Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Grafting onto Protein. I. Graft Copolymerization of Poly(methyl Acrylate) onto Gelatin

B. N. Misra[a]; I. K. Mehta[a]; D. S. Sood[a]
[a] Department of Chemistry, Himachal Pradesh University, Simla, India

To cite this Article Misra, B. N. , Mehta, I. K. and Sood, D. S.(1981) 'Grafting onto Protein. I. Graft Copolymerization of Poly(methyl Acrylate) onto Gelatin', Journal of Macromolecular Science, Part A, 15: 3, 457 — 465
To link to this Article: DOI: 10.1080/00222338108074385
URL: http://dx.doi.org/10.1080/00222338108074385

J. MACROMOL. SCI.–CHEM., A15(3), pp. 457-465 (1981)

Grafting onto Protein. I. Graft Copolymerization of Poly(methyl Acrylate) onto Gelatin

B. N. MISRA, I. K. MEHTA, and D. S. SOOD

Department of Chemistry
Himachal Pradesh University
Summer Hill, Simla-171005, India

ABSTRACT

Poly(methyl acrylate) has been graft copolymerized onto a soluble protein, gelatin, in aqueous medium by using ceric ammonic nitrate (CAN) as the redox initiator. Graft copolymerization was carried out at 35, 45, and 55°C for various reaction periods. Maximum percent grafting occurred at 45°C. Nitric acid was found to influence grafting. Percent grafting has been determined as a function of (1) concentration of CAN, monomer, and nitric acid; (2) time; and (3) temperature.

INTRODUCTION

As early as 1937, Flory [1] discovered that polymers can be modified by grafting of appropriate vinyl monomers by the chain transfer process. Many natural polymers such as collagen [2] and rubber [3] have been graft copolymerized using different initiating systems. We have reported grafting of various vinyl monomers onto starch [4-6], cellulose [7, 8] and wool [9-14] in our previous communications. Very few studies on grafting onto soluble proteins have been made. Recently Imai et al. [15] were able to modify ovalbumin by grafting polystyrene. Japanese workers [16] studied the grafting of methyl methacrylate onto blood protein using Bu_3B as initiator.

Poly(styrene) and poly(acrylonitrile) were grafted to silk [17] by gamma irradiation. Nayudamma and co-workers [2] have reported grafting of methyl acrylate onto collagen using ceric sulfate as initiator.

Gelatin, which results from the loss of structure of collagen, is unique among proteins owing to the absence of an appreciable internal order. Therefore, in aqueous solution at sufficiently high temperature, peptide chains take up a random configuration which is analogous to the linear chain of synthetic high polymers. In order to explore the utility of gelatin and starch in the leather industry, it was found necessary to modify gelatin through grafting. Recently Santappa et al. studied the grafting of ethyl acrylate [18] and methyl acrylate [19] onto gelatin using persulfate as initiator. Kuwajima and co-workers [23] have studied the grafting of methyl methacrylate onto gelatin by using potassium peroxysulfate as initiator.

Grafting onto gelatin may give a product of good mechanical properties, high elasticity, and thermal stability, which can be used in coating formulations of leather finishes. A comprehensive research program has been undertaken in our laboratory to effect grafting of a variety of vinyl monomers onto gelatin by using various initiating systems that would selectively afford grafting. In our previous work on wool grafting [9-14] it was observed that both acceptor and donor vinyl monomers could be successfully grafted to wool fiber in presence of ceric ion initiator. In the present article we report studies on the grafting of methyl acrylate onto gelatin by using ceric ammonium nitrate (CAN) as a redox initiator. Percent grafting has been determined as a function of various reaction variables, and the results are reported in Table 1.

EXPERIMENTAL

Materials and Method

Gelatin (Oxoid, England) was in the form of granules and was used as received. Methyl acrylate was washed with 5% NaOH three to four times and dried over anhydrous sodium sulfate. Dried monomer was distilled and the middle fraction was used.

Ceric ammonium nitrate (B.D.H.) was used as received, and a known weight was dissolved in nitric acid of known strength. Nitrogen was purified by passing it through freshly prepared pyrogallol solution.

