

Functionalization of Poly(vinyl chloride) Through Radiation-Induced Grafting

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SYNOPSIS

Poly(vinyl chloride) was irradiated in air with γ -rays. The hydroperoxidized poly(vinyl chloride) when heated with acrylic acid in water was grafted with poly(acrylic acid), thus introducing the elements of glutaric acid on the polymer. Percentage weight gain was investigated as a function of total dose, monomer concentration, and time of reaction. The effect of adding methanol to water as a medium of reaction was studied in terms of percentage weight gain on grafting. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the lowest-cost and best-known polymers and is used for diverse applications in industry. It is strong, has excellent fire-resistant properties, and is relatively inert. The chlorine atom in PVC is easily knocked off by high-energy radiations and this has been a popular synthetic approach for the preparation of graft copolymers. The source of high-energy radiations may be a Co^{60} or other radioactive sources, X-rays, or a linear accelerator. Functionalization or introduction of functional groups, as a result of grafting, is an important parameter in dyeing, response to adhesives, and bonding to form polymer composites.

PVC film was radiochemically grafted with polyvinylpyridine *in vacuo* by Chapiro and Mankowski¹ in the temperature range of 20 to -78°C . The film after quaternization with HCl had good swellability in water and was suitable for anion-exchange membrane.² Polystyrene or its derivatives were grafted on PVC in the presence of plasticizers using γ -radiation³ for specialized applications. The grafts could be made rigid, flexible, crosslinkable, or curable depending upon their industrial applications. Styrene, acrylonitrile, acrylic ester, and dienes as grafting monomers gave grafts with specific prop-

erties and uses.^{4,5} Gaspassini et al.⁶ performed radiation-induced graft copolymerization of acrylic acid onto PVC and found that only minor cross-linking had occurred. Adhesives, useful for bonding metals, were prepared by chemically induced grafting of PVC with acrylic acid.⁷ PVC films plasticized with dioctyl phthalate were modified by radiochemical grafting with poly(acrylic acid) (PAA). The grafted films possessed increased hygroscopicity, vapor permeability, and tensile strength for use as leather substitutes.⁸ PVC powder on radiochemical grafting of PAA was suitable as an ion-exchange resin.⁹

Functionalization of a polymer is also a primary process when the polymer is intended to be used as a reagent for carrying out organic reactions. Carboxylic groups are introduced by grafting PAA and these are the sites which are amenable for further chemical transformation of the polymer into a polymeric reagent. Since the solubility or swellability of a polymer in solvents will alter on functionalization, the compatibility of a polymeric reagent with a given solvent will depend on the functional groups introduced and on the extent of grafting. Grafting of PAA, in effect, is tantamount to the introduction of elements of glutaric acid into PVC. The primary aim of the present study was to determine the percentage weight gain on grafting of PAA under various parameters, as the success with a polymeric reagent often rests upon an optimum concentration of reagent groups.

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EXPERIMENTAL

PVC powder of chromatographic grade (lot #S-149-9) was received from Polysciences, Washington, PA. Acrylic acid (AAc), used as a monomer, was freshly distilled. PVC was irradiated in air by a 2100 Ci cobalt-60- γ -gamma radiation source installed in a Gamma Chamber-900, supplied by BARC, Bombay, India.

General Procedure

PVC powder was irradiated in air in the gamma chamber at a constant dose rate (0.84 MR/h) for preset periods of time. The irradiated PVC powder (100 mg) was added to a solution of AAc in water and the reaction mixture was heated at 120°C in an oil bath for 3 h. The grafted polymer was thoroughly washed with warm water on a weighed sintered crucible for completely removing the homopolymer, PAA, formed during the reaction. The crucible was dried at 50°C to a constant weight. Percentage weight gain on grafting was calculated from the increase in the initial weight of the PVC powder in the following manner:

Percentage weight gain on grafting

$$= \frac{W_1 - W_0}{W_0} \times 100$$

where W_1 = weight of grafted PVC powder after complete removal of the homopolymer, and W_0 = weight of original PVC powder.

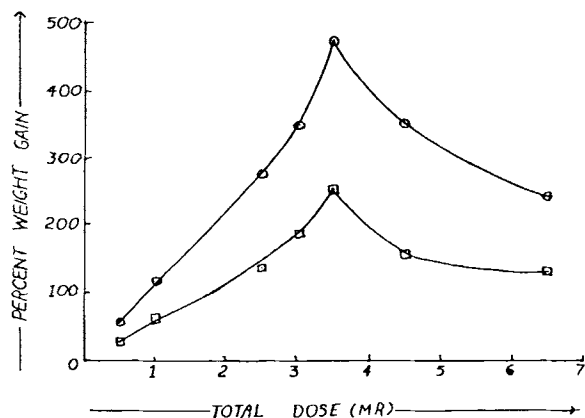


Figure 1 Effect of total dose on the percentage weight gain on grafting of AAc on PVC [PVC 100 mg, water 3 mL, temp 120°C; (○—○) AAc 2 mL; (□—□) AAc 1 mL].

