Gamma-Radiation-Induced Graft Copolymerization of Acrylamide onto Crosslinked Poly(*N*-vinylpyrrolidone)

C. S. PANDE, N. GUPTA

Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla-171005, India

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ABSTRACT: Crosslinked poly(*N*-vinylpyrrolidone) (PVPy) beads were irradiated with γ-rays in air from a ^{60}Co source. Preirradiated beads were grafted with polyacrylamide by refluxing with acrylamide in water or dioxane. Conditions for optimum grafting were determined under a variety of reaction parameters, such as the total dose, duration, and temperature of heating, and the molar concentration of acrylamide used. The effect of the addition of methanol to the aqueous medium during grafting was also studied. The pendant carboxamide groups of PVPy-*g*-polyacrylamide were transformed into amino, aminoethylamido, and hydrazide functionalities terminating in primary amino or hydrazido groups. These provide sites for immobilizing proteins through their amino or carboxyl groups and, also, handles for attaching reagent molecules. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2163–2168, 1999

Key words: PVPy; irradiation; grafting; proteins

INTRODUCTION

Crosslinked poly(*N*-vinylpyrrolidone) (PVPy) is produced by copolymerization of *N*-vinylpyrrolidone and a crosslinking agent in aqueous systems containing substantial quantities of an inorganic salt.[1,2] Typically, under a nitrogen atmosphere, a solution of *N*-vinylpyrrolidone, AlBN, and methylene bisacrylamide is added with stirring to a 10% aqueous solution of disodium hydrogen phosphate and sodium sulfate heated to 50–65°C. Alternative crosslinking agents used are ethylene dimethacrylate, the dimethacrylates of the higher ethylene glycols, and divinylbenzene.[1] Sodium chloride may be substituted for sodium sulfate.[2] Poly(*N*-vinylpyrrolidone) has also been crosslinked with α-ω-diolefins, such as 1,7-octadiene,[3] diazo compounds, or oxidizing agents.[4–6]

Highly purified PVPy in a beaded form is a stable powder that is practically odorless and tasteless (pH 6.0–7.5), insoluble in water and all other common solvents, and chemically inert. PVPy is one of the most nontoxic polymers known and finds several applications in the medical field. PVPy swells in aqueous and alcoholic media, dioxane, and DMF, a property that makes it an excellent support for developing into a reagent for organic synthesis. We have been looking for introducing functional groups by free-radical-initiated grafting of a variety of monomers. The present article examines the graft copolymerization behavior of acrylamide on heating with PVPy, which has been irradiated with γ-rays in air from a ^{60}Co source. A detailed study of the grafting was made under a variety of reaction parameters, for example, total dose, temperature and duration of the reaction, reaction media, monomer concentration, and mole fraction of MeOH in H_2O–MeOH media. The carboxamide groups of the grafted chain were transformed into amino, hydrazido, and aminoethylamido functionalities by treating with hypochlorite, hydra-

Correspondence to: C. S. Pande.

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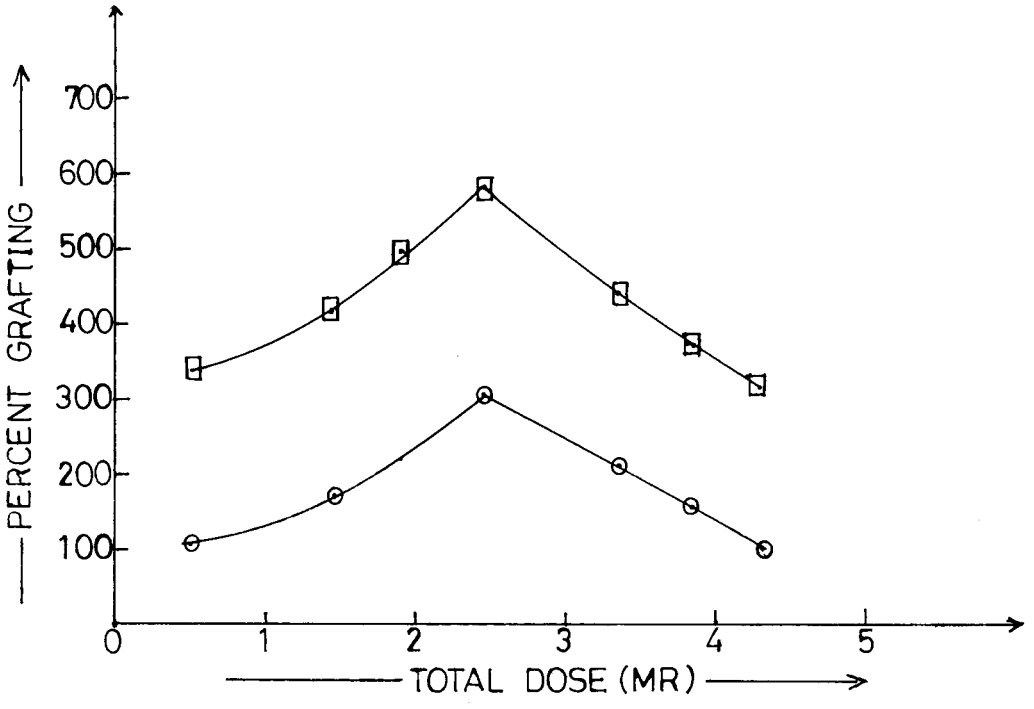


