

# Graft Copolymerization of Acrylonitrile onto Poly(Vinyl Alcohol) in Presence of Air Using Ceric Ammonium Nitrate-Natural Gums

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**ABSTRACT:** In an attempt to overcome the problem of polymerization of vinyl monomers in presence of oxygen, polymerization was done by using some plant gums. The effect of some plant gums were studied on the graft copolymerization of acrylonitrile (AN) on to poly(vinyl alcohol) using ceric ammonium nitrate (CAN) as initiator in presence of air. Percent of grafting was determined as a function of nitric acid, concentration of monomer, time, and temperature. The rate of polymerization and maximum grafting (151%) were high compared with those in absence of the gum both in air or even in an inert atmosphere. Thus, it was definitely observed that the graft copolymerization is affected by the gum. From the differential scanning calorimetric (DSC) studies the glass-transition temperature  $T_g$  of polyacrylonitrile (PAN) is found to be 56°C. Thermal stabilities were checked by thermogravimetric analysis (TGA) and this indicated that the grafted copolymers were resistant to moisture absorption. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1586–1590, 2000

**Key words:** graft copolymerization; ceric(IV) initiation; plant gum; aqueous medium in air

## INTRODUCTION

Graft reaction is usually carried out in aqueous solution either with free radical producing initiator or with ionic catalysts. A wide range of monomers has been successfully grafted to poly(vinyl alcohol) (PVA) in aqueous solution.<sup>1–5</sup> Because water<sup>6</sup> is known to be the only solvent where PVA can be dissolved, grafting has been done in aqueous medium so far. The monomer and the initiator must be soluble in water to achieve grafting on PVA. The discovery of Mino and Kaizerman<sup>7</sup> and

other workers<sup>8,9</sup> has shown that ceric ion is capable of forming redox system with alcohol, and a number of polyhydroxy compounds such as starch,<sup>10,11</sup> cellulose,<sup>12</sup> and PVA have been grafted copolymerized with a number of vinyl monomers by employing the ceric ion technique. Japanese workers<sup>13</sup> used a novel initiator system comprising  $\text{LiBr}-\text{S}_2\text{O}_8^{2-}$  without homopolymer formation. Onescu et al.<sup>14</sup> prepared acrylic fiber in presence of  $\text{K}_2\text{S}_2\text{O}_8$  and  $\text{Na}_2\text{S}_2\text{O}_3$  at 70°C. Misra and coworkers<sup>15</sup> used fenton's reagent. Ion et al.<sup>16</sup> were able to achieve copolymerization including acrylonitrile and vinyl acetate with  $\text{K}_2\text{S}_2\text{O}_8-\text{NaHSO}_3$  initiator at 60°C. Qui<sup>17</sup> selected macromolecules such as poly(ether-urethane) and ceric ion graft reaction. However

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greater amount of  $O_2$  is dissolved in aqueous medium in vinyl polymerization, where oxygen acts as retarder initiator. Most polymerization reactions are commonly carried out in an inert atmosphere to meet out the problem of retardation by atmospheric oxygen. We have solved this problem of oxygen removal and identified a redox-pair, ceric ammonium nitrate-natural gums that helps graft reaction onto the PVA in aqueous medium and in airy atmosphere.

## EXPERIMENTAL

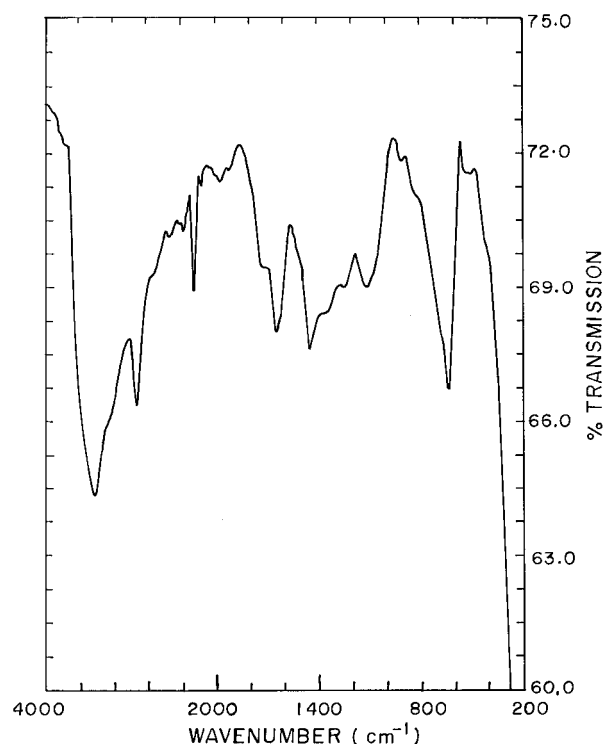
### Materials

PVA white crystalline solid was obtained from British Drug House (BDH, reagent grade) having viscosity average molecular weight of 14 000 and contained 1% of residual PVA. Acrylonitrile (AN), ceric ammonium nitrate (CAN) (Merck), dimethyl formamide (DMF), were purified according to the usual procedures.<sup>18</sup>  $HNO_3$  (BDH) was of analytical grade and used without further purification.

