



Research Article

Green Synthesis of Graft Copolymers Based on Starch and Acrylic Monomers by Solid Phase Polymerization Technique

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Abstract

The solid phase polymerization technique for preparing graft copolymers involving polysaccharide and acrylic monomer (s) which is hazards free and effective is reported first time in this paper. In the authors' laboratory a series of graft copolymers based on starch and acrylamide (AM), N-methylacrylamide (NMA), N,N-dimethylacrylamide (DMA) acrylic acid (AA) and methylacrylate (MA) were successfully synthesized with high yield by solid phase method. The synthesized graft copolymers were characterized by FTIR spectroscopy and XRD analysis.

Keywords: Solid phase polymerization; Graft copolymer; Starch; Acrylamide; Dimethylacrylamide; Acrylic acid

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1. Introduction

Graft copolymerization of the acrylic monomers onto the polysaccharides' backbone is a technique to get materials having wide range of applications [1-3] due to the merging of the properties of both the polysaccharides and the synthetic polymers. The graft copolymers between polysaccharide and the acrylic monomers were prepared by using various techniques [4-9] in the solution phase. Of the various methods free radical initiation process in aqueous medium is most popular. But the conventional grafting process required high temperature (70-90°C), inert atmosphere (N₂ or Ar) and long reaction time to complete the polymerization process.

Here we have developed a solid phase polymerization technique for preparing graft copolymers of polysaccharide (Starch) and acrylic monomers which requires short reaction time, air atmosphere (inert atmosphere is not required) and low temperature i.e. hazards free process. In authors' laboratory a series of graft copolymers involving starch and other acrylic monomers namely AM, NMA, DMA, AA and MA were prepared by solid phase polymerization technique using ceric ammonium nitrate (CAN) and potassium persulfate (PPS) as the initiators separately.

2. Experimental Section

2.1 Materials

Acrylamide (AM), starch (St), acetone, methanol, dichloromethane (DCM), ceric ammonium nitrate (CAN), N-methylacrylamide (NMA), acrylic acid (AA) and methylacrylate (MA) are procured from Loba Chemie, Mumbai, India. N, N-dimethylacrylamide (DMA) is procured from Sigma Aldrich, Missouri, United States. Middle fraction of the vacuum distilled DMA and double distilled water were used in the synthesis.

2.2 Synthesis of graft copolymers

The synthesis of graft copolymers namely St-g-PAM, St-g-PNMA, St-g-PDMA, St-g-PAA and St-g-PMA were synthesized using solid phase polymerization technique. In this process CAN and PPS were used as the initiator separately. The typical process of preparing St-g-PAM was as follows; 2.5 g of starch and 6.0 g of acrylamide were taken in a mortar and grinding by pestle for about 2-3min. Ceric ammonium nitrate (0.3 g) was mixed with the mixture and the mixture was thoroughly grounded 1 min after the addition of 9-10 drops of water into the mixture. At this stage the grafting reaction was started vigorously. Same procedure was followed for preparing St-g-PNMA, St-g-PDMA, St-g-PAA and St-g-PMA. Again all the aforementioned graft copolymers were synthesized using PPS initiator (0.1 g) separately. In this case hot air blower (Hair drier; 1000W, Philips) was used to increase the temperature of the reaction mixture up to 70°C for the dissociation of K₂S₂O₈ to the free radicals. The synthetic details are given in Table 1 and Table 2. A pictorial representation of the synthetic process is shown in Scheme 1.



Scheme 1 Pictorial representation of graft copolymer synthesis

Table 1 Synthetic details of the graft copolymers using 2.5 g starch, 6.0 g of monomer (s) and 0.3 g of CAN at 25 °C.

Polymer	Time (min)	Grafting				(%H)
		Yield	(%C)	(%G)	(%E)	
St-g-PAM	2	8.5	93.3	324	95.2	4.7
St-g-PNMA	3	8.6	92.2	320	93.0	6.9
St-g-PDMA	10	8.2	83.3	300	91.4	8.5
St-g-PAA	15	7.5	71.7	272	90.6	9.3
St-g-PMA	25	7.8	63.9	256	82.0	17.9

$$\%Conversion(\%C) = \frac{(wt \text{ of graft copolymer} - wt \text{ of polysaccharide})}{amount \text{ of AM / NMA / DMA / AA / MA}} \times 100$$

$$\%Grafting \text{ ratio} (\%G) = \frac{wt \text{ of graft polymer}}{wt \text{ of polysaccharide}} \times 100$$

$$\%Grafting \text{ efficiency} (\%E) = \frac{Wt. \text{ of grafted product}}{Wt. \text{ of polymer formed}} \times 100$$

$$Homopolymer (\%H) = 100 - \%Grafting \text{ efficiency}$$

Table 2 Synthetic details of the graft copolymers using 2.5 g starch, 6.0 g of monomer (s) and 0.1 g of PPS at 70 °C.