Graft Copolymerization

One gram of gelatin was dissolved in 100 mL of boiled distilled water in a three-necked flask. The temperature of the reaction

TABLE 1. Effect of Concentrations of CAN, HNO_3, MA, Time, and Temperature on Percent Grafting of P(MA) onto Gelatin[a]

No.	$[CAN] \times 10^3$ (mol/L)	$[HNO_3] \times 10^2$ (mol/L)	$[MA] \times 10^2$ (mol/L)	Time (min)	Temperature (°C)	% Grafting	% efficiency
1	8.3	28.8	33.1	30	45	0	0
2	"	"	"	60	"	234.27	81.94
3	"	"	"	120	"	226.63	79.26
4	"	"	"	150	"	175.16	61.26
5	1.2	"	"	60	"	63.87	22.34
6	5.0	"	"	"	"	138.46	48.83
7	10.5	"	"	"	"	164.51	57.54
8	8.3	0	"	"	"	0	0
9	8.3	14.4	"	"	"	47.18	16.50
10	"	21.6	"	"	"	185.80	65.00
11	"	43.2	"	"	"	128.66	45.00
12	"	28.8	"	"	35	194.78	68.12
13	"	"	"	"	55	112.00	39.17
14	"	"	11.0	"	45	0	0
15	"	"	55.2	"	"	314.85	66.26
16	"	"	76.2	"	"	369.78	55.43
17	"	"	110.4	"	"	802.53	84.21

[a]Gelatin = 1 g, H_2O = 100 mL.

mixture was brought to the water bath temperature. A definite amount of catalyst (CAN) was dissolved in a definite volume of HNO_3 of known strength and was added to the reaction flask. Purified nitrogen gas was passed through the reaction flask for 30 min. A known weight of monomer was added directly to the reaction mixture. Graft copolymerization was carried out at different temperatures for various reaction periods. A continuous supply of nitrogen was maintained throughout the reaction period.

After the completion of the reaction, the ingredients were poured into acetone and kept for 48 h. The grafted gelatin was precipitated out, and any loosely bound homopolymer was dissolved in acetone. The grafted gelatin was filtered, dried, and finally weighed.

Percentage of grafting and efficiency were calculated as follows:

$$\% \text{ grafting} = \frac{W_1 - W_0}{W_0} \times 100$$

$$\% \text{ efficiency} = \frac{W_1 - W_0}{W_2} \times 100$$

where W_0, W_1, and W_2 are the weights of gelatin, grafted gelatin, and monomer, respectively.

Evidence of Grafting

Evidnece of grafting was obtained from the infrared spectra of the grafted copolymers. Pure gelatin has amide absorptions centered around 1650 and 1550 cm^{-1} (Fig. 1). Pure poly(methyl acrylate) has

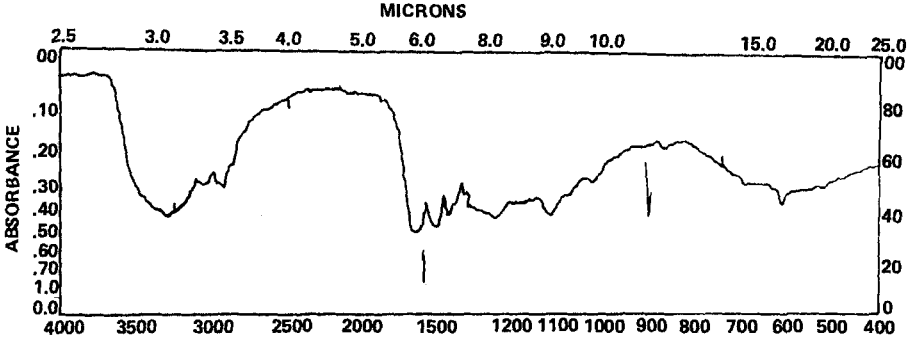

FIG. 1. Infrared spectrum of pure gelatin.

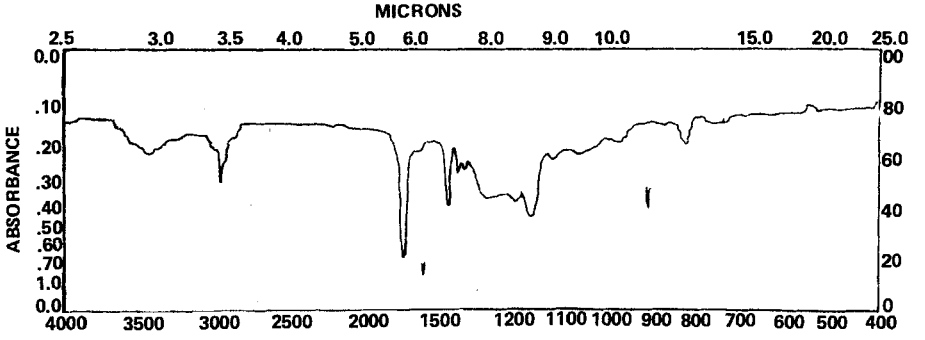

FIG. 2. Infrared spectrum of gelatin-g-poly(methyl acrylate).

absorption due to carbonyl group centered at 1730 cm^{-1}. Figure 2 shows the spectrum of the graft copolymer having absorption bands due to the amide of gelatin and the ester carbonyl groups of poly-(methyl acrylate).

RESULTS AND DISCUSSION

In gelatin the reactive groups are primarily hydroxyl, carboxyl, and amino functions. These groups are known to form a complex with ceric ion. The complex decomposes to generate free radical sites onto gelatin. In analogy with the ceric ion initiated mechanism for wool grafting, the following mechanism is proposed to explain the grafting of poly(MA) onto gelatin:

$$G + Ce^{4+} \rightleftharpoons \text{Complex}_1 \longrightarrow G^{\cdot} + Ce^{3+} + M^{+} \quad (1)$$

$$M + Ce^{4+} \rightleftharpoons \text{Complex}_2 \longrightarrow M^{\cdot} + Ce^{3+} + H^{+} \quad (2)$$

$$G^{\cdot} + M \longrightarrow GM^{\cdot} \xrightarrow{Mn} G(M)^{\cdot}_{n+1} \quad (3)$$

$$M^{\cdot} + nM \longrightarrow (M)^{\cdot}_{n+1} \quad (4)$$

$$G\,(M)^{\cdot}_{n+1} + M \longrightarrow \text{graft} \quad (5)$$

$$G\,(M)^{\cdot}_{n+1} + Ce^{4+} \longrightarrow G(M)_{n+1} + Ce^{3+} \quad (6)$$

$$(M)^{\cdot}_{n+1} + Ce^{4} \longrightarrow (M)_{n+1} + Ce^{3+} \quad (7)$$

Homopolymer

where G = gelatin and M = monomer.

Thus it is clear that ceric ion reacts both with gelatin and monomer to produce graft and homopolymer, respectively.

Effect of Catalyst Concentration

It is observed from Table 1 that with an increase in catalyst concentration, grafting increases and reaches a maximum value of 234.27% at a ceric ion concentration of 8.30×10^{-3} mol/L. With a further increase in the ceric ion concentration, the percent grafting decreases. The decrease in grafting with increasing ceric ion concentration is attributed to the fact that at higher concentration the complex formation between the monomer and ceric ion assumes predominance over that between gelatin and ceric ion. This would be expected since methyl acrylate (MA), having a smaller steric requirement, will easily enter into complex formation with ceric ion. This would favor formation of homopolymer at the cost of grafting. Also, since more and more of the monomer is utilized in the complex formation, the gelatin macroradical (G°) does not find enough monomer in its vicinity to produce the graft.

Effect of Acid Concentration

It is observed from Table 1 that there exists an optimum concentration of acid which affords maximum grafting. Beyond this concentration of nitric acid, the percent grafting decreases. Nitric acid may influence grafting by two factors:

1. The change in concentration of active species of cerium(IV) in the presence of acid
2. The decrease in the monomer concentration because the equilibrium constant for the complex of monomer with ceric ion decreases with increasing concentration of acid

In aqueous medium, ceric(IV) is believed to combine with water in the following manner:

$$Ce^{4+} + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} [CeOH]^{3+} + H^{+} \quad (8)$$

$$2[CeOH]^{3+} \xrightarrow{K_2} [Ce\text{–}O\text{–}Ce]^{6+} + H^{+} \quad (9)$$

Thus ceric ion exists as $[Ce]^{4+}$, $[CeOH]^{3+}$, and $[Ce{-}O{-}Ce]^{6+}$ in water solution. The concentration of these species is found to vary with the concentration of the acid. At higher concentration Reactions (8) and (9) shift more toward the formation of these species, and the species at higher concentration tend to decrease the percent grafting. Termination of growing polymeric chains and growing grafted chains [20, 21] by ceric ion is known.

The zero grafting obtained in the absence of nitric acid may indicate that $[Ce{-}O{-}Ce]^{6+}$, having a larger size, inhibits the formation of the complex between