

Role and Relevance of Polarity and Hindrance of Vinyl Monomers in Graft Copolymerization onto Potato Starch

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ABSTRACT: The graft copolymerization of the vinyl monomers that were prepared by reactions of methyl acrylate and 4-aminoazobenzene derivatives, such as 4-aminoazobenzene, 4-amino-4'-methyl azobenzene, 4-amino-4'-nitro azobenzene, and 4-amino-3',5'-dinitro azobenzene, onto potato starch were carried out by the initiation of potassium persulfate. The evidence of grafted copolymers was investigated by using FTIR spectroscopy and acid hydrolysis technique. The relationship between grafting efficiency and monomer structure as well as polarity was studied. The experimental results showed that the graft copolymerization is independent of the polarity of the vinyl monomers and that the structures of monomers exhibit a marked influence on the graft copolymerization, namely, the larger the substitute is, the lower the grafting efficiency will be. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 896–899, 2002

Key words: graft copolymerization; potato starch; polarity; spatial hindrance; *p*-acryloazoanilide derivatives

INTRODUCTION

A literature survey on graft copolymerization of vinyl monomers onto starch reveals that most of the articles, in general, deal with the synthesis of the starch graft copolymer involving the study of the effect of reaction variables, such as monomer and initiator concentrations, period, and temperature, on grafting.^{1,2} However, only a few articles emphasized the relationship between monomer structure and grafting efficiency. At present, two views conflict with each other. Reyes et al.,³ in their study of graft copolymerization of vinyl monomers in aqueous medium using ceric ammonium nitrate (CAN) as initiator, reported that the grafting efficiency decreases with the decrease in polarity, in the order of: acrylonitrile > acrylic acid > methyl methacrylate > vinyl acetate > styrene. Misra et al.⁴ initiated graft copolymer-

ization of acrylonitrile and methyl acrylate onto starch, employing benzoyl peroxide in aqueous medium, and reported that the former shows higher grafting efficiency than the latter; they attributed it to the higher polarity and solubility of acrylonitrile over methyl acrylate. Zhuo et al.⁵ carried out the graft copolymerization of vinyl monomers such as acrylonitrile, methyl acrylate, methyl methacrylate, butyl acrylate, and butyl methacrylate onto granular corn starch by the initiation of CAN. The experimental results showed that the structure of monomers exhibited a marked influence on the graft copolymerization; the grafting efficiency can be enhanced by using a monomer with less spatial hindrance and stronger polarity. In stark contrast, Athawale and Rathi⁶ reexamined the relevance of polarity and solubility of vinyl monomers in graft polymerization onto starch, employing a wide spectrum of vinyl monomers, and concluded that the graft polymerization is independent of the polarity and solubility of the vinyl monomer and that no interrelation exists between the grafting ability of a vi-

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Table I Graft Copolymerization of Vinyl Monomers onto Starch in Inverse Emulsion

Graft Monomer	Abbreviation	<i>G</i> (%)	<i>GE</i> (%)
$\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{CH}_3$	AMAM	45.66	83.23
$\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_5$	ADAM	53.00	85.50
$\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{NO}_2$	ANAM	41.45	81.33
$\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_3(\text{NO}_2)_2$	ADNAM	37.08	78.85

nyl monomer and its polarity and solubility. In the case of *n*-alkyl acrylates and methacrylates, as the length of the *n*-alkyl group increases, the grafting percentage and homopolymer content decrease, due to their increase in steric hindrance. Thus, the question arose as to whether any relation really exists between the polarity of monomer and its ability toward grafting. Hence, in the present study, an attempt was made to investigate the same by synthesis of *p*-acryloazoanilide derivatives grafted onto potato starch copolymers, having the potential utilization in heavy metal ions removal and the industries of paper or textile manufacturing.

EXPERIMENTAL

Materials and Methods

Potato starch (AGU) was purchased from Yellow River Beer Co. Ltd. (China). It was dried at 60°C for 20 h before use. The graft monomers (see Table I) were prepared by referring to Kozul et al.'s method⁷ and run with methyl acrylate and *p*-aminoazobenzene derivatives in glacial acetic acid. All the chemicals used were analytical reagent grades.

Graft Copolymerization in Inverse Emulsion⁸

The reactions were carried out in 250-mL three-neck flasks equipped with a stirrer and condenser and immersed into a thermostat water bath. The N₂ gas was purged into the flask to remove the presence of oxygen during the operation. The starch slurry prepared from 2.00 g AGU and 60 mL distilled water was preheated at 90°C for about 45 min with stirring. After it was gelatinized, the flask contents were cooled to room tem-

perature, and then 80 mL paraffin liquid and 1.00 g Span-80 were added to the reaction mixture. The reaction mixture was mixed homogeneously and then heated slowly to 50°C; the required amount of monomer and 0.5M K₂S₂O₈ solution (1.35 g K₂S₂O₈ dissolved in 50 mL 0.5M NaOH) was added and the mixture was stirred for 3 h. When the reaction was complete, the product was cooled and poured into 200 mL ethanol to induce precipitation. The graft products were washed three times with ethanol/water (4 : 1) and then the products were oven dried at 50°C to constant weight.

Extraction of Homopolymer and Determination of Graft Level

The above crude products were extracted with benzene in a Soxhlets extractor for 24 h to remove homopolymer, and pure copolymers were then dried at 50°C to constant weight.

The percentage of grafting (*G*%) and grafting efficiency (*GE*%) were determined by the formula reported by Silong et al.¹:

Percentage of grafting

$$= \frac{\text{weight of grafting polymer}}{\text{weight of backbone}} \times 100$$

Grafting efficiency

$$= \frac{\text{weight of grafted polymer}}{\text{weight of grafted polymer} + \text{weight of homopolymer}} \times 100$$

EVIDENCE FOR GRAFTING

Infrared (IR) Spectroscopy

IR spectra of the grafted copolymers were recorded on a Fourier transform IR spectrometer

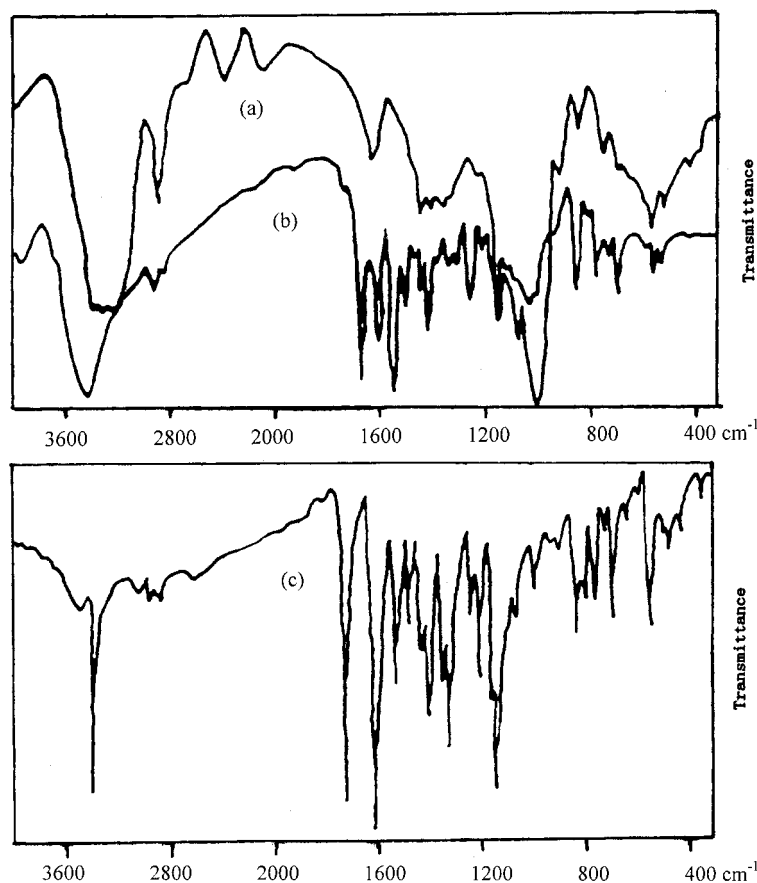


Figure 1 FTIR spectra of (a) potato starch; (b) poly(4-acryloazoanilide)-grafted potato starch; and (c) side-chain poly(4-acryloazoanilide).

(Perkin–Elmer 1725, Norwalk, CT), using KBr pellets for sample preparation.

Acid Hydrolysis

To separate the grafted polymer from the starch backbone, the grafted copolymer was subjected to acid hydrolysis. In the case of water-insoluble polymers, on refluxing the grafted polymer in 1*N* hydrochloric acid, the carbohydrate component was hydrolyzed, leaving behind the hydrophobic particles of the grafted polymer, the identity of which was confirmed by IR spectroscopy.

RESULTS AND DISCUSSION

IR Spectroscopy

IR spectrum of AGU is shown in Figure 1(a); it indicates the characteristic absorption bands of starch at 3430 and 1652 cm^{-1} due to O—H stretching and bending modes, respectively. Additional characteristic adsorption bands of AGU

appear at 2932 and 1014 cm^{-1} due to C—H stretching and bending, respectively. IR spectrum of purified poly(4-acryloazoanilide)-grafted AGU shows a new characteristic absorption band at 1667 cm^{-1} of C=O stretching mode in addition to the same absorption bands of starch, as shown in Figure 1(b). The spectrum of the side-chain polymer was similar to the spectrum of 4-acryloazoanilide, as shown in Figure 1(c).

The IR spectrum of the other three polymers were omitted because their peaks are similar to the IR spectrum of starch-grafted poly(4-acryloazoanilide) and the functional groups' adsorption bands such as —NO₂ and —CH₃ are overlapped with the characteristic peaks of starch. However, their formation was confirmed by the acid hydrolysis technique.

Effect of Polarity and Hindrance of Monomers on Grafting

Of the various vinyl monomers used in the present work, ADNAM and ANAM were the most

polar monomers and AMAM was the least polar with ADAM having polarity in between the two extremes. All the four monomers are water insoluble, so their solubility has no need to be considered.

Table I lists the results of the various vinyl monomers under the experimental conditions described above.

Based on the earlier assumptions³⁻⁵ that the more polar the monomer is, the more its grafting on starch will be, it was expected that ADNAM will show the highest grafting efficiency, followed by the other vinyl monomers, and AMAM will show the least grafting efficiency, in consonance with their polarity. However, a study of Table I reveals that no such trend is observed.

AMAM and ADAM, having a negligibly small difference in polarity, show a wide difference in the $G\%$ value, which attributed that AMAM exerts more hindrance effect on graft polymerization than ADAM does. This is further confirmed by the fact that ADNAM, a highly polar monomer, shows lower $G\%$. Thus, it can be said that there does not necessarily exist any specific relation between the polarity of the monomer and its grafting onto starch. However, the structure of vinyl monomers exhibit a marked influence on the graft polymerization.

CONCLUSION

The graft copolymerization is independent of the polarity of the vinyl monomers. However, interrelation exists between the grafting ability of a vinyl monomer and its stereo structure that the larger the substitute is, the lower the $GE\%$ will be.

REFERENCES

1. Rahman, L.; Silong, S.; Zin, W. D.; Rahman, M.; Ahmad, A.; Haron, J. *J Appl Polym Sci* 2000, 76, 516–523.
2. Wang, Y.; Yang, W.; Cui, D. *Gaofenzi Xuebao* 1996, 1, 111–115.
3. Reyes, Z.; Rist, C. E.; Russell, C. R. *J Polym Sci, Part A: Polym Chem* 1966, 4 (5), 1031–1043.
4. Misra, B. N.; Dogra, R.; Kaur, I.; Sood, D. S. *Indian J Chem, Sect A* 1979, 17 (4), 390–392.
5. Zhuo, R. X.; Huang, L.; Zhu, Z. F. *J Wuhan Univ (Natural Sci ed.)* 1998, 44, 163–166.
6. Athawale, V. D.; Rathi, S. C. *React Funct Polym* 1997, 34, 11–17.
7. Kozul, M.; Stiplosek, Z.; Kojic, J.; Orhanovic, Z. *Synth Commun* 1997, 27 (21), 3711–3722.
8. Lu, S. J.; Liu, R. X.; Wei, N. Q.; Yang, G. Z.; Liu, H. B. *J Qiqihar Light Ind Inst* 1997, 13 (2), 5–8.