Polymer	Time(min)	Grafting				(%H)
		Yield	(% C)	(%G)	(%E)	
St-g-PAM	5	8.4	88.3	312	92.8	7.1
St-g-PNMA	5	8.2	83.3	300	91.4	8.5
St-g-PDMA	40	7.9	76.7	284	89.8	10.1
St-g-PAA	45	7.8	70.0	268	85.9	14.1
St-g-PMA	60	7.7	61.7	248	80.5	19.4

$$\%Conversion(\%C) = \frac{(wt \text{ of graft copolymer} - wt \text{ of polysaccharide})}{amount \text{ of AM / NMA / DMA / AA / MA}} \times 100$$

$$\%Grafting \text{ ratio} (\%G) = \frac{wt \text{ of graft polymer}}{wt \text{ of polysaccharide}} \times 100$$

$$\%Grafting \text{ efficiency} (\%E) = \frac{Wt. \text{ of grafted product}}{Wt. \text{ of polymer formed}} \times 100$$

$$Homopolymer (\%H) = 100 - \%Grafting \text{ efficiency}$$

2.3 Purification of graft copolymers

Different type of homo-polymers, poly (acrylamide) [PAM], poly (N-methylacrylamide) [PNMA], poly (N, N-dimethylacrylamide) [PDMA], Poly (acrylic acid) [PAA] and poly (methylacrylate) [PMA] were removed from the synthesized graft copolymers by solvent extraction technique [9-12]. The extracted homo-polymers were collected to calculate the different grafting parameters (Table 1 and Table 2). The solvent used to remove the homo-polymers are formamide and acetic acid (1:1 by volume) for PAM, water for PNMA, methanol for PDMA, methanol and water mixture (6:1 by volume) for PAA and acetone for PMA. The graft copolymers were re-precipitated using excess quantity of acetone. The graft copolymers were then dried in a vacuum oven pulverized and sieved through a 125 μ sieve.

3. Characterization of graft copolymers

Purified synthesized graft copolymers, starch and homo-polymers were subjected for FTIR analysis by Perkin Elmer Spectrophotometer (L 16000300 Spectrum Two LiTa, Llantrisant, UK) and XRD studies (Rigaku Miniflex-600, (Japan) x-ray diffractometer). Powder XRD studies were carried out using $\text{CuK}\alpha$ radiation ($\lambda = 0.154056 \text{ nm}$).

4. Results and discussion

From Table 1 and Table 2 it is obvious that greater grafting yields for all the graft copolymers were occurred in case of CAN than that of PPS initiator. This is mainly due to following facts; ceric ion generates free radical sites onto the polysaccharide backbone rapidly by formation of a complex between the hydroxyl groups of the polysaccharide and the Ce (IV) for which homo-polymerization becomes less. Potassium persulphate (PPS) forms macro-radicals at high temperature onto the polysaccharide backbone by hydrogen abstraction from the $-\text{OH}$ groups present in the polysaccharide backbone. Here percentage of homo-polymerization becomes greater due to the direct attack of the radical generated by the decomposition of PPS to the acrylic monomer (s).

Grafting yield is higher in case of AM compare to NMA, DMA and AA because of the higher reactivity of AM molecules. The presence of one methyl group in NMA and two methyl groups in DMA decreases the reactivity of NMA and DMA molecules. Therefore, total time requirement for polymerization is higher in case of DMA and lower in case of AM. For AA and MA time requirement is higher because of their low reactivity. Same results were occurred in PPS initiator also.

FTIR spectra of graft copolymers and homo-polymers are shown in Figure 1 and Figure 2 respectively for proof of grafting.