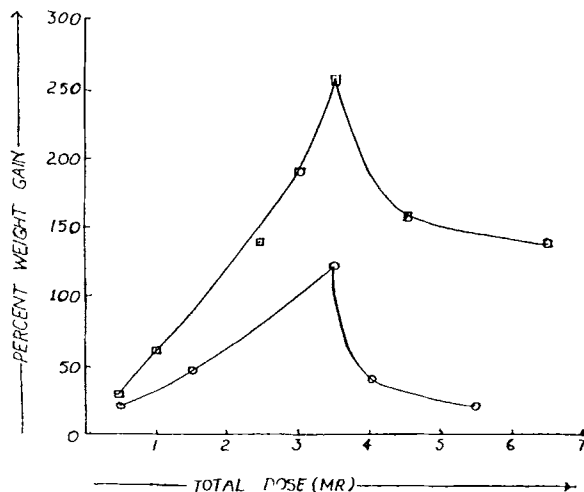


Figure 2 Effect of total dose on the percentage weight gain on grafting of acrylic acid on PVC in methanol medium [PVC 100 mg, AAc 1 mL, temp 120°C (○—○) methanol 3 mL; (□—□) water 3 mL].

Percentage weight gain on grafting was determined as a function of total dose, reaction time, and monomer concentration. Percentage weight gain was also determined by carrying out the reaction in a mixture of methanol and water of varying composition.

Effect of Total Dose on Grafting

PVC powder (100 mg) was irradiated for different periods of time. Irradiated samples were heated for 3 h at 120°C with AAc (2 mL) in water (3 mL). The reaction was repeated by taking 1 mL of AAc, keeping other parameters unchanged. Results are presented in Figure 1.

Effect of Total Dose on Grafting in Methanol Medium

Percentage weight gain on grafting of AAc onto preirradiated PVC in methanol was studied as a function of total dose. Figure 2 shows the results.

Effect of Mol Fraction of Methanol in Water as a Reaction Medium

Percentage weight gain on grafting was studied in a mixture of methanol and water as a function of mol fraction of MeOH and results are shown in Figure 3.

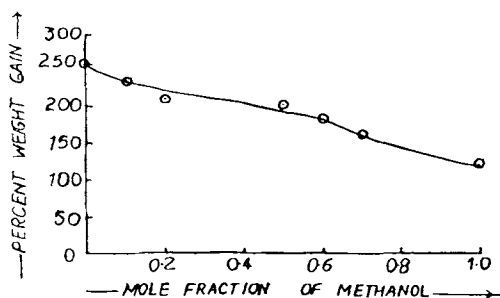


Figure 3 Effect of mol fraction of methanol in water on the percentage weight gain on grafting of AAc on PVC (PVC 100 mg, AAc 1 mL, temp 120°C, time of irradiation 42 h, methanol 3–0 mL, and water 0–3 mL).

Effect of Molar Concentration

At a fixed dose, the percentage weight gain on grafting was studied as a function of monomer concentration in water. Beginning from a very low concentration of 0.15 mL AAc in 3 mL of water, the concentration was gradually raised until it reached to 2 mL of AAc in 3 mL of water. Results are presented in Figure 4. It is evident that the percentage weight gain went on increasing throughout the experimental range. It was not possible to go beyond this level of concentration because, then, the amount of homopolymer was very high and its removal from the graft became a formidable task.

Four experiments were run by taking the same amount of PVC, time of irradiation, and time of reaction and different amounts of AAc in water but keeping its concentration constant. Table I records the results.

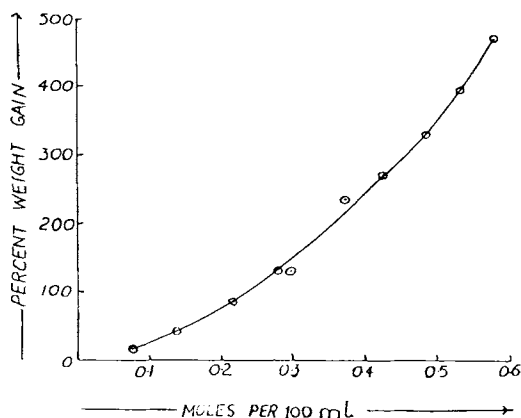


Figure 4 Effect of molar concentration on the percentage weight gain on grafting of AAc on PVC (PVC 100 mg, AAc 0.15–2 mL, water 3 mL, temp 120°C, time of irradiation 42 h).

