

Water-soluble and amphiphilic polymers

11. Graft polymerization of acrylic acid on poly(vinyl alcohol)

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SUMMARY

The graft polymerization of acrylic acid (AA) on poly(vinyl alcohol) (PVAL) has been investigated by using either potassium persulfate (KPS) or ceric ammonium nitrate (CAN) as an initiator. In the case of KPS initiation, the formation of the graft polymer always lags behind the homopolymer formation. The graft polymer is separated by acetone, and the increase of reaction temperature favors the homopolymer formation at the early stage. In the case of CAN initiation, graft polymers with a high PAA content can hardly be obtained when the polymerization is performed under nitrogen and at < 0.06 mol/L HNO_3 concentration. It has been found that incorporation of a small amount of oxygen in a protective nitrogen gas accelerates markedly the graft polymerization, and that the resulting graft polymers can not be separated by acetone precipitation technique in most cases. The Dalian nitrogen (containing 0.7% oxygen) is a good protective gas for CAN-initiated PVAL-AA graft polymerization.

INTRODUCTION

Although ceric ion-induced graft polymerization of hydroxyl-containing polymers was first discovered by Mino and Kaizerman in 1958 by using poly(vinyl alcohol) (PVAL) as a substrate (1), most work in recent years, however, has been focused on the modification of starch or cellulose (2–8). Also, there is little information about persulfate-initiated graft polymerization of acrylic acid (AA) on hydroxyl-containing polymers (9). In this work, we intend to compare the graft polymerization behaviors of AA on PVAL initiated by potassium persulfate (KPS) and ceric ammonium nitrate (CAN), and some new observations are reported.

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EXPERIMENTAL

Materials—Poly(vinyl alcohol) (\overline{DP} = 1750, fully hydrolyzed) was extracted with acetone and dried in vacuum before use. AA was purified by reduced—pressure distillation. KPS, CAN, nitric acid, and acetone were reagent grade and used as received.

Graft polymerization—PVAL—AA graft polymerization was carried out in a 500 mL flask equipped with a mechanical stirrer and a condenser. In a typical graft polymerization, 3.0 g PVAL was dissolved in 90 mL doubly—distilled water at 80—90°C. After cooling down to room temperature and adding 3.0 g AA, the reaction mixture was purged with nitrogen for 30 min, equilibrated to certain reaction temperature in a thermostat, and then 10 mL of an initiator solution (0.02 mol/L KPS aqueous solution or 0.03 mol/L CAN solution in 0.1 mol/L HNO₃) purged with nitrogen was introduced to start the polymerization. The reactions were performed under a slight positive pressure of nitrogen. In KPS—initiated polymerization, only Fushun high purity nitrogen (99.999%, according to the manufacturer) was used as the protective gas, while nitrogen gases used in CAN—initiated graft polymerization were Fushun nitrogen, Dalian nitrogen (containing 0.7% oxygen), and nitrogen gases with a controlled amount of oxygen, which were obtained by mixing Fushun nitrogen and air.

Measurements— Following expressions were used for calculation:

$$\text{total conversion}(\%) = \frac{\text{total weight of AA polymer}}{\text{weight of used AA monomer}} \times 100\%$$

$$\text{grafted PAA}(\%) = \frac{\text{weight of grafted PAA}}{\text{weight of used AA monomer}} \times 100\%$$

$$\text{grafting efficiency}(\%) = \frac{\text{weight of grafted PAA}}{\text{total weight of AA polymer}} \times 100\%$$

The total conversion was obtained by titrating the unreacted monomer, similar to Sigga's procedure for determination of unsaturated compounds (10). Acetone precipitation was used to separate AA homopolymer. According to Mukhopadhyay et al. (11), AA homopolymer is not precipitated by acetone, and the precipitate is the graft polymer along with PVAL homopolymer. When this separation procedure was feasible, the grafted PAA was measured by acid—base titration of aqueous solutions of the

precipitates.

RESULTS AND DISCUSSION

Figure 1 shows typical results of PVAL-AA graft polymerization when Fushun nitrogen was used as a protective gas. Although both KPS (9,12) and CAN may be used to initiate graft polymerization of hydroxyl-containing polymers, the polymerization behaviors are quite different in PVAL-AA system.

In the case of KPS initiation, monomer conversion increases with reaction time, just similar to KPS-initiated homopolymerization of AA in absence of PVAL. Homo-PAA can easily be separated from the graft polymer and unreacted PVAL by acetone precipitation. It is of special interest to note that the formation of graft polymers always lags behind the homo-PAA formation. As depicted in Figure 2, homopolymerization is predominant at the early stage, the graft polymer is still not detectable when monomer conversion reaches about 20%, beyond which the process

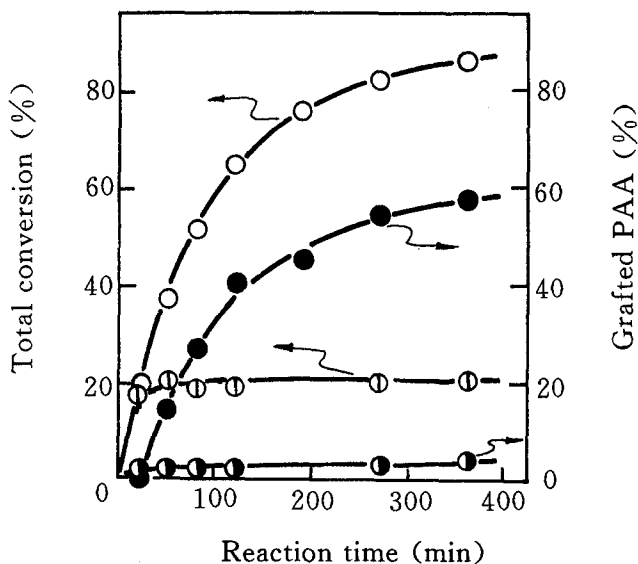


Figure 1. Variation of total monomer conversion and grafted PAA with reaction time (high purity Fushun nitrogen; $[PVAL]=30$ g/L; $[AA]=30$ g/L)
 ○ ● —KPS initiation, $[KPS]=2 \times 10^{-3}$ mol/L, Temp. = 45°C
 ⊙ ● —CAN initiation, $[CAN]=3 \times 10^{-3}$ mol/L
 $[HNO_3]=0.01$ mol/L, Temp. = 35°C

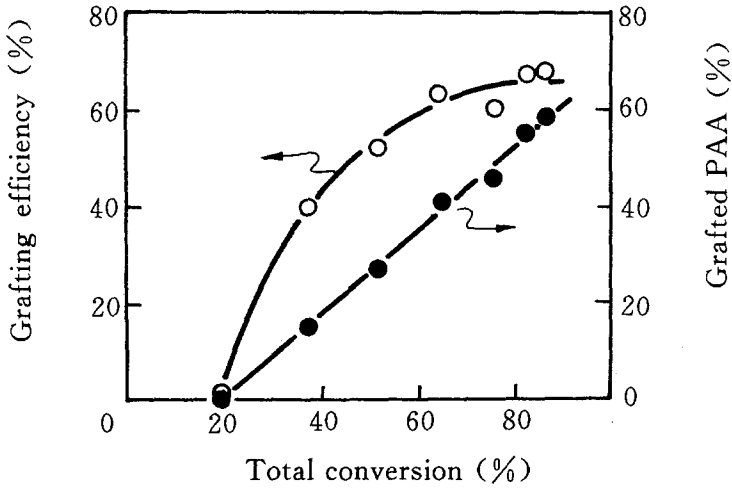


Figure 2. Dependence of grafting efficiency and grafted PAA on total monomer conversion
 ([KPS] = 2×10^{-3} mol/L; [PVAL] = 30 g/L; [AA] = 30 g/L; Temp. = 45°C)

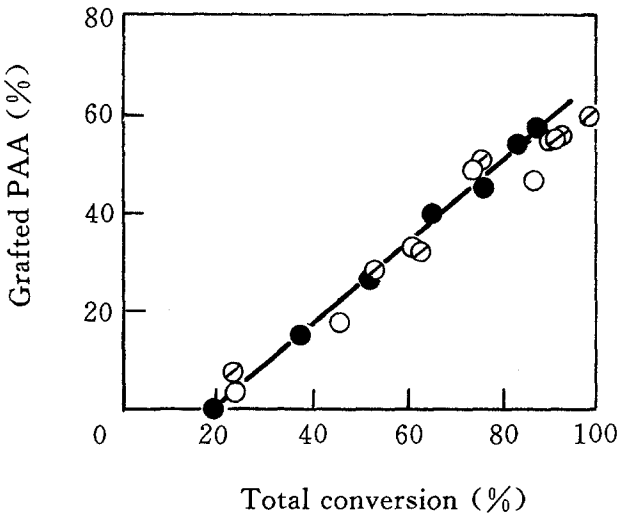


Figure 3. Effect of KPS concentration on PVAL-AA graft polymerization
 ([AA] = 30 g/L; [PVAL] = 30 g/L; Temp. = 45 °C)
 KPS concentration: ● 2×10^{-3} mol/L
 ○ 4×10^{-3} mol/L; ⊗ 6×10^{-3} mol/L

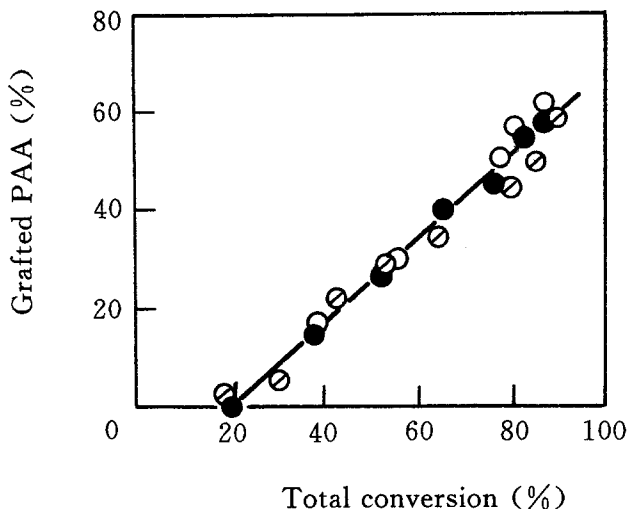


Figure 4. Effect of PVAL/AA ratio on KPS-initiated PVAL-AA graft polymerization ($[KPS]=2 \times 10^{-3}$ mol/L; $[AA]=30$ g/L; Temp. = 45°C)
 PVAL/AA: ● 1/1; ◐ 2/1; ○ 3/1

is mainly governed by graft polymer formation.

Figure 3 and 4 show the effects of KPS concentration and PVAL/AA ratio on the relationship between grafted PAA and total monomer conversion, respectively. It can be seen that there was little, if any, influence of initiator concentration and PVAL/AA ratio on the grafting efficiency. On the other hand, reaction temperature is an important factor affecting the PVAL-AA graft polymerization. As shown in Figure 5, total monomer conversion reaches 73.1% after 20 min reaction at 75°C , while grafted PAA is only 19.4%, indicating that increasing reaction temperature favors the homopolymer formation at the early stage.

For CAN-initiated PVAL-AA graft polymerization under Fushun high purity nitrogen, monomer conversion goes to a maximum value at 20 min, which is only about 20%, and then levels off, as shown in Figure 1. Grafted PAA is also very low. Figure 6 (curve 1) shows the effect of nitric acid concentration on total monomer conversion. It can be seen that the monomer conversion is always relatively low in the lower acid concentration region (<0.06 mol/L), and then increases with the further increase of acid concentration. It seems that graft polymers with a high PAA content can hardly be obtained when the graft polymerization is carried out under nitrogen and at <0.06 mol/L HNO_3 concentration.

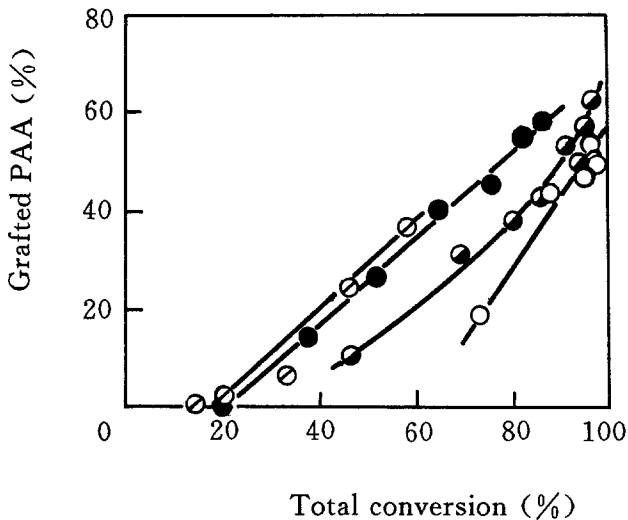


Figure 5. Effect of reaction temperature on KPS-initiated PVAL-AA graft polymerization ($[KPS]=2 \times 10^{-3}$ mol/L; $[PVAL]=30$ g/L; $[AA]=30$ g/L)
 ○ -30°C ; ● -45°C ; ◐ -60°C ; ○ -75°C

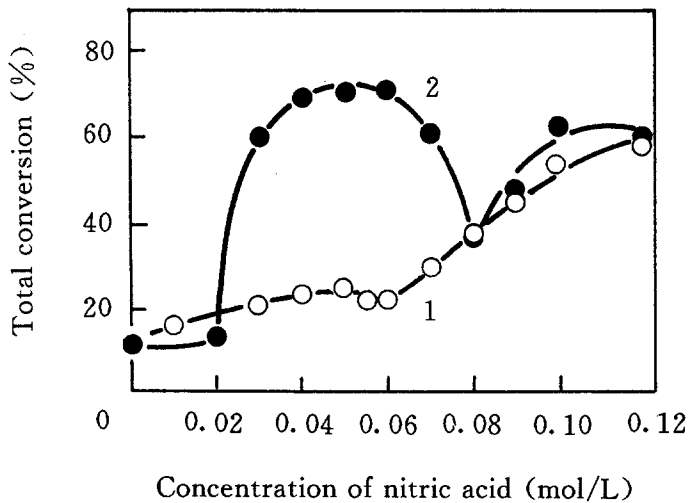


Figure 6. Effect of a protective gas on the ceric ion-initiated PVAL-AA graft polymerization ($[CAN]=2 \times 10^{-3}$ mol/L; $[PVAL]=30$ g/L; $[AA]=30$ g/L; Temp. = 35°C ; Time = 2 hrs)
 1—Fushun nitrogen; 2—Dalian nitrogen

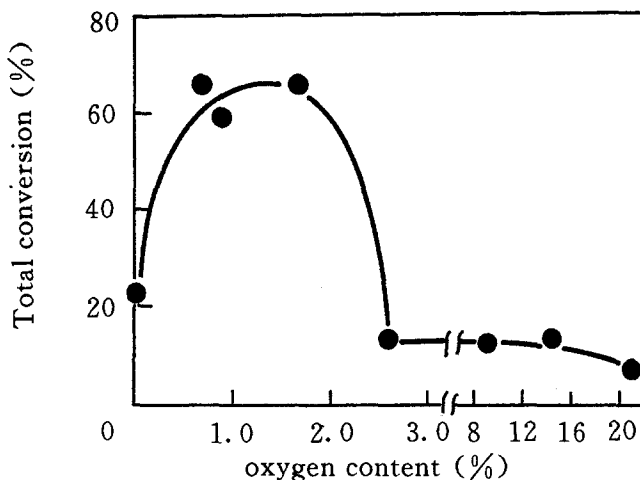


Figure 7. Effect of oxygen content in the protective gas on PVAL-AA graft polymerization
 ($[\text{CAN}] = 2 \times 10^{-3}$ mol/L; $[\text{HNO}_3] = 0.04$ mol/L; $[\text{PVAL}] = 30$ g/L
 $[\text{AA}] = 30$ g/L; Temp. = 35°C ; Time = 2 hrs)

Interestingly, the graft polymerization is greatly accelerated at the acid concentration of 0.03–0.07 mol/L when the Dalian nitrogen (containing 0.7% oxygen) is used as a protective gas, as shown in Figure 6 (curve 2). Unlike the graft polymers obtained by persulfate initiation, however, the resulting graft polymer can not be separated by acetone precipitation in most cases. Acetone solutions were apparently turbid. The weight of the precipitate was often less than that of PVAL added. The precipitate was even hardly seen sometimes. Due to the difficulty of separation of graft polymers by acetone precipitation, it is not possible so far to obtain data of grafted PAA or grafting efficiency. The great change of solubility behavior indicates not only that the graft polymerization of AA on PVAL does occur, but also that the structure of the graft polymers obtained by CAN-initiated polymerization under Dalian nitrogen is different from that of PVAL-AA graft polymers synthesized by KPS initiation. The results also show that the Dalian nitrogen is a good protective gas for CAN-initiated PVAL-AA graft polymerization.

The fact of acceleration of PVAL-AA graft polymerization by the use of the Dalian nitrogen stimulated us to study the influence of oxygen content incorporated in a protective gas on the graft polymerization. As shown in Figure 7, the nitrogen with oxygen content in the range of 0.7–1.7% has the best effect on the PVAL-AA graft polymerization.

Some investigators found that grafting from cellulose with certain

monomers such as acrylonitrile under certain conditions was unaffected by the presence of oxygen(4). Generally speaking, however, the inclusion of air was found to cause a decrease in grafting yield due to the inhibiting effect of oxygen(4, 8). The reason why a small amount of oxygen in a protective nitrogen benefits the CAN—induced PVAL—AA graft polymerization is not clear. Further investigation is needed in order to elucidate the role played by the small amount of oxygen in the graft polymerization.

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