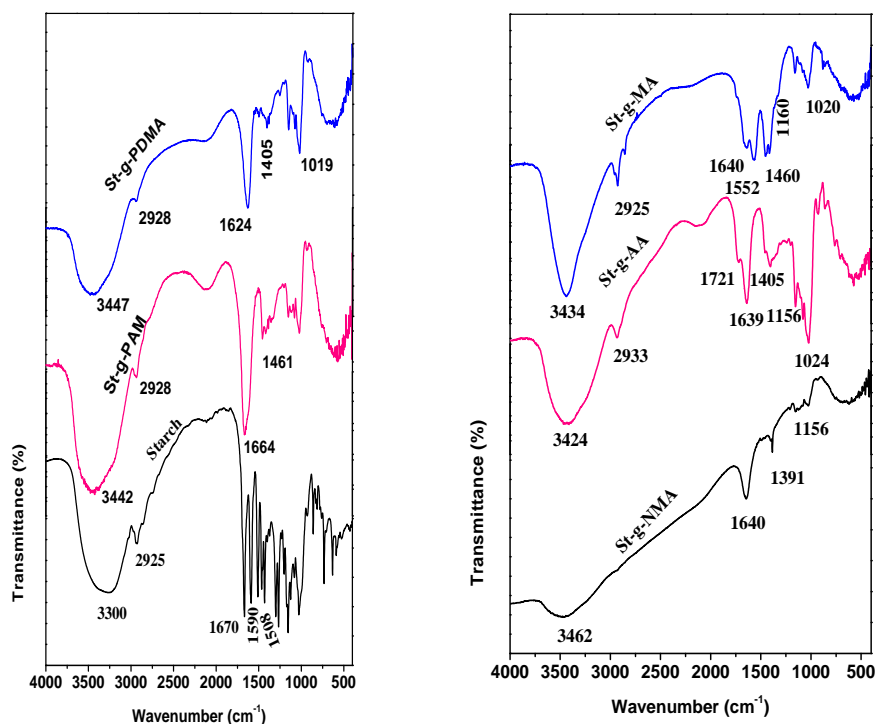


Figure 1 FTIR spectra of starch, St-g-PAM, St-g-PDMA, St-g-NMA, St-g-PAA and St-g-PMA.