Raw plant gums were collected from the stems of *Moringa Olefera* (Sajina) from different locality and dried in vacuum at 40°C. The detail composition and structure have already been reported.<sup>19,20</sup> The acetone extract of the gum was dried under vacuum and the dried powder was used for polymerization processes.

### Graft Copolymerization

PVA, 0.44 g (0.01 mol based on  $(-CH-CH(OH)-)$  as the repeated unit) was dissolved in 48 mL of a distilled water in a 100-mL conical flask and a measured amount of AN from a stock solution was taken to it. The flask was sealed with addition of the gum. Next, 2 mL aqueous CAN solution of specified concentration was injected into the flask. The flask was placed in the center of two tube lights (220 V-40 W, Philips India Ltd.) separating 12 cm. The induction periods for polymerization were noted by observing the appearance of the white turbidity. After requisite time intervals the precipitated polymer was filtered in a grouch crucible and washed with hot water and then dried under vacuum at 60°C. The product was purified by soxhleting with DMF. The final product was isolated and dried till constant. The above process was also repeated for the different molar ratio of PVA/AN, temperature, and acid concentration. Percent grafting and



**Figure 1** Infrared (IR) spectra of graft copolymer of polyvinyl alcohol-acrylonitrile.

percent efficiency were determined in the following manner.

$$\% \text{ Grafting} = \frac{w_2 - w_1}{w_1} \times 100$$

$$\% \text{ Efficiency} = \frac{w_2 - w_1}{w_3} \times 100$$

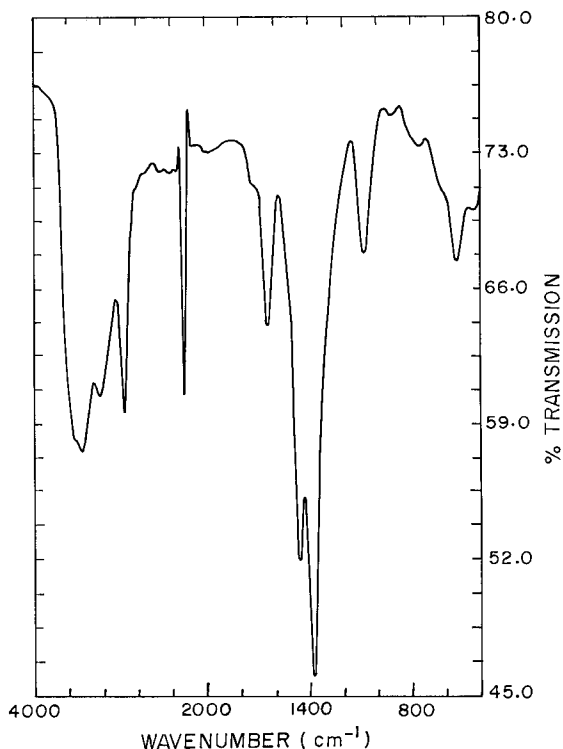
Where  $w_1$ ,  $w_2$ , and  $w_3$  denote respectively the weight of PVA, grafted PVA-g-AN after solvent extraction, and weight of monomer added.

## RESULTS AND DISCUSSION

### Evidence of Grafting

#### Gravimetric Estimation

The graft copolymerization was followed gravimetrically. The increase in the weight of the residue for each copolymerization, compared with control reaction, confirms the occurrence of grafting. The control reaction was carried out with



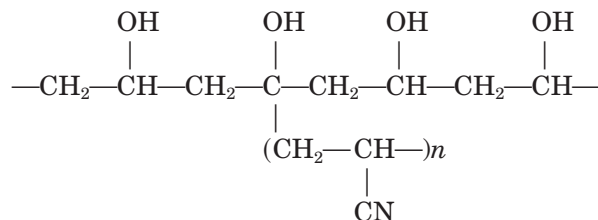
**Figure 2** Infrared spectra of graft polyacrylonitrile (PAN).

.44 g of PVA using  $0.45 \times 10^{-2} \text{ mol/L}^{-1}$  CAN at  $28^\circ\text{C}$  for 120 min.

### Spectroscopic Analysis

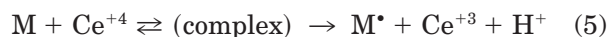
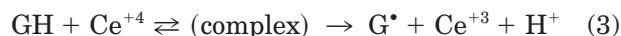
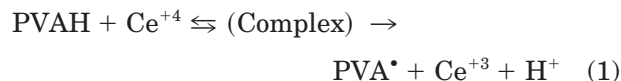
The IR spectra of grafted copolymer PVA-g-AN along with PVA is studied. The characteristic absorption band at  $2260 \text{ cm}^{-1}$  due to CN group and a broad band at  $3424 \text{ cm}^{-1}$  are due to the hydroxyl group in PVA in the polymer, confirmed the formation of PVA-g-AN (Figs. 1 and 2).

The structure of PVA-g-AN is presented as follows<sup>21</sup>:



A mechanism for grafting of AN onto PVA is proposed by the complex formation between PVAH and ceric ion. The complex then decomposes to generate the macroradical (PNA), which

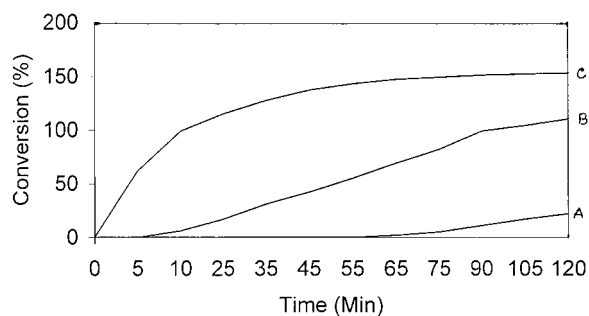
then reacts with monomer to produce grafts. The gum (GH) also forms a complex with ceric ion and its decomposition gives sufficient amount of monomer radicals that promoted the grafting reaction.



The gums contain pyrogallol derivative<sup>22</sup> that can easily form a complex with  $\text{Ce}^{+4}$  ion, which on decomposition forms macro free radicals. Therefore grafting reaction of AN onto the gum may be avoided.

### Effect of $[\text{H}^+]$ ion on Graft Copolymerization

The initiation with ceric ion in the graft copolymerization depends very much on the  $[\text{H}^+]$  of the system<sup>23</sup> and a weakly acidic system is usually used. Saldick,<sup>24</sup> and Ananthanarayanan and Santappa<sup>25</sup> carried out the polymerization of vinyl monomers by ceric ion in several acidic medium and observed that the rate of polymerization varies with the kind of acid used. Kabota and Ogiwara<sup>26</sup> showed that the maximum grafting is ef-



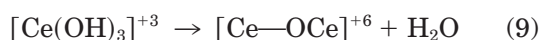
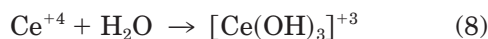
**Figure 3**

**Table I Effect of Monomer on the Grafting of AN on to PVA**

PVA (g)	AN (mol)	% of Grafting	Graft Efficiency (%)
0.44	0.112	46.6	28.1
0.44	0.2	48.8	34.4
0.44	0.4	93.6	36.9
0.44	0.6	151.6	37.7
0.44	0.7	164.1	34.02

[Gum] = 0.2 (%); [CAN] = 0.45 mol · L<sup>-1</sup>; Temp. = 300C; Time = 90 (min)

ected by the kind of acid and is increased in the order HNO<sub>3</sub> > HCL > H<sub>2</sub>SO<sub>4</sub>. The effect of H<sup>+</sup> ion on the course of polymerization has been studied by the of nitric acid (HNO<sub>3</sub>) in the range of 1.4 × 10<sup>-2</sup> to 14.6 × 10<sup>-2</sup> mol/L<sup>-1</sup>. It was observed that when H ion was kept below 1.4 × 10<sup>-2</sup> mol/L<sup>-1</sup> no characteristic polymerization occurs. This is explained by the fact that ceric ion in water is believed to react in the following manner:



Thus, ceric ion exists as Ce<sup>+4</sup>, [Ce(OH)<sub>3</sub>]<sup>+3</sup>, and [Ce—O—Ce]<sup>+6</sup> in water solution. The observed zero polymerization at zero nitric acid concentration indicates the inability of [Ce—O—Ce]<sup>+6</sup> to form a complex with monomer. The increase observed is well explained as the function of [H<sup>+</sup>]. With increasing nitric acid concentration in the range of (14–14.6) × 10<sup>-2</sup> mol/L<sup>-1</sup>, the equilibria (eq. 8) and (eq. 9) moderately shift toward forma-

tion of Ce<sup>+4</sup> and [Ce(OH)<sub>3</sub>]<sup>+3</sup>, thereby facilitating the radical generation steps. But on increasing [H<sup>+</sup>] beyond 14.6 × 10<sup>-2</sup> mol/L<sup>-1</sup> the rate of formation of Ce<sup>+4</sup> and [Ce(OH)<sub>3</sub>]<sup>+3</sup> increases, which may be confirmed by an orange-colored solution formation. These species at higher concentration affect polymerization efficiency adversely by termination of growing propagated chain. Similar observations have been reported by Misra et al.<sup>27</sup> who observed that methyl methacrylate and acrylic acid would be grafted to wool.

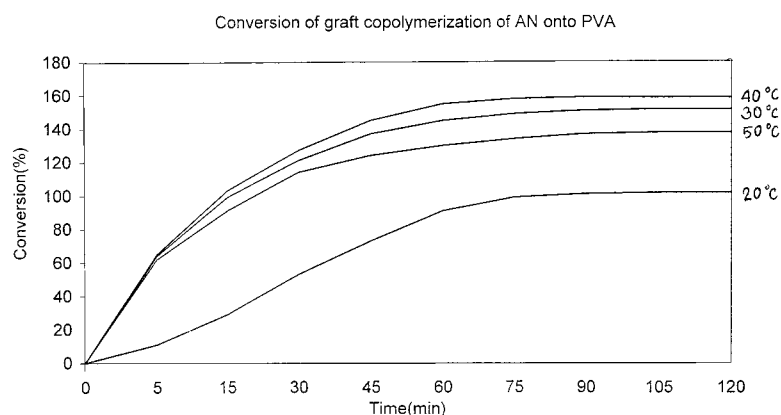
In the kinetic study of aqueous graft copolymerization of AN onto PVA it is found that the rate of copolymerization was remarkable high in the presence of the gum compared with those in absence of the gum both in air or even in an inert atmosphere in Figure 3. It indicates that the gum not only acts as an oxygen scavenger but also as an accelerator for the free radical generation.

#### Effect of Monomer Concentration on Graft Copolymerization

It is observed that with the increase in monomer concentration the percent grafting increases to give a maximum grafting of 151%. Further increase in monomer concentration the percent grafting essentially remain constant (Table I).

#### Effect of Temperature

Grafting of AN onto PVA was carried out at 20, 30, 40, and 50°C. It is apparent from Figure 4 afforded maximum grafting at 40°C. Further increase in temperature decreased the percent grafting. This indicates that at higher temperature, termination of grafted chain growth by process (eq. 7) may be responsible for the decrease in percent grafting.

**Figure 4**

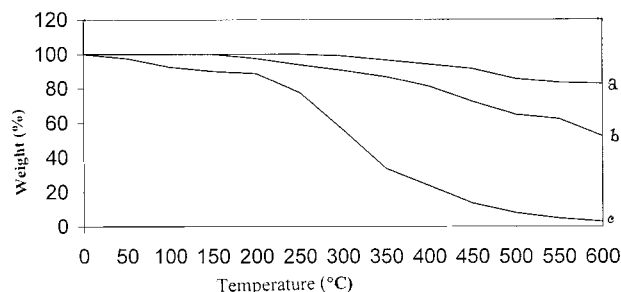


Figure 5

### Thermal Behavior

The thermal behavior of PVA-g-AN prepared with and without gum was studied by thermogravimetric analysis (TGA) (Fig. 5). The TGA curve of PVA had an inflexion between 100–135°C due to the removal of absorbed moisture. No such inflexions were observed in the TG curve of PVA-g-AN. This indicated that the grafted copolymer was resistant to moisture absorption. The resistance to absorb moisture of the graft copolymer was also examined in the following way. Accurately weighted 0.5 g of the graft copolymers was kept in a desiccator for 2 weeks and then the sample was weighted accurately. This operation was carried out once again after keeping the sample outside the desiccator for another 2 weeks. The weight of that compound was found to be same as taken initially. It was observed that the graft copolymer decomposed in two stages.<sup>28</sup> At a particular temperature the percent weight loss of PVA-g-AN prepared with the gum in air atmosphere is less than that of PVA-g-AN prepared without gum in N<sub>2</sub> atmosphere. The char residue at 600°C is also higher for PVA-g-AN obtained with the gum. Therefore, PVA-g-AN obtained with the gum is more thermostable than that obtained without the gum. The more thermostable PVA-g-AN polymer obtained with the gum to its higher molecular weight, stereoregularity, and crystallinity.<sup>29</sup>

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