Figure 1 Effect of total dose on the percentage of grafting of acrylamide on PVPy (PVPy, 100 mg; water, 3 mL; temperature, 112–115°C): (○——○) acrylamide, 0.014 mol; (□——□) acrylamide, 0.028 mol.

zine, and ethylenediamine, respectively. The modified polymers can be applicable in chromatographic support systems and useful for anchoring biomolecules and reagent groups for organic reactions. Studies on these applications will be presented in a future communication.

EXPERIMENTAL

Materials and Methods

Crosslinked PVPy in a beaded form was a gift from Fluka. Acrylamide was recrystallized before use. The resin was irradiated in air from a 2100 Ci ^{60}Co γ-radiation source at a constant dose rate (0.080 MR h) for different periods of time.

General Procedure for Grafting

Irradiated PVPy beads were suspended in distilled water, followed by the addition of acrylamide. The reaction mixture was gently refluxed in an oil bath maintained at 112–115°C. The contents were then filtered through a weighed cintered crucible and washed thoroughly with distilled water to ensure complete removal of the homopolymer, polyacrylamide. The grafted copolymer was dried at 50°C to a constant weight. The percentage of grafting was expressed as the percentage of increase in the weight of the crosslinked PVPy as a result of grafting.

The percentage of grafting was determined as a function of the total dose of irradiation, the time of reaction, and the mole fraction of methanol when the reaction was carried out in aqueous methanol as the reaction medium. The percentage of grafting was also determined in samples irradiated with increasing doses and in dioxane as the medium of reaction at two different temperatures. With molar concentration of acrylamide as the variant, the effect on the percentage of grafting was determined at different doses. A set of experiments was run where the only variable parameter was the volume of a 3.5*M* acrylamide solution. Results are presented in Tables I–III and Figures 1–3.

Evidence of Grafting

The IR spectrum (KBr pallet) of the grafted copolymer showed peaks at 3400 cm^{-1} due to N—H (str) and at 1605 cm^{-1} due to N—H (def), indicating that acrylamide has been grafted onto PVPy.

Preparation of PVPy-*g*-polyvinylamine

To 50 mL of NaOBr solution prepared according to the method of Allen and Wolf,[7] PVPy-*g*-polyacrylamide (200% grafting, 200 mg) was added. A stream of nitrogen was bubbled through the solution at 0°C for 4 h and at 20°C overnight. The polymer was filtered and washed thoroughly with deareated water, 1*N* HCl, and water. Titrimetric estimation of HCl retained by the polymer revealed that ~ 80% of amide groups of the polymer had been converted into amino groups.