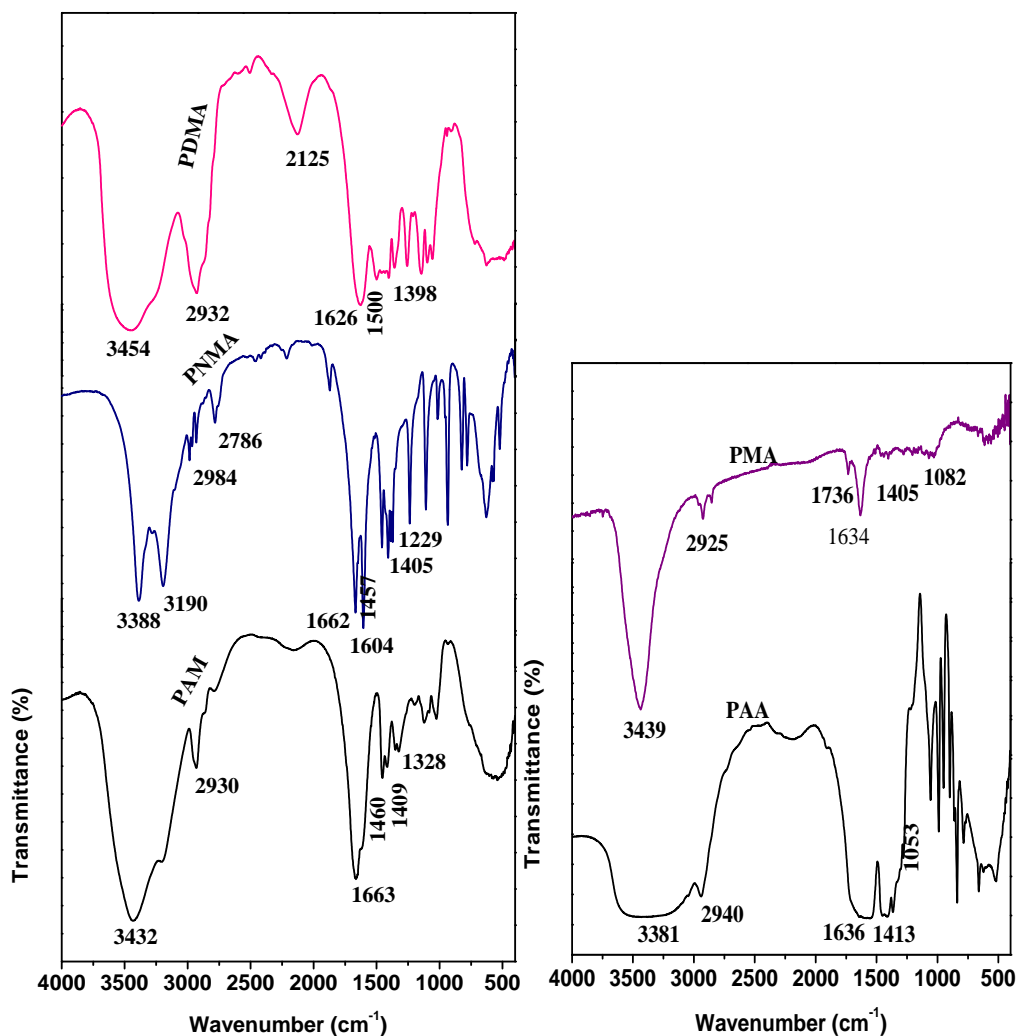


Figure 2 FTIR spectra of PAM, PNMA, PDMA, PAA and PMA

In St-g-PAM; the peak at 1664 cm^{-1} is for amide $>\text{C}=\text{O}$, 1461 cm^{-1} is for C-N groups, 2928 cm^{-1} is for saturated C-H units and 3447 cm^{-1} is for hydroxyl (-OH) groups. Since PAM was removed from the graft copolymer completely, presence of amide $>\text{C}=\text{O}$, C-N groups in the graft copolymers is an evidence of grafting.

For St-g-PDMA ; the peak at 1624 cm^{-1} appears is for amide $>\text{C}=\text{O}$, at 1405 cm^{-1} is for the C-N groups, at 3447 cm^{-1} is for -OH groups present at the starch backbone. The peak at 2928 cm^{-1} is for the saturated C-H units. Since PDMA were removed from the graft copolymer completely, presence of amide $>\text{C}=\text{O}$, C-N groups in the graft copolymers is an evidence of grafting.

For St-g-NMA; the peak at 1640 cm^{-1} is for amide $>\text{C}=\text{O}$, 1391 cm^{-1} is for C-N groups and 3462 cm^{-1} is for hydroxyl (-OH) groups. Since PNMA was removed completely from the graft copolymer, presence of amide $>\text{C}=\text{O}$, C-N groups in the graft copolymers is an evidence of grafting.

For St-g-AA ; the peak at 1639 cm^{-1} is for $-\text{COOH}$, 1405 cm^{-1} is for C-N groups, 2933 cm^{-1} is for saturated C-H units and 3434 cm^{-1} is for hydroxyl (-OH) groups. Since PAA was removed from the graft copolymer completely, presence of $-\text{COOH}$ groups in the graft copolymers is an evidence of grafting.

For St-g-MA; the peak at 1640 cm^{-1} is for $-\text{COOMe}$, 1460 cm^{-1} is for C-N groups, 2925 cm^{-1} is for saturated C-H units and 3434 cm^{-1} is for hydroxyl ($-\text{OH}$) groups. Since PMA was removed from the graft copolymer completely, presence of $-\text{COOMe}$ groups in the graft copolymers is an evidence of grafting.

Similar results were also reported as proof of grafting where the graft copolymers were prepared by solution phase polymerization technique [2, 9, 12-14].

From the XRD plots (Figure 3) it is obvious that the peaks which are originally present in starch backbone shifted in the graft copolymers, because of the change in morphology after grafting of PAM, PNMA, PDMA, PAA and PMA chains onto the starch backbone. Morphological changes suggest that the grafting reaction onto starch backbone take place.

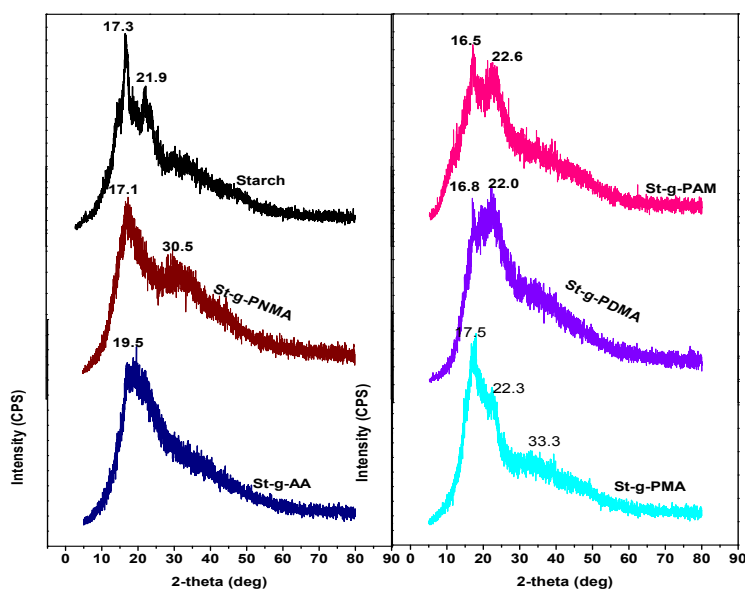


Figure 3 X-ray diffraction plots of starch, St-g-PAM, St-g-PDMA, St-g-PNMA, St-g-PAA and St-g-PMA.

