Polymer Bulletin 4, 635–640 (1981)

Polymer Bulletin

Grafting onto Wool

13. Graft Copolymerization of Acrylic Acid onto Reduced Wool in the Presence of Ceric Ammonium Nitrate as Redox Initiator

B.N. Misra, Inderjeet Kaur and R.K. Sharma

Chemistry Department, Himachal Pradesh University, Simla-171005, India

SUMMARY

In order to study the role of -SH group of wool in graft copolymerization, an attempt has been made to study grafting of acrylic acid (AAc) onto reduced wool in aqueous medium using ceric ammonium nitrate (CAN) as redox initiator. HNO_3 was found to catalyze the graft copolymerization. Reduction of wool was effected with thioglycolic acid (TGA) in aqueous medium. Percentage of grafting was determined as a function of concentration of (i) CAN, (ii) vinyl monomer (AAc), (iii) nitric acid, (iv) time and (v) temperature. Under optimum conditions, poly(acrylic acid) was grafted to the reduced wool to the extent of 9.14%, the unreduced wool under optimum conditions afforded maximum grafting of poly(AAc) to the extent of 12.24%. Reduction of wool does not promote grafting of AAc in the presence of CAN.

INTRODUCTION

Ceric ion has been extensively used as a redox initiator for effecting grafting of a variety of vinyl monomers onto starch (FANTA et al. 1971, SRIVASTAVA et al. 1976), cellulose (MISRA et al. 1976, 1978), poly(vinyl alcohol) (ODIAN et al. 1968). In the presence of polyhydric alcohols ceric ion forms a complex which disproportionates by a one electron transfer process to generate macro radical on the polymeric backbone where grafting occurs.

$$\text{R-cellOH} + Ce^{+4} \rightleftharpoons B \longrightarrow \text{R cell}\dot{O} + Ce^{+3} + H^{+}$$

Since in this process, active sites are exclusively generated on the backbone polymer, grafting occurs without homopolymer formation. Functional groups other than hydroxyl such as $-NH_2$, -SH, -CHO, -COOH and -SS- are also known to form complexes with ceric ion. Wool is a natural polypeptide that contains -OH, $-NH_2$, -SH, -CHO, -COOH, -SS- and imino groups which can form complexes with ceric ion. It is, therefore, natural that attempts are being made to modify wool fiber by graft copolymerization in the presence of ceric ion initiator. We have studied grafting of MA, MMA, VAc, AAc and EA onto wool by using ceric ammonium nitrate in the presence of nitric acid. Relative reactivities of different vinyl monomers towards grafting onto wool have been

0170-0839/81/0004/0635/$01.20

evaluated (MISRA et al. 1977, 1978, 1979, 1980). However, it has not been possible to identify the functional groups of wool responsible for grafting. It appears that $-NH_2$, -SH and -OH may play major role in providing active sites for graft copolymerization. Data are available (KANTOUCH et al. 1971) that indicate that a definite role is played by both $-NH_2$ and -OH during ceric ion initiated grafting. Relatively less attention has been paid to identify the role of -SH group of wool in ceric ion initiated grafting.

Sulphur compounds are known to participate in initiating, modifying and promoting vinyl polymerization. LIPSON (1949) reported graft copolymerization to wool through -SH groups formed by the reduction of cystine in wool. The role of cystine in the polymerization occurring in the presence of sulphur containing proteins was illustrated by LIPSON and HOPE (1950) who showed that methacrylic acid polymerises in the presence of cystine and ammonium persulphate. Recently NEGESHI et al. (1967) investigated grafting of MMA onto wool in the presence of $LiBr-S_2O_8^{-2}$ initiating system and concluded that -SH of wool provides sites for grafting. In the present article attempts have been made to determine the role of -SH group by carrying out grafting of AAc onto reduced wool in the presence of CAN. Wool contains a very small amount of cysteine and therefore wool was treated with thioglycolic acid (TGA) in order to convert -SS- linkages into -SH groups. Percentage of grafting of AAc onto TGA treated wool has been determined as functions of various reaction variables.

EXPERIMENTAL

Material and Methods

Himachali wool and acrylic acid were purified as described (MISRA et al. 1977, 1980).

Ceric ammonium nitrate (BDH) was used as received.

Nitrogen was purified by passing through freshly prepared alkaline pyrogallol solution.