Table I Grafting with Different Amounts of AAc (Keeping the Molar Concentration Constant, 3.5M); PVC 100 mg, Irradiation Time 42 h

AAc	Water	Percentage Weight Gain on Grafting
1 mL	3 mL	258
2 mL	6 mL	247
3 mL	9 mL	254
4 mL	12 mL	266

Effect of Time of Reaction

Percentage weight gain was studied as a function of time of reaction at 120°C. Keeping other parameters constant, the time of reaction was varied from 1 to 4 h. Results are presented in Figure 5.

Effect of Heating an Aqueous Suspension of Irradiated PVC Powder

PVC powder (500 mg) was irradiated in air with a total dose of 0.504–7.200 MR. The irradiated powder was heated in water for 3 h at 94 or 120°C (sealed tube). The powder was then washed, dried, and weighed. Loss in weight on possible dehydrochlorination was determined. The loss in weight was < 2%, which corresponds to the loss of 1 molecule of hydrogen chloride from more than 29 monomeric units in PVC.

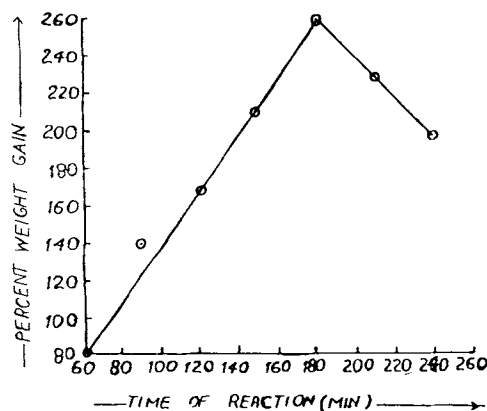
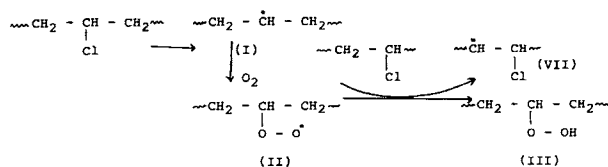


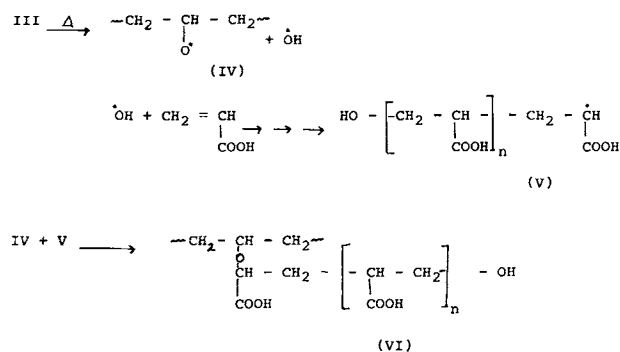
Figure 5 Effect of time of reaction on the percentage weight gain on grafting of acrylic acid on PVC (PVC 100 mg, AAc 1 mL, water 3 mL, time of irradiation 42 h, temp 120°C).

RESULTS AND DISCUSSION

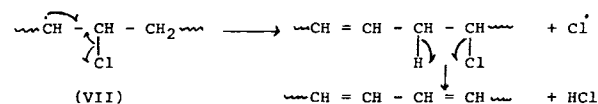
When PVC is irradiated with γ -rays in air, the C—Cl bond is cleaved homolytically, giving rise to a free radical (I) which on reaction with oxygen forms a peroxy radical (II). II abstracts a hydrogen inter- or intramolecularly, thus forming macromolecular hydroperoxide (III):



On heating, III forms alkoxy radical (IV) and $\dot{\text{O}}\text{H}$. In the presence of AAc, $\dot{\text{O}}\text{H}$ initiates its polymerization and the PAA radical (V) is terminated by combining with IV, forming the grafted PVC (VI). Evidence of grafting was indicated by the presence of a sharp peak at $1670\text{--}1680\text{ cm}^{-1}$ (for >C=O) in the grafted copolymers:



The homopolymer, PAA, is formed by the dimerization of V or by any other termination process. It is also known that on irradiation PVC eliminates HCl, leading to unsaturations in the molecule:

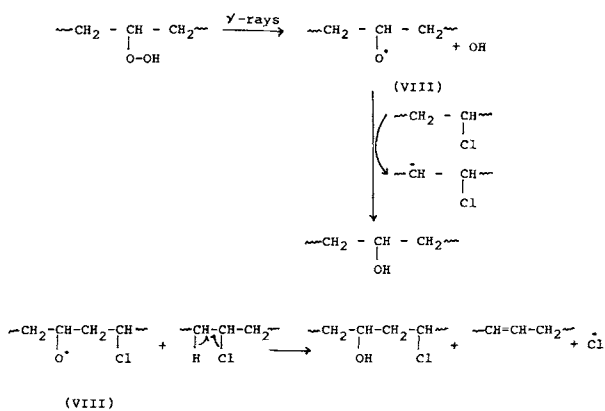


Formation of as many as nine such conjugated double bonds have been reported.