5. Conclusion

It is concluded that the graft copolymers of St-g-PAM, St-g-PNMA, St-g-PDMA, St-g-PAA and St-g-PMA were successfully synthesized by solid phase polymerization technique. Different characterization techniques suggest the grafting reaction occurred on starch backbone.

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References

1. Singh RP, Karmakar GP, Rath SK, Karmakar NC, Pandey SR, Tripathy T, Panda J, Karmakar K, Jain S K, Lan NT. Biodegradable Drag Reducing –Agents and Flocculants Based on Polysaccharides: Materials and Applications, Polym Eng Sci. 2000, 40:46-60

2. Kolya H, Pal S, Pandey A, Tripathy T. Preparation of gold nanoparticles by a novel biodegradable graft copolymer sodium alginate-g-poly (N,N-dimethylacrylamide-co- acrylic acid) with anti micro bacterial application, *Eur Polym J*, 2015, 66:139-148
3. Dao V H, Cameron NR, Saito K. Synthesis, properties and performance of organic polymers employed in flocculation applications, *Polym Chem*. 2016, 7:11-25
4. Liu Y, Liu Z, Zhang Y, Deng K. Graft copolymerization of Methyl acrylate onto Chitosan initiated by Potassium diperiodateonickelate (IV) , *J Macromol Sci Part A*, 2002, A 39 (1 &2):129-143
5. Mino G, Kaizerman SA. A new method for the preparation of graft copolymers. Polymerization initiated by ceric ion redox system, *J Polym Sci.*, 1958, 31:242-243
6. Wang M, Xu L, Zhai M, Li Peng J, Wei JG. γ -ray radiation-induced synthesis and Fe(III) ion adsorption of carboxymethylated chitosan hydrogels, *Carbohydr Polym*, 2008, 74:498-503
7. Singh V, Tiwari A, Tripathy DN, Sanghai R, Microwave enhanced synthesis of chitosan-*graft*-polyacrylamide, *Polymer*, 2006, 47:254-260
8. Duke FR, Bremer RF. The Theory and Kinetics of Specific Oxidation. IV. The Cerate 2,3-Butanediol Reactions in Perchlorate Solutions, *J. Am. Chem. Soc.* 1951, 73:5179-5181
9. Kolya H, Sasmal D, Tripathy T, Novel Biodegradable Flocculating Agents Based on Grafted Starch Family for the Industrial Effluent Treatment, *J Polym Environ*, 2016, (In press) DOI: 10.1007/s10924-016-0825-0
10. Sasmal D, Kolya H, Tripathy T. Amylopectin-g-poly(methylacrylate-co-sodium acrylate): An efficient Cd(II) binder, *Int J Biol Macromolec.* 2016, 91:934-945
11. Sasmal D, Singh RP, Tripathy T. Synthesis and flocculation characteristics of a novel biodegradable flocculating agent amylopectin-g-poly(acrylamide-co-N-methylacrylamide) *Colloids and Surface A: Physiochem. Eng. Aspects.* 2015, 482:575-584
12. Kolya H, Tripathy T. Metal complexation studies of amylopectin-graft-poly[(N,N-dimethylacrylamide)-co-(acrylic acid)]: a biodegradable synthetic graft copolymer, *Polym. Int.* 2015; 64, 1336-1351
13. Kolya H, Tripathy T. Grafted Polysaccharides Based on Acrylamide and N,N-Dimethylacrylamide: Preparation and Investigation of Their Flocculation Performances, *J. Appl. Polym. Sci.* 2013, 127:2786-2795
14. Kolya H, Das S, Tripathy T. Synthesis of Starch-g-Poly-(N-methylacrylamide-co-acrylic acid) and its application for the removal of mercury (II) from aqueous solution by adsorption, *Eur. Polym. J.* 2014, 58:1-10