Graft Copolymerization of Water-Soluble Monomers Containing Quaternary Ammonium Group on Poly(Vinyl Alcohol) Using Ceric Ions

San-Yan Zheng, Zhi-Chun Chen, De-Shui Lu, Qi Wu, Xian-Fu Lin

Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China

ABSTRACT: Graft copolymerization of water-soluble monomers containing quaternary ammonium onto PVA was studied in an aqueous medium using ceric ammonium nitrate-nitric acid as the redox initiator. To optimize the reaction conditions for obtaining a maximum percent of grafting, the concentrations of methacryloxyethyl trimethylammonium chloride (DMC) monomer, ceric ammonium nitrate, and temperature were varied, and the effects on the grafting copolymerization were discussed. Under optimum conditions, a series of water-soluble monomers containing quaternary ammonium, such as methacryloxyethyl trimethylammonium chloride (DMC), DMAEMA·C_2H_5Br, DMAEMA·C_4H_9Br, DMAEMA·$C_{16}H_{33}Br$, and DMAEMA·C_7H_7Cl, were successfully grafted onto PVA. The resulting grafted PVA were characterized with IR, NMR, and viscosity measurements. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2186–2191, 2005

**Key words:** ceric ammonium nitrate; graft copolymerization; PVA; quaternary ammonium group; water-soluble monomer

INTRODUCTION

Poly(vinyl alcohol) (PVA) is the only polyvinyl-type synthetic polymer that has been confirmed to be biodegradable.[1] This feature and its water solubility imply the advantages of easier degradation and elimination. Due to its biocompatibility, PVA can be used for a variety of biomedical applications, preferably in the form of hydrogel. PVA has been chemically modified with different compounds, such as 10-undecenoyl chloride,[2] 2,3-epoxypropyltrimethylammonium chloride,[3,4] aldehydes,[5] carboxylic acid,[6] anhydrides,[7] and so forth. But the rate and extent of grafting by this method are usually low due to hindered diffusion of preformed polymers. Grafting of vinyl monomers onto natural polymers like guar gum,[8] starch,[9,10] and cellulose[11–14] by employing the ceric ion technique has been studied. Graft copolymerization is a powerful tool for obtaining polymers with new properties and applications. Graft copolymers are finding application in development of selective permeable membranes[15] and outstanding sorption agents and in fabrication of drug delivery systems. Above all, the method of graft copolymerization in comparison to the method of chemical modification can obtain higher graft yield. Among graft copolymerization methods, redox-initiated grafting offers advantages because, in the presence of redox systems, grafting can be carried out under milder conditions with minimum side reactions, but the graft yield is still very high. Although various monomers such as acrylonitrile,[16] butyl acrylate,[17] itaconic acid,[18] and so on have been used for PVA modifications, studies on graft copolymerization of water-soluble monomers containing quaternary ammonium groups onto PVA are not reported at present. The graft copolymerization of PVA with ammonium-containing monomers has attracted greater interest. PVA grafted by ammonium-containing monomers has a broad utility in many areas, for example, as a flocculating agent in water treatment, retention aids in the manufacture of mineral-filled paper, and effective clay or shale hydration inhibitors in oilfield treatment.

In this study, we attempted to prepare new water-soluble grafted PVA by grafting methacryloxyethyl trimethylammonium chloride (DMC) onto PVA in the presence of a HNO_3/CAN (ceric ammonium nitrate) initiation system. For this purpose, the effects of various factors, such as the initiator concentration, monomer concentration, and reaction temperature, on the grafting of DMC onto PVA were studied. Other monomers with ammonium-groups, such as DMAEMA·C_2H_5Br, DMAEMA·C_4H_9Br, DMAEMA·$C_{16}H_{33}Br$, and DMAEMA·C_7H_7Cl, were grafted onto PVA on the basis of the optimum reaction conditions of DMC grafted onto PVA, and the resulting grafted PVA were characterized with IR, NMR, and viscosity measurements.

Correspondence to: X. F. Lin (llc123@css.zju.edu.cn).
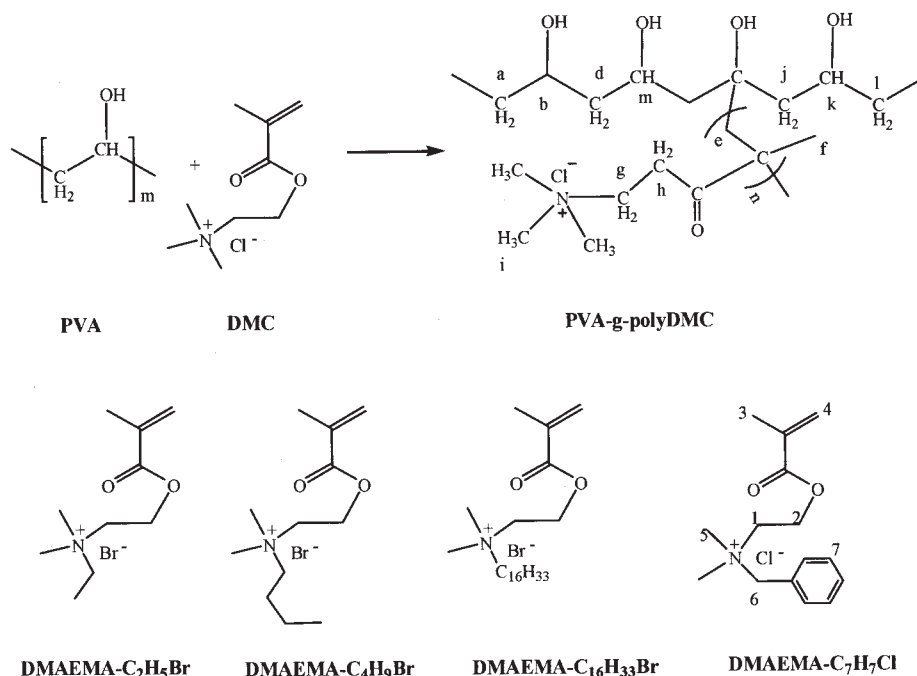
Figure 1 Graft copolymerization of water-soluble monomers containing quaternary ammonium group on poly(vinyl alcohol) using ceric ions.

EXPERIMENTAL

Materials

PVA white crystalline solid obtained from Shanghai Chemical Company (Shanghai City, P. R. China) with average degree of polymerization 1750 ± 50, and molecular weight 8×10^4 was used. Methacryloxyethyl trimethylammonium chloride (DMC, 76 wt % in water) was purchased from Wuxi Xinyu Chemical Industry Co., LTD (Wuxi, P. R. China). The other monomers with quaternary ammonium group were self-synthesized. The ceric ammonium nitrate (CAN) and nitric acid were reagent grade chemicals and used without further purification.

Synthesis of quaternary 2-(dimethylamino)ethyl-2-methacrylate derivatives

N-(2-Methacryloyloxy)ethyl-N,N-dimethylethyl-ammonium bromide (DMAEMA-C$_2$H$_5$Br) was prepared as described earlier[19] using DMAEMA and ethyl bromide as starting materials. The synthesized monomers were isolated and purified by precipitation many times from acetone and dried in a vacuum oven at 35°C for 24 h. The other monomers, such as DMAEMA·C$_4$H$_9$Br, DMAEMA·C$_{16}$H$_{33}$Br, and DMAEMA·C$_7$H$_7$Cl, were prepared by the same methods (Fig. 1).
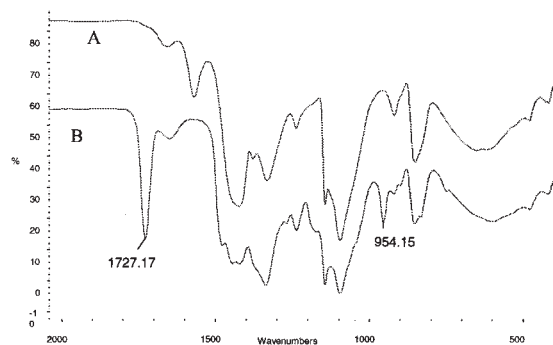
Graft copolymerization

The graft copolymerization of DMC onto PVA was carried out by adding a calculated amount of PVA

(0.44 g) to 50 mL water in a 100 mL three-necked round-bottom flask that was fitted with a magnetic stirrer, an N$_2$ gas inlet, a reflux condenser, and a thermometer, and kept in a water bath maintained at 35°C. The solution was purged with nitrogen gas for about 30 min after adding DMC monomer into the flask, then a calculated amount of nitric acid and CAN was added to initiate the graft copolymerization. A constant supply of nitrogen in the reaction mixture was maintained until graft copolymerization was accomplished. The mixture was kept at 35°C for 3h. At the end of the reaction, the mixture was poured into a beaker containing an excess amount of methanol, separated by filtration, and washed repeatedly with methanol to remove unreacted DMC and existing PDMC. The purified grafted products were finally dried in vacuum at 60°C for 24h. Graft copolymerization of different monomers containing quaternary ammonium onto PVA was also done according to the aforementioned methods. The percent graft yield (mol %) was calculated by ^{1}H NMR spectroscopy.

Characterization methods

Infrared spectra of grafted and ungrafted PVA were measured with a Nicolet Nexus FTIR 470 spectrophotometer. ^{1}H NMR spectra were recorded at 500 MHz with a Bruker DRX 500 NMR spectrometer. D$_2$O was used as solvent, and Me$_4$Si was used as an internal reference. Viscosity measurements were performed by an Ubbelohde viscometer at 25°C. The reduced viscos-

Figure 2 FTIR spectra of PVA (A) and graft copolymer of PVA-g-DMC (B).

ity of the graft copolymers was measured in H_2O solution (PVA, c = 0.5% w/v; PVA-g-polyDMC, c = 0.25% w/v).

RESULTS AND DISCUSSION

Characterization of PVA-g-poly(DMC)

The existence of the grafting was first confirmed by observing the difference between the IR spectra of PVA and the grafted copolymer. As seen from Figure 2, the IR spectrum of the grafted copolymer shows not only the characteristic absorption bands of PVA but also additional characteristic absorption bands of the carboxylic ester carbonyl group at $1727 cm^{-1}$ and the quaternary groups at $954.7 cm^{-1}$. This indicates that the monomer DMC has been grafted onto PVA.

Further evidence of the grafting was provided by the ^{1}H NMR spectrum (Fig. 3). From the ^{1}H NMR spectrum of PVA-g-DMC, we can observe a signal centered at 3.3 ppm, which was due to the methyl
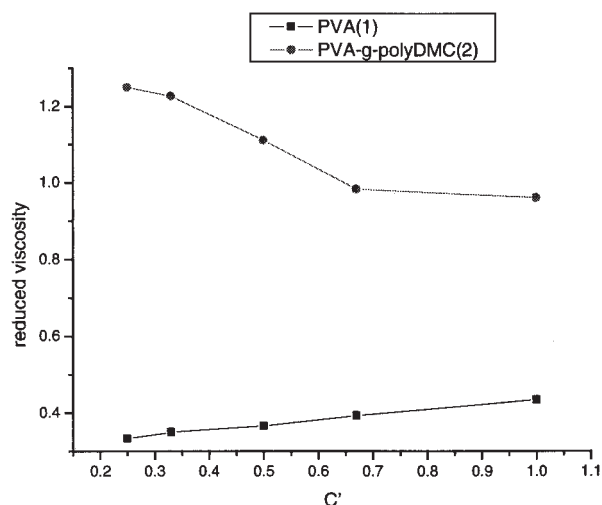
Figure 4 Reduced viscosity plots for the PVA (c = 0.5% w/v) and the PVA-g-polyDMC (c = 0.25% w/v), measured in water at 25°C. C′ is relative concentration, c = c′ × c_0 (c is actual concentration, c_0 is initial concentration).

proton of DMC. A signal corresponding to the methine proton of the PVA appears at 4.0 ppm. A similar result was reported in the literature. Imai and coworkers[20] modified PVA with vinyl sulfoxide and reported signals at 4.0 ppm due to the methine proton. According to the integral area ratio of the methyl proton of DMC to the methylene proton of PVA, we calculated the percent of graft yield (mol %).

The PVA and the PVA-g-polyDMC (graft yield = 9.9 mol %) were also characterized by viscosity measurements in water at 25°C. Figure 4 gives the reduced viscosity ($\eta_{sp/c'}$) plots of the PVA (c = 0.5% w/v) and PVA-g-polyDMC(c = 0.25% w/v). When the PVA is grafted by DMC, reduced viscosity of the
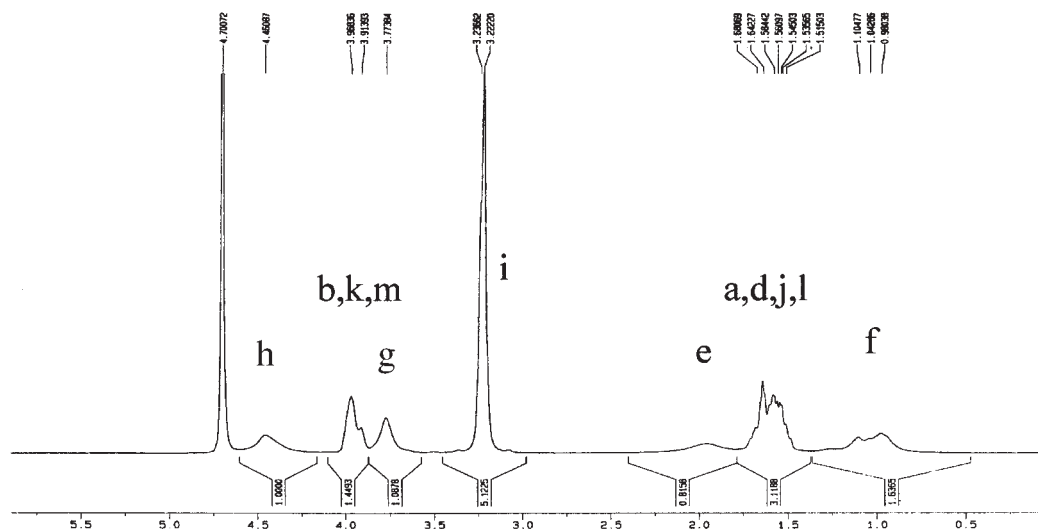
Figure 3 ^{1}H NMR spectrum of the graft product of PVA with DMC (D_2O, 500MHz, graft yield of DMC is 36.5 mol %). Assignments of a-m are marked in Figure 1 **(PVA-g-polyDMC)**.

TABLE I
Graft Yield Obtained from the Calculation of ¹H NMR Spectra

Entry	Monomer	Graft yield (mol %)
1	DMC	36.5
2	DMAEMA-C_2H_5Br	2.9
3	DMAEMA-C_7H_7Cl	23.7
4	DMAEMA-C_4H_9Br	2.1
5	DMAEMA-$C_{16}H_{33}Br$	0

graft copolymer shows the analogue to polyelectrolytes.[21] Comparing PVA with PVA-g-polyDMC, the reduced viscosity of PVA-g-polyDMC exhibits the trend of a parabola plot. This is probably because the graft copolymer has brought PVA the characteristics of polyelectrolytes. The result confirms that DMC has succeeded in grafting onto PVA. Moreover, there will be an obvious difference in viscosity behavior between the grafted product and a physical mixture of PVA and DMC homopolymers. The plot of $\eta_{sp/c'}$ versus c of unquaternized PVA homopolymer is straight lines, and the $\eta_{sp/c'}$ values are lower than those of the quaternized PVA grafted product. The viscosity behavior of the physical mixture of PVA and DMC homopolymer is the additivity results of a polyelectrolyte and a common polymer.

Characterization of graft copolymers of DMAEMA-C_2H_5Br, DMAEMA-C_4H_9Br, DMAEMA-$C_{16}H_{33}Br$, and DMAEMA-C_7H_7Cl on PVA

Graft copolymers of DMAEMA-C_2H_5Br, DMAEMA-C_4H_9Br, DMAEMA-$C_{16}H_{33}Br$, and DMAEMA-C_7H_7Cl (Fig. 1) on PVA were characterized by IR and NMR. For example, the assignment of the NMR spectrum of the graft copolymer PVA-g-poly(DMAEMA-C_7H_7Cl) was as follows: δ (ppm), 0.8 (m, CH$_3$-3′), 1.5 (m, CH$_2$-a,d,j,l,e), 2.98(s, Me-5′), 3.98(m, H-2′), 3.89(m, CH-k′), 4.45(m, CH$_2$-6′, CH$_2$-1′), 7.4(m, C_6H_5-7′) (the number of a-j and 1–7 were marked in Fig. 1). DMAEMA·C_7H_7Cl was assigned as follows: δ (ppm), 1.83 (s, 3H, Me-3), 3.03 (s, 6H, Me-5), 3.70 (t, 2H, H-2), 4.50 (s, 2H, H-6), 4.59 (t, 2H, H-1), 5.65 (s, 1H, H-4), 6.05 (s, 1H, H-4), 7.45 (d, 5H, H-7). Analysis of NMR revealed that the DMAEMA·C_7H_7Cl was successfully grafted onto PVA. The IR spectrum of the grafted copolymer PVA-g-poly(DMAEMA-C_7H_7Cl) showed the characteristic absorption bands of DMAEMA·C_7H_7Cl and PVA. Characterization results confirmed the structure of graft copolymer of DMAEMA-C_2H_5Br, DMAEMA-C_4H_9Br, and DMAEMA-C_7H_7Cl on PVA.

The graft yields of different monomers are shown in Table I. From Table I, we can see that the PVA grafted by water-soluble monomers shows graft yield content in the range 0.0–0.40. Comparison of the graft yield of

quaternized monomer with the two different anions studied (Cl⁻ and Br⁻) shows that the nature and size of the halogen counter ion have important influence. As the monomer is quaternized with bromoalkyl, the graft yield is very low. The reason is probably due to the bromine ion, which makes the initiator (ceric ammonium nitrate) inactive. Furthermore, the results of Table I showed that the different chain length of quaternized monomer influenced the graft yields. The graft yield decreases when the monomer is quaternized from methyl chloride to cetane alkylogens.

Effect of monomer concentration on graft copolymerization

To optimize the experimental conditions for a maximum graft yield, the graft copolymerization of DMC has been carried out as a function of concentration variation of monomer, initiator, and reaction temperature.

The graft copolymerization has been done at different concentrations of DMC ranging from 1.6×10^{-1} to 10.0×10^{-1} mol dm^{-3} at constant concentration of the ceric ammonium nitrate (10.0×10^{-3} mol dm^{-3}) and nitric acid (8.0×10^{-2} mol dm^{-3}) at 35°C. The effect of monomer concentration on percent grafting as well as percent conversion is shown in Figure 5. The percent grafting increased as the monomer concentration increased from 1.6×10^{-1} mol dm^{-3} to 5.0×10^{-1} mol dm^{-3}, and thereafter, it decreased with further increase of monomer concentration. The rapid increase of graft yield by increasing monomer concentration up to 5.0×10^{-1} mol dm^{-3} could be due to the greater availability of grafting sites to the monomer. However, the decreasing trend of percent grafting beyond the optimum monomer concentration was probably ascribed to the competition between homopolymerization and graft copolymerization, where the former prevailed over the latter at higher DMC concentration.
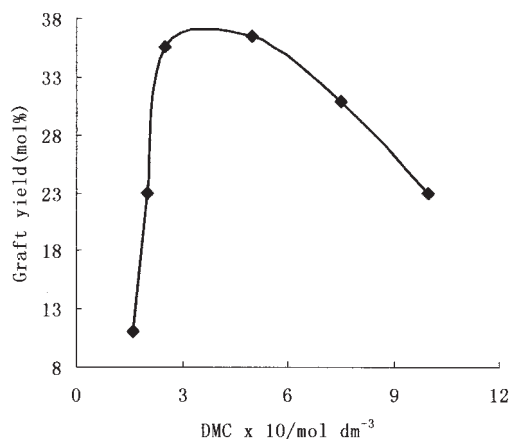

Figure 5 Effect of DMC concentration on percent grafting.

Enhancement in percent conversion at higher DMC concentration could be associated with the greater availability of monomer molecules in the vicinity of PVA as well as in the polymerization medium. This greater availability would favor greater opportunity for DMC to graft PVA, and also allow greater collision of initiated DMC molecules with its own molecules, thereby promoting homopolymerization. This analysis was in agreement with the results obtained in the grafting of AA onto starch.[22] On the other hand, the drop in conversion with increasing DMC concentration is also due to the covering of the initiation sites on the PVA backbone with growing DMC grafts. As the DMC concentration increases even more, the monomer "sees" a cationic cloud around the PVA and is repelled by the charge—eliminating the ability to initiate polymerization.

Effect of temperature on graft copolymerization

The graft copolymerization of DMC onto PVA was studied at different temperatures (20°C, 30°C, 35°C, and 40°C). Figure 6 showed that the optimal temperature for the HNO_3/CAN (ceric ammonium nitrate) initiation system was 35°C. The percent of grafting increased gradually with temperature in the range of 20–35°C and decreased quickly at 40°C. The maximum graft extent was 36.5%. A relatively high grafting percent could also be obtained even at the low temperature of 20°C. The lower grafting percent at higher temperature may be because the termination rate of free radicals on the grafted monomer increased with the further increase of temperature.

Effect of concentration of ceric ammonium nitrate on graft copolymerization

When the concentration of the ceric ammonium nitrate was in the range from 5.0×10^{-3} mol dm^{-3} to 25.0×10^{-3} mol dm^{-3}, the effect of the CAN concentration
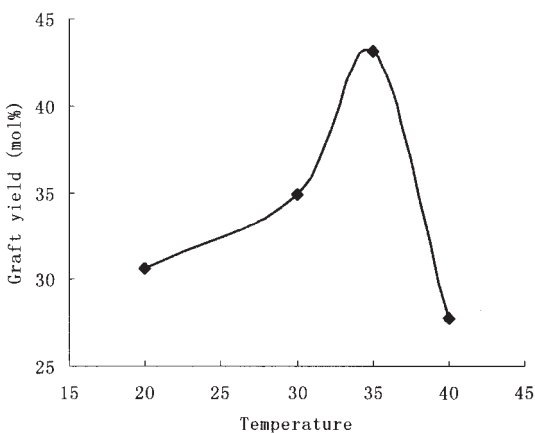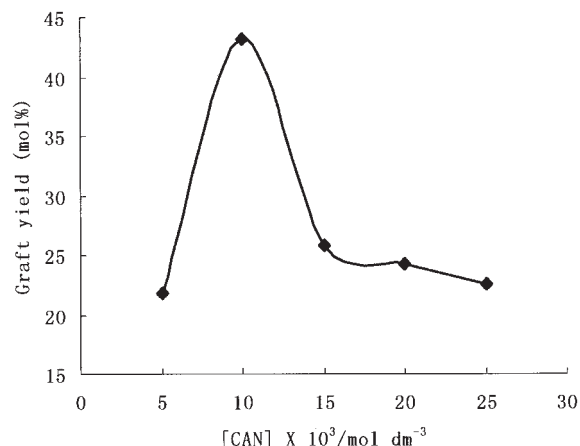

Figure 7 Effect of CAN concentration on percent grafting.

on grafting is shown in Figure 7. It can be found that the optimal CAN concentration was 10.0×10^{-3} mol dm^{-3}. For the grafting of DMC onto PVA, the increase in the grafting percent with an increase in the CAN concentration from 5.0×10^{-3} mol dm^{-3} to 10.0×10^{-3} mol dm^{-3} maybe resulted from the production of more radical sites, which was favorable for grafting. However, a decrease of grafting percent at a higher CAN concentration may be due to the efficiency of Ce(IV) taking part in the termination of growing grafted chains and homopolymerization. With the increase of the concentration of the initiator, the color of the product gradually changed from flavescent to brown because of the excessive initiator.

Reaction mechanism

Although several reports have been published on the graft copolymerization mechanisms of the vinyl monomer onto PVA, the proposed mechanism used in this study was based on the same principle as that used by Zhang.[17] The first step of the mechanism is that the cerium ion attacks the PVA molecules and forms a PVA-ceric complex. The Ce^{4+} ion in the complex is then reduced to a Ce^{3+}, and a hydrogen atom is oxidized. Consequently, a free radical is formed onto PVA, and the polymeric PVA free radical formed may react with the monomer to initiate graft copolymerization. In the presence of vinyl monomers, the PVA free radical was added to the double bond of the vinyl monomer, resulting in a covalent bond between the monomer and PVA to create the chain reaction for propagation. Termination of the graft copolymerization is through a combination of two radicals.

CONCLUSIONS

Water-soluble quaternary ammonium monomers grafted PVA were synthesized by the methods of using ceric

Figure 6 Effect of temperature on percent grafting.

ammonium nitrate as the catalyst. The main factors affecting the grafting percent, including the initiator concentration, monomer concentration, and temperature, were studied. With this study, the optimum reaction conditions for obtaining the maximum grafting degree were found. Different monomers with ammonium-groups, such as DMAEMA·C_2H_5Br, DMAEMA·C_4H_9Br, DMAEMA·$C_{16}H_{33}Br$, and DMAEMA·C_7H_7Cl were studied under the optimum conditions. The resulting grafted PVA were characterized with IR, NMR, and viscosity measurements.

References

1. Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G. Encyclo Polym Sci Eng; Wiley: New York, 1989.
2. Gimenez, V.; Reina, J. A.; Mantecon, A.; Cadiz, V. Polymer 1999, 40, 2759.
3. Stober, R.; Kohn, E.; Bischoff, D. U.S. Pat. 4, 822, 851.
4. Beresniewicz, A.; Hassall, A. U.S. Pat. 4, 775, 715 (1988).
5. Huang, R. Y. M.; Rhim, J. W. Polym Int 1993, 30, 129.
6. Gubb, D. T.; Kearney, F. R. J Appl Polym Sci 1990, 39, 695.
7. An, Y.; Koyama, T.; Hanabusa, K.; Shirai, H.; Ikeda, J.; Yonenieo, H.; Itoh, T. Polymer 1995, 36, 2297.
8. Sharma, V. K.; Soni, P. L. J Appl Polym Sci 2002, 86, 3250.
9. Rahman, L.; Silong, S.; Wan, M. Z.; Rahman, A. B. J Appl Polym Sci 2002, 76, 516.
10. Geogre, F. F.; Robert, C. B.; Russell, C. R. J Appl Polym Sci 1970, 14, 2601.
11. Gupta, K. C.; Khandekar, K. J Appl Polym Sci 2002, 86, 2631.
12. Gupta, K. C.; Sahoo, S. Biomacromol 2001, 2, 239.
13. Gupta, K. C.; Sahoo, S.; Khandeker, K. Biomacromol 2002, 3, 1087.
14. Zhang, L. M.; Chen, L. Q. J Appl Polym Sci 2002, 83, 2755.
15. Chiang, W. Y.; Lin, Y. H. J Appl Polym Sci 2002, 86, 2854.
16. Jana, S, C.; Maiti, S.; Biswas, S. J Appl Polym Sci 2000, 78, 1586.
17. Zhang, G. Z.; Zhang, H.; Xie, F. C.; Hu, X. Q.; Luo, X. Y. J Appl Polym Sci 2000, 75, 977.
18. Isiklan, N.; Sanli, O. J Appl Polym Sci 2004, 93, 2322.
19. Hamid, S. M.; Sherrington, D. C. Polymer 1987, 17, 325.
20. Imai, K.; Shiomi, T.; Tezuka, Y. J Macromol Sci Chem A 1985, 22, 1359.
21. Li, G. J.; Shen, J. R.; Zhu, Y. L. J Appl Polym Sci 1996, 62, 2247.
22. Hebeish, A.; El-Rafie, M. H.; Higazy, A.; Ramadan, M. Doki Starch/Starke 1996, 48, 175.