Effect of total dose on grafting of PAA was studied in water. Maximum grafting (475%) was observed at 2520 min (3.528 Mrad) when 2 mL (0.028 mol) of monomer was taken. Beyond this dose, percentage weight gain decreases gradually. When the amount of monomer was reduced to 1 mL, the percentage weight gain decreased but the maximum was ob-

served at the same dose (Fig. 1). In comparison, the rates of grafting at $[\text{AAc}] = 0.028\text{ mol}$ and at $[\text{AAc}] = 0.014\text{ mol}$ are nearly the same initially (0.20%/min and 0.17%/min, respectively). Beyond 1800 min, the rate of grafting at a higher concentration of AAc increases rapidly (0.24%/min) until it reaches the maximum. At lower concentration, it, rather, slows down (0.066%/min).

Percentage weight gain on grafting of AAc was studied as a function of total dose in water and in methanol as solvents. Results are shown in Figure 2. Percentage weight gain on grafting initially increased with increasing total dose in both the media, reached a maximum (258% [aq.] and 123% [MeOH]) at a dose of 3.53 Mrad, and decreased on further increasing of the dose. Increase in weight with increasing total dose was due to the formation of more hydroperoxide groups which provided a larger number of sites for grafting. Decrease in grafting beyond an optimum total dose may involve the cleavage of hydroperoxide groups, leading to the formation of macroxy radicals (VIII). The macroxy radical can abstract a hydrogen atom in an inter- or intramolecular manner to generate hydroxy groups on the polymeric backbone along with the formation of unsaturation:

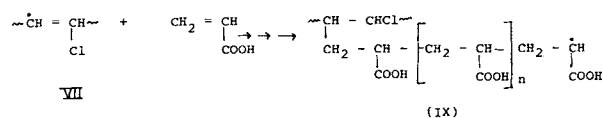


Such effects do not contribute toward grafting and, hence, decreases the percentage weight gain on grafting.

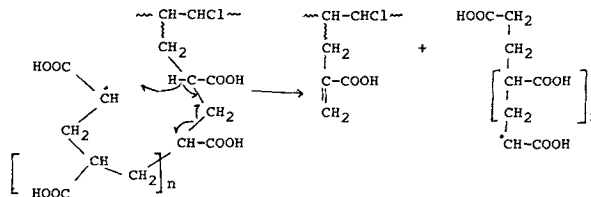
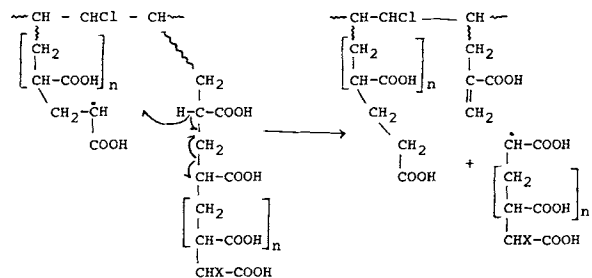
The gain in weight on grafting was much less (123%) in methanol than in water (258%). In methanol, the growing polymeric chains are terminated to produce the homopolymer via a chain-transfer process while such processes are almost absent in water. The same effects are reflected when the percentage weight gain is studied as a function of mol fraction of MeOH in the $\text{H}_2\text{O} - \text{MeOH}$ system (Fig. 3). As the mol fraction of MeOH increases, the percentage weight gain decreases.

Percentage weight gain on grafting was studied as a function of monomer concentration. As the molar concentration of the monomer increases, the percentage weight gain also increases (Fig. 4). Keeping the molar concentration of the monomer in water constant while varying the total amount of water and the monomer, the gain in weight remained unchanged (Table I). These results clearly indicate that the percentage weight gain on grafting onto PVC depends on the molar concentration and not upon the number of moles of the monomer present in the reaction mixture.

Figure 5 shows the dependence of percentage weight gain on the time of reaction. Upon a reaction time of 3 h, the percentage weight gain increases linearly and then there is a linear decrease. The process of grafting occurs not only through chain transfer of the PAA radical **V** to the PVC as presented earlier; it is also possible when polymeric radicals like **VII** initiates the polymerization of AAC:



A radical like **IX** will have sufficient dimensional flexibility to reach and abstract a hydrogen atom from itself by "back biting" or from an adjoining grafted PAA chain or radical through a process involving β -scission:



If these processes become competing reactions, the gain in weight on grafting should fall.

We acknowledge with appreciation the helpful discussions with Dr. (Mrs.) I. K. Mehta during the course of this work.

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Received January 19, 1995

Accepted April 27, 1995