Thioglycolic acid of reagent grade (Pfizer) was used as received.

Reduction: One gram of purified and dried wool was immersed in 0.5% solution of thioglycolic acid for 48 hours. The wool was then washed with water and methanol several times, dried and weighed.

Graft Copolymerization: Reduced wool (1.0 gm) was dispersed in 200 ml of deareated distilled water. A known weight of catalyst (CAN), dissolved in known strength of HNO_3 was added to the reaction mixture. The reaction flask was flushed with nitrogen for 30 minutes prior to monomer addition. Appropriate amount of monomer was added dropwise to the reaction mixture. A continuous flow of nitrogen was maintained throughout the reaction. After the reaction was over, the mixture was filtered and the residue was extracted with acetone for 48 hours. The grafted wool was then dried and weighed until constant weight was obtained.

Percentage of grafting and efficiency were calculated as follows and the results are presented in Table 1.

$$\%\ \text{Grafting} = \frac{W_2 - W_1}{W_1} \times 100, \quad \%\ \text{Efficiency} = \frac{W_2 - W_1}{W_3} \times 100$$

where W_1, W_2 and W_3 are the weights of reduced wool, grafted wool after acetone extraction and the weight of the monomer added, respectively.

RESULTS AND DISCUSSION

It is well known that treatment of wool with TGA increases the thiol content of wool. Cystine disulfide is reduced to -SH group of cystein. Since -SH groups are susceptible to air oxidation to -SS- groups, grafting was carried out onto freshly reduced wool. Sulfhydryl groups are quite reactive and capable of forming complexes with ceric ion. Reduction of wool was, therefore, expected to afford enhanced grafting. In a previous paper (MISRA et al. 1980) grafting of AAc onto untreated wool by using CAN as redox initiator was reported. Both untreated and reduced wool required a small amount of nitric acid which acted as a catalyst for the production of graft. It has been reported earlier (MISRA et al. 1980) that poly(AAc) is poorly grafted to untreated wool in the presence of CAN and under optimum conditions poly(AAc) could be grafted to untreated wool only to the extent of 12.24%. This was attributed to the greater reactivity of AAc towards homopolymerization. The present study indicates that reduction of wool did not promote grafting of AAc. It is observed from Table I that under optimum conditions, poly(AAc) was grafted to reduced wool only to the extent of 9.14%.

Effect of concentration of CAN

It is observed from Table I that maximum grafting of AAc onto reduced wool occurs at $[Ce^{4+}] = 2.0 \times 10^{-3}$ Moles/lit. Further increase in the concentration of Ce^{4+} progressively reduces percentage of grafting. It seems that at higher concentration Ce^{4+} preferentially terminates the growing grafted chain. Similar observation was also made during grafting of AAc onto untreated wool (MISRA et al. 1980). The following mechanism (eq.1-7) is suggested to explain the decrease in percent grafting of AAc onto reduced wool:

$$R\text{-}S\text{-}S\text{-}R + 2HS - CH_2COOH \longrightarrow 2RSH + HOOC\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}COOH \quad (1)$$

$$2RSH + 2Ce^{4+} \longrightarrow R\text{-}S\text{-}S\text{-}R + 2Ce^{3+} + 2H^{+} \quad (2)$$

$$R\text{-}S\text{-}S\text{-}R + Ce^{4+} \longrightarrow \text{Wool oxidation product} \quad (3)$$

$$RSH + Ce^{4+} \longrightarrow RS - Ce^{3+} + H^{+} \quad (4)$$

$$2\ RS\text{-}Ce^{3+} + 2RSH \longrightarrow 2\ RS\text{-}Ce^{2+} + R\text{-}S\text{-}S\text{-}R + 2H^{+} \quad (5)$$

$$2RSH + Ce^{4+} \longrightarrow R\text{-}S\text{-}Ce\text{-}SR^{2+} + 2H^{+} \qquad (6)$$

$$2\ R\text{-}S\text{-}Ce\text{-}SR^{2+} + 2RSH \longrightarrow 2\ R\text{-}S\text{-}Ce\text{-}SR^{+} + RS\text{-}SR + 2H^{+} \qquad (7)$$