Preparation of PVPy-*g*-polyacrylhydrazide

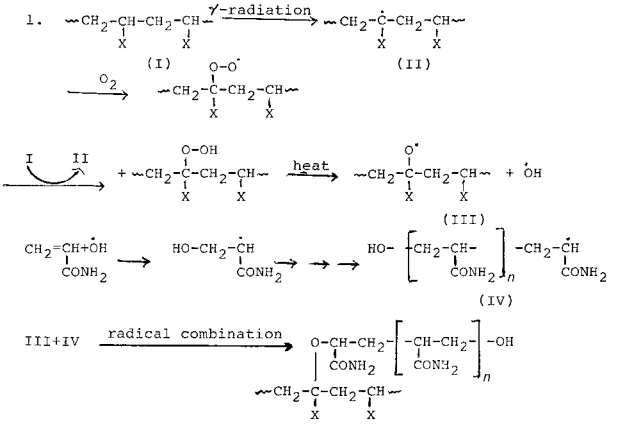
PVPy-*g*-polyacrylamide (200% grafting, 200 mg) was treated with hydrazine at 47°C according to the method of Inman and Dintzis.[8] After thorough washing and titrating with 0.1*N* HCl, it was found that approximately 75% of the amide groups had been converted to the hydrazide groups.

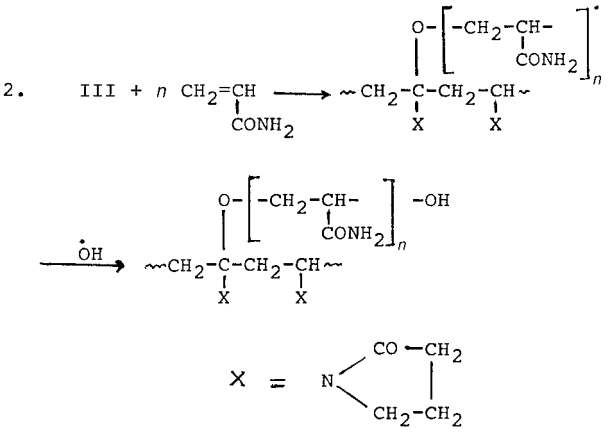
Preparation of PVPy-*g*-poly(*N*-aminoethylacrylamide)

PVPy-*g*-polyacrylamide (200% grafting, 200 mg) was treated with ethylenediamine at 90°C according to the method of Inman and Dintzis.[8] The polymer treated with 0.1*N* HCl showed that approximately 60% of amide groups on the polymer had been transformed.

RESULTS AND DISCUSSION

Assuming that the grafting of polyacrylamide onto preirradiated PVPy takes place through the following possible mechanisms





it becomes evident that exposing PVPy to a higher dose will increase the concentration of III and ȮH, which will result in the formation of larger amounts of graft copolymer by either of the two mechanisms considered (Fig. 1). Irradiation beyond a point results in excessive radical sites on the polymer backbone. The concentration of initiator radicals ȮH in the medium becomes so high that they tend to terminate the homopolymer radicals IV and polymer radicals II by combining with them and compete with grafting. The result is that the homopolymer formation is promoted at the cost of grafting.[9]

The percentage of grafting was studied as a function of reaction time (Fig. 2). Grafting increased linearly up to 180 min, followed by a regular decrease up to 240 min. Again, there was an increase in the percentage of grafting between 240 and 330 min of reaction. A similar trend was noticed when PVPy was grafted with polyvinylpyridine.[10] The decrease in grafting may be attributed to a back biting mechanism.[11] An increase in the percentage of grafting on prolonged heating may be the result of the grafting of large homopolymer species trapped inside the beads.

The profile of the percentage of grafting as a function of temperature and total dose in two different media is presented in Table I. If we compare the results of grafting in dioxane at 112–115°C and at 127–130°C [column (B) and (C) in Table I], it will be seen that grafting at higher temperature is consistently higher at all doses studied. Not only does the higher temperature favor the homolytic fission of hydroperoxide groups of the irradiated PVPy creating radical sites, it also brings the reacting species into more intimate contact by the gentle boiling of the medium and a decrease in its viscosity. Comparing columns (A) and (B) in Table I, the lower percentage of grafting under (B) is attributed to the

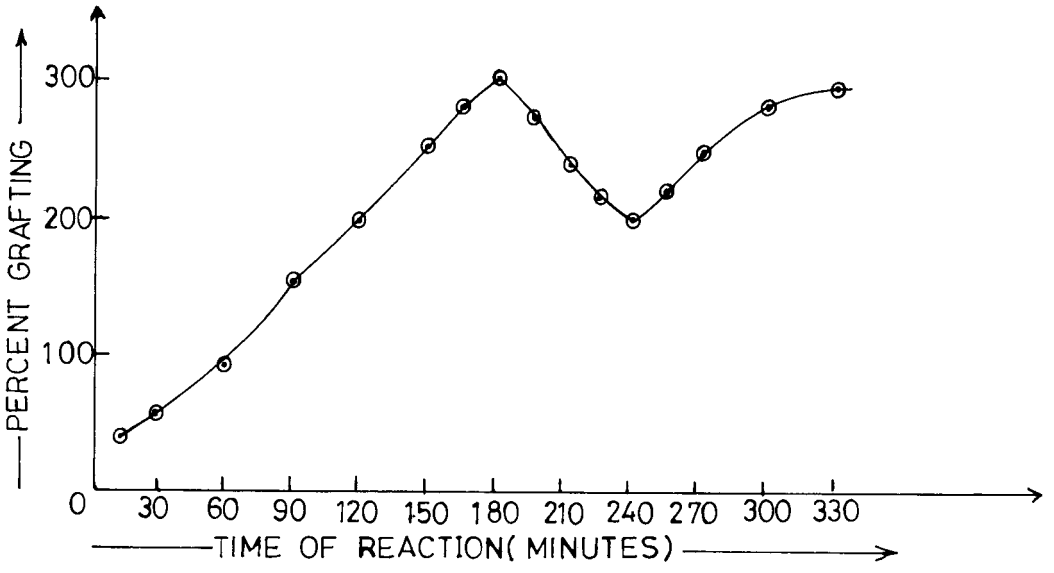


Figure 2 Effect of the time of reaction on the grafting percentage of acrylamide on PVPy (PVPy, 100 mg; acrylamide, 0.014 mol; water, 3 mL; temperature, 112–115°C; total dose, 2.4 MR).

higher chain-transfer constant of dioxane, as well as the poor mixing of the reacting species. The aqueous mixture boils at 112–115°C, while the mixture in dioxane does not boil at this temperature. Comparison of columns (A) and (C) reveals the same trend that a higher reaction temperature favors grafting, effectively overshadowing the negative effect of a higher chain-transfer constant of the medium. Summing up, grafting is favored by (1) a high reaction temperature, (2) a low chain transfer constant of the medium, and (3) efficient mixing of the reacting species.

The effect of molar concentration of acrylamide on grafting was studied at a fixed total dose, which shows a regular increase through the range studied (Fig. 3). According to the proposed mechanism as well, the percentage of grafting should increase with an increase in the molar concentration of the monomer. Grafting remained unchanged when the moles of the monomer present in solution were allowed to change while keeping the molar concentration constant (Table II).

The effect of the addition of methanol in water as a medium of grafting was studied at a fixed total dose in sealed tubes at 112–115°C. Table III presents the results. It was observed that the percentage of grafting increases as the mole fraction of methanol in the reaction mixture decreases. These results agree with the higher chain transfer constant of MeOH, as compared to that of water. A small positive contribution of pressure was also noticed on the

Table I Effect of Temperature on the Percentage of Grafting of Acrylamide (0.014 mol) on PVPy (100 mg) in Different Reaction Media and with Increasing Total Dose

Total Dose (MR)	(A) Water (3 mL; 112–115°C)	(B) Dioxane (3 mL; 112–115°C)	(C) Dioxane (3 mL; 127–130°C)
0.48	110	32	143
1.44	170	74	238
1.92	220	85	315
2.40	306	95	397
3.36	209	71	268
3.84	157	64	205
4.32	101	49	156

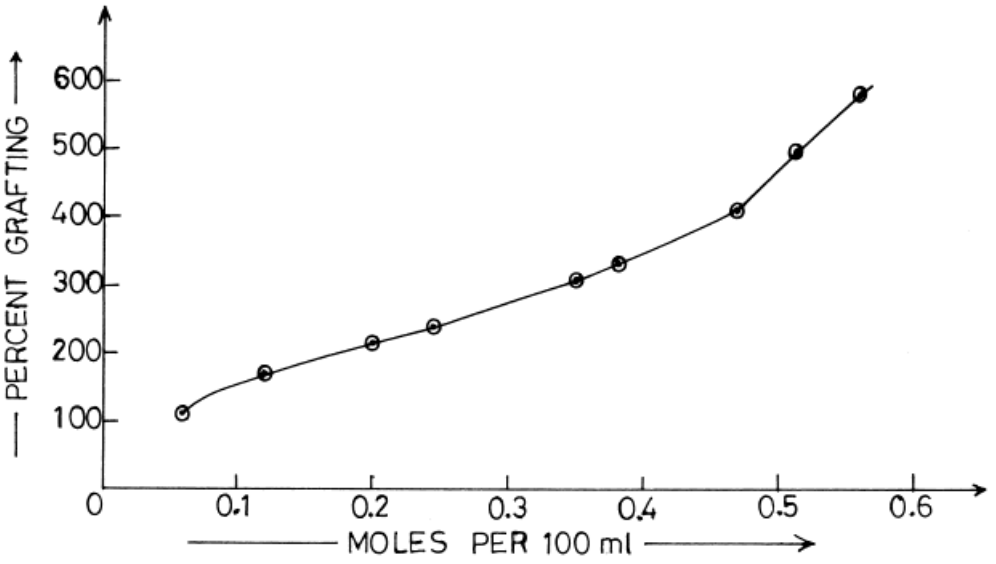


Figure 3 Effect of molar concentration on the percentage of grafting of acrylamide on PVPy, (PVPy, 100 mg; water, 3 mL; temperature, 112–115°C; total dose, 2.4 MR).

percentage of grafting when the reaction was done in closed tubes.

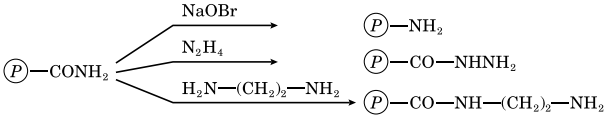
The backbone polymer (PVPy) contains tertiary amide functionalities in the form of the cyclic lactam, *N*-substituted pyrrolidone pendants. This imparts into PVPy the property of swelling in aqueous medium. If the physical properties are to be retained in grafted PVPy, it is important that the grafted homopolymer should be as closely related to PVPy as possible. Grafting of polyacrylamide and its chemical transformation described here is an appropriate choice in this direction.

The carboxamide groups of the grafted chains are not very reactive as such but could be conveniently transformed chemically into amino, hydrazido, and aminoethylamido functionalities by treatment with sodium hypobromite, hydrazine, and ethylenediamine, respectively.

Table II Grafting with Different Amounts of Acrylamide, Keeping the Molar Concentration Constant at 3.5*M*

3.5*M* Aqueous Acrylamide (mL)	Percentage of Grafting
3	306
6	305
9	306
12	304

PVPy, 100 mg; total dose, 2.4 MR; temperature, 112–115°C; reaction time, 3 h.



where *P* is the polymer.

All of them have a basic —NH_2 group at the terminii of the pendants and can be made to react with carboxyl, amino, and various other groups by simple chemistry, as follows:

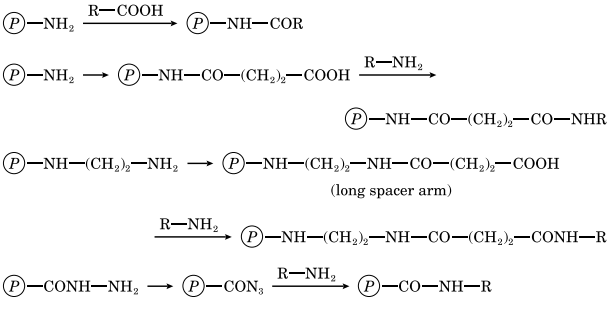


Table III Effect of Mole Fraction of MeOH in H_2O—MeOH in Sealed Tubes at 112–115°C

Mole Fraction in MeOH	Percentage of Grafting
1.0	144
0.5	167
0.3	221
0.1	285

PVPy, 100 mg; acrylamide, 0.014 mol; total dose, 2.4 MR.

The various classes of compounds that can be so anchored are proteins and, also, small active (chemically or biologically) molecules. Enzymes covalently bound to the carriers (immobilized enzymes) through their functional groups not essential for biological activity are convenient to handle both in a batch process or as packed columns in the laboratory or in industry. Carriers obtained through grafting, as in the present work, do not have hydrophobic regions and therefore should not denature sensitive enzymes bound to them. By choosing appropriate molecules for anchoring to the carrier, it can be used for separation through affinity chromatography or as a supported reagent for organic reactions.

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