-DVB powder (100 mg) was done for different periods of time. Irradiated samples were gently refluxed for 3 h (at 90°C) with acrylic acid (1 mL) in benzene (3 mL). The experiments were repeated with 2 mL of acrylic acid. Figure 1 presents the results.



**Figure 1** Effect of total dose on the percentage of grafting of acrylic acid on PS-DVB [PS-DVB = 100 mg, benzene = 3 ml, temp = 90°C, (○—○) acrylic acid = 1 mL, (□—□) acrylic acid = 2 mL].

**Table I Effect of Reaction Media with Increasing Total Dose on the Percentage Grafting of Acrylic Acid on PS-DVB\***

Total Dose (MR)	0.48	1.44	1.92	2.4	3.36	3.84	4.32	5.28	5.76
Medium: Water (3 mL) Temp: 105°C % Grafting	0	0	0	0	0	0	0	0	0
Medium: Benzene (3 mL) Temp: 90°C % Grafting	107	190	233	275	355	295	210	143	120
Medium: Toluene (3 mL) Temp: 90°C % Grafting	0	0	0	0	0	0	0	0	0
Medium: Toluene (3 mL) Temp: 125°C % Grafting	282	345	368	405	465	380	305	260	227

\* PS-DVB, 100 mg; acrylic acid, 1 mL.

### EFFECT OF REACTION MEDIA ON GRAFTING

Samples of PS-DVB (100 mg) irradiated for different periods of time were refluxed for 3 h (at 105°C) with acrylic acid (1 mL) in water (3 mL). Similar experiments were run with toluene (3 mL) as reaction medium (at 90°C and at gentle reflux at 125°C). Results are shown in Table I.

### EFFECT OF TEMPERATURE OF REACTION ON GRAFTING IN BENZENE AND TOLUENE MEDIA

In order to investigate the effect of temperature on grafting in benzene and toluene, four samples of PS-DVB (100 mg) were irradiated with a total dose of 3.36 MR. Irradiated samples were transferred to tubes, and 1 mL of acrylic acid was added to each tube. Benzene (3 mL) was added to two of them, and the tubes were sealed. One of the tubes was heated in an oil bath at 90°C and the other at 125°C for 3 h. Toluene (3 mL) was added to each of the two remaining tubes, after which they were sealed. One was heated at 90°C and the other at 125°C for 3 h. Results of percentage of grafting are reported in Table II.

### EFFECT OF REACTION TIME ON GRAFTING

Keeping other parameters constant (PS-DVB, 100 mg; acrylic acid, 1 mL; benzene, 3 mL; temperature,

90°C; and time of irradiation, 42 h, percentage of grafting was studied as a function of time of reaction, which varied from 1 to 5 h. Results are presented in Figure 2.

### EFFECT OF MOLAR CONCENTRATION OF ACRYLIC ACID ON GRAFTING

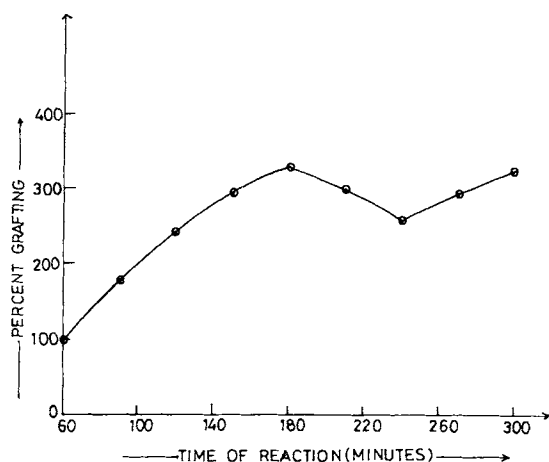
Percentage of grafting was determined as a function of monomer concentration. Preirradiated (3.36 MR) PS-DVB (100 mg) in benzene (3 mL) was taken for each experiment, and the molar concentration of acrylic acid varied from 0.069 to 0.580 mol/100 mL. Reaction was carried out for 3 h at 90°C. Figure 3 shows the results.

Four separate experiments were run by carrying out the reaction in different volumes of 3.65 M acrylic acid in benzene. Results are presented in Table III.

**Table II Effect of Temperature on Grafting in Benzene and Toluene Media in Sealed Tubes\***

Medium	Temperature	
	90°C	125°C
Benzene (3 mL)	384	482
Toluene (3 mL)	30	472

\* Total dose, 3.36 MR; PS-DVB, 100 mg; acrylic acid, 1 mL.



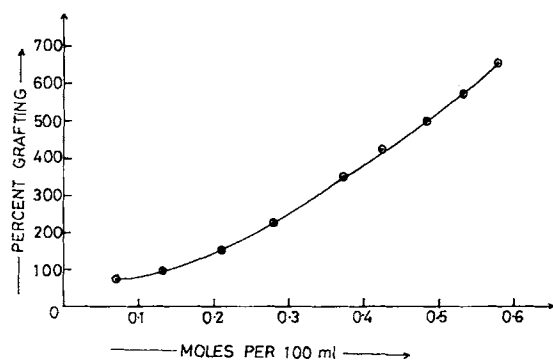
**Figure 2** Effect of time of reaction on the grafting percentage of acrylic acid on PS-DVB (PS-DVB = 100 mg, acrylic acid = 1 ml, benzene = 3 mL, temp = 90°C, time of reaction = 42 h).

### EFFECT OF MOL FRACTION OF ALCOHOLS IN BENZENE-ALCOHOL REACTION MEDIUM

Two binary systems, i.e., benzene-MeOH and benzene-*n*-BuOH were taken for determining the percentage of grafting as a function of mol fraction of MeOH and *n*-BuOH, respectively. Results are shown in Figure 4.

### EFFECT OF MOHR SALT ON PERCENTAGE OF GRAFTING

Keeping the total dose for irradiation fixed at 3.36 MR, two similar experiments were run using  $10^{-4}$  and 0.003 mmol of Mohr salt, respectively.



**Figure 3** Effect of molar concentration on the percentage of grafting of acrylic acid on PS-DVB (PS-DVB = 100 mg; acrylic acid, 0.5–2 mL; benzene = 3 mL, temp = 90°C; time of reaction = 42 h).

**Table III** Grafting with Different Amounts of Acrylic Acid, Keeping the Molar Concentration at 3.65M\*

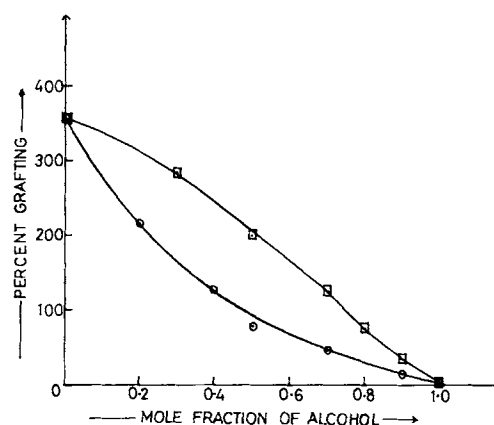
3.65M Acrylic Acid in Benzene (mL)	Percentage of Grafting
3	355
6	354
9	357
12	359

\* PS-DVB, 100 mg; irradiation time, 42 h; temp., 90°C.

### EFFECT OF IRRADIATION AND GRAFTING ON THE SWELLING PROPERTIES OF PS-DVB

Two samples of PS-DVB (100 mg) were irradiated for 42 h (total dose 3.36 MR). One sample of irradiated polymer was heated in benzene (3 mL) for 3 h at 90°C. The other sample was heated in benzene (3 mL) containing 3.65M acrylic acid for 3 h at 90°C. After removing the homopolymer, the sample was dried.

One hundred milligrams of each of the original PS-DVB, irradiated PS-DVB, irradiated and heated PS-DVB, and irradiated and grafted PS-DVB were suspended in  $\text{CH}_2\text{Cl}_2$  for 50 h; and the bed volumes were measured. The dry samples were next suspended in DMF for 50 h, and the bed volumes were again measured. Results were recorded in (Table IV).



**Figure 4** Effect of mole fraction of alcohols in benzene-alcohol reaction medium [PS-DVB = 100 mg; acrylic acid = 1 ml; temp = 90°C; time of reaction = 42 h; benzene, 0–3 ml; (○—○) butanol, 0–3 mL; (□—□) methanol, 0–3 mL].

**Table IV Bed Volume of PS-DVB (100 mg) at Different Stages of Grafting Experiment**

	Bed Volumes (mL)	
	in CH <sub>2</sub> Cl <sub>2</sub>	in DMF
Original PS-DVB	0.41	0.28
Irradiated PS-DVB	0.42	0.29
Irradiated and heated PS-DVB	0.41	0.27
Irradiated and grafted (107%) PS-DVB	0.16	0.20

## EVIDENCE OF GRAFTING

The infrared spectrum of PS-DVB-*g*-poly(AAc) showed sharp peak at 1670–1680 cm<sup>-1</sup> (for C=O), which is strong evidence of the grafting of polyacrylic acid.

## RESULTS AND DISCUSSION

An increase in total dose produces more hydroperoxide groups during irradiation. On subsequent heating for grafting of polyacrylic acid, it generates more hydroxyl radicals; hence, grafting increases on increasing total dose to an optimum value. On excessive irradiation, there is an overcrowding of the radical sites on backbone carbon or as macroxy oxygen. In this situation, not all sites are approachable through diffusion by large polyacrylic acid radicals, and these tend to dimerize and terminate. This situation suits the graft copolymerization of acrylic acid by radical sites on the polymer, and grafting by chain transfer becomes a relatively minor process. The result is a reduced grafting yield. Overcrowding by the radical sites on PS-DVB could also cause cross-linking. Our results on the swelling of the polymer, however, indicate that direct cross-linking between PS chains has not occurred by pairing of radicals formed on irradiation, probably because of steric effects. On the other hand, cross-linking through polyacrylic acid chains cannot be ruled out.

At the higher monomer concentration, the rate of increase in grafting up to the maximum was higher than the corresponding rate at the lower monomer concentration. This difference can be attributed to a higher concentration of the monomer at the active sites on the polymer. As the total dose of irradiation is increased beyond the maximum grafting, there is a steeper decrease in the percentage of grafting at the higher monomer concentration. This is because of the increase in the concentration of hydroxyl radicals, which (being small in size) easily diffuse out

of the polymer beads and enhance polymerization of acrylic acid in the solution. Polyacrylic acid radicals cannot diffuse easily into the beads and terminate by dimerization. The barrier to the diffusion of polyacrylic acid radicals into the beads is provided by a) their size; b) their restricted movement on account of their viscous gelatinous mass that is formed in benzene or toluene; and c) their polar nature, which resists entry into a hydrophobic environment. The result is that grafting through chain transfer is curtailed. Graft copolymerization now occurs mainly through radical sites on the polymer backbone. This explains relative slopes of the curves in Figure 1 beyond the maximum.

Percentage of grafting was studied as a function of total dose in water, benzene, and toluene to see the effects of different media on the percentage grafting. The reactions were carried out at temperatures where the heterogenous reaction mixture was gently boiling to keep it well stirred. Results are shown in Table I. There was no grafting when water was used as a medium at 105°C. This may be attributed to the fact that the polymer does not swell in aqueous medium, and this resists the entry of reactant molecules into the interior of the beads. Percentage of grafting was higher in toluene at 125°C than in benzene at 90°C at any of the total doses of irradiation studied, with the optimum dose being the same in each case (Table I). When the reactions were carried out in toluene at 90°C, there was no grafting at any of the experimental doses. The swelling of the polymer is pretty high in both the media, and it appeared to be due to something other than the chain transfer constants of the media alone. It turned out to be the effect of the temperature of the reactions, which was different in each medium. The higher rate of grafting in toluene at higher temperature overshadowed the loss due to the relatively higher chain transfer constant of toluene. There was an increase of about 8% in the percentage of grafting at 90°C in benzene medium on carrying out the reaction in a sealed tube. When the

same reaction was done at 125°C in a sealed tube, the percentage of grafting increased by 35%. Other parameters remaining the same, grafting in the toluene medium increased from zero in an open tube to 30% in a sealed tube at 90°C. The corresponding figures at 125°C were 465 and 472%, respectively. There seems to be a small but positive role of increased pressure on grafting in sealed tubes (Table II).

Effect of the time of reaction was studied on the percentage of grafting of acrylic acid on PS-DVB (Fig. 2). There was a regular increase in the percentage of grafting as the time of reaction was increased from 60 to 180 min. It then showed a decreasing trend when heating was continued further. A minimum was observed at 240 min, after which it again rose and reached 323% at the end of 300 min of heating. This may be explained by taking into consideration the various energy transfer processes that occur in the irradiated mixture. A growing grafted chain is capable of attacking the neighboring grafted chain, which results in chain scission. This "backbiting" results in the reduction of the length of grafted branches, leading to reduced percentage grafting.<sup>18</sup> Subsequent increasing trend in the percentage of grafting may possibly be the result of the accumulation of homopolymer radicals or homopolymer with olefinic bonds, which are grafted to the graft copolymer. A cross-linked polymer would offer resistance to the free diffusion of the homopolymer species in and out of the pores. In this situation, the chances for the grafting of entrapped chains onto PS-DVB are increased.

Percentage of grafting was studied as a function of monomer concentration. Results are presented in Figure 3. The percentage of grafting increases with an increase in molar concentration of the monomer. It remained unchanged when the mols of monomer in solution was allowed to change while keeping the molar concentration constant (Table III). Percentage of grafting is a function of the molar concentration of monomer and concentration of the active sites on the backbone polymer. On keeping the total dose constant, the concentration of active sites may be assumed to remain constant. Under this condition, the percentage of grafting should increase with an increase in the monomer concentration. Figure 3 agrees with this mechanism.

The effect of increasing the ratio, benzene : alcohol in the binary medium on the percentage of grafting of polyacrylic acid, was studied at the optimum conditions of reaction. Results are presented in Figure 4. It was observed that as the mol fraction of MeOH and *n*-BuOH decreases, the percentage of

grafting increases. In pure methanol and *n*-butanol, there was no grafting. First, PS-DVB does not swell in these alcohols, causing a resistance to the diffusion of monomer to the interior of the beads. Second, the chain transfer property of the alcohols causes the termination of the free radicals competing for grafting at the surface of the PS-DVB beads. Results obtained with methanol and *n*-butanol are in accordance with Garnett's observation on the effect of alcohols on radiation-induced grafting of vinyl monomers onto cellulose. Dilli and Garnett<sup>19</sup> observed that higher alcohols, because of their higher chain transfer constants, caused a lower grafting.

Swelling of cross-linked polymers in a suitable solvent is often associated with the amount of cross-linking in the resins. Cross-linking during an experiment reduces the swelling property of a cross-linked polymer, which is often taken as an index to cross-linking. We were interested in knowing if irradiation, heating, or grafting causes any additional cross-linking in the polymer. Table IV shows that irradiation and irradiation followed by heating causes no change in the bed volumes in CH<sub>2</sub>Cl<sub>2</sub> and DMF. Hence, there should not be any additional cross-linking by radical pairing between different PS chains during irradiation and heating. Polyacrylic acid is soluble in DMF. Hence, the grafted copolymer should swell in DMF without any difficulty. A 28% reduction in the bed volume could possibly arise on account of the reduced mass of PS-DVB in the grafted copolymer. The bed volume is reduced by 40% in dichloromethane, which is not unexpected since dichloromethane is a non-solvent for polyacrylic acid. Some contribution to the cross-linking through polyacrylic acid chains can occur.

To see the effect of Mohr salt on the percentage grafting, two experiments were run with low concentration (10<sup>-4</sup> mmol) and high concentration (0.003 mmol) of Mohr salt under optimum conditions of reaction. Grafting increased from 355 to 437% at the lower concentration of Mohr salt and decreased to 302% at the higher concentration. Mohr salt at a low concentration is known to inhibit homopolymer formation.

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