From the above mechanism, it is observed that reaction (2) leads to rebuilding of disulfide linkages. If this reaction predominates it would be expected that reduced wool would yield the same amount of graft as the unreduced wool. This is actually observed. The unreduced wool under optimum conditions afforded maximum grafting of AAc to the extent of 12.24% (MISRA et al. 1980), and the reduced wool under optimum conditions produced maximum grafting of AAc to the extent of 9.14% (Table 1). With EA in the presence of Ce^{4+}, it was observed that there is considerable decrease in percent grafting onto reduced wool (MISRA et al. 1980) This was explained by assuming that additional -SH groups resulting from reduction of disulfide linkages are involved in reaction that leads to production of a variety of oxidised product. These side reactions do not assume importance in ceric ion initiated grafting of poly(AAc) on to reduced wool. With both untreated and reduced wool, the percentage of grafting is less and this is due to acrylic acid being soluble in water shows a strong tendency to polymerize to give homopolymer at the expense of grafting.

Effects of concentration of nitric acid, monomer, time and temperature on graft copolymerization onto reduced wool were similar to those observed during grafting of AAc onto unreduced wool (MISRA et al. 1980).

Thus it is concluded that -SH groups of wool are not responsible for effecting grafting of acrylic acid in the presence of Ce^{4+} initiator.

ACKNOWLEDGEMENT

Financial assistance from DAE, Govt. of India is gratefully acknowledged. I.K.Mehta and R.K.Sharma are grateful to DAE, India for the award of Senior and Junior Research Felllowships, respectively.

TABLE 1

Effect of concentration of HNO_3, CAN, AAc, Temperature and Time on percent grafting[a]

Sr.No.	[CAN] x 10^3 mole/1	[HNO_3] x 10^2 mole/1	[AAc] x 10^2 mole/1	Temp. °C	Time min.	% Grafting	% Efficiency
1.	2.00	14.4	36.7	45	180	9.14	1.74
2.	3.00	"	"	"	"	7.79	1.48
3.	5.1	"	"	"	"	5.69	1.08
4.	6.3	"	"	"	"	2.90	0.55
5.	7.5	"	"	"	"	6.35	1.21
6.	2.00	10.8	"	"	"	4.73	0.93
7.	"	18.0	"	"	"	4.21	0.83
8.	"	21.6	"	"	"	3.39	0.64
9.	"	14.4	"	30	"	6.90	1.31
10.	"	"	"	60	"	7.27	1.38
11.	"	"	"	45	90	2.08	0.39
12.	"	"	"	"	150	3.35	0.64
13.	"	"	22.0	"	180	3.57	1.13
14.	"	"	51.4	"	"	7.20	0.98

[a] TGA treated wool = 1.0 gm

H_2O = 200 ml

REFERENCES

FANTA, G.F., BUSS, R.C., RUSSELL, C.R. and RIST, C.E., J. Appl. Polym. Sci., 15, 1889 (1971).

KANTOUCH, A.A., HEBEISH, A. and BENDAK., A., Eur. Polym. J., 7(2), 153 (1971).

LIPSON, M., Nature, 164, 576 (1949).

LIPSON, M. and HOPE, R., Aust, J. Chem., 3A, 324 (1950).

MISRA, B.N., JASSAL, J.K. and PANDE, C.S., J. Polym. Sci., Polym. Chem. Ed., 16, 295 (1976).

MISRA, B.N., JASSAL, J.K. and PANDE, C.S., Ind. J. Chem., 16A, 1033 (1978).

MISRA, B.N. and CHANDEL, P.S., J. Polym. Sci., Polym. Chem. Ed., 15, 1545 (1977).

MISRA, B.N., MEHTA, I.K. and DOGRA, R., J. Macromol. Sci.-Chem., A(12)10, 1513 (1978).

MISRA, B.N., MEHTA, I.K. and DOGRA, R., J. Appl. Polym. Sci., 24, 1595 (1979).

MISRA, B.N., MEHTA, I.K. and DOGRA, R., J. Appl. Polym. Sci., 25, 235 (1980).

MISRA, B.N., MEHTA, I.K. and SHARMA, R.K., Polymer Bulletin, 3, 115 (1980).

NEGESHI, M., ARAI, K. and OKADA, S., J. Appl. Polym. Sci., 11, 2427 (1967).

ODIAN, G. and KHO, J.H.T., Polymer Preprints, Amer. Chem. Soc., Division of Polym. Chem., 9, 675 (1978).

Received May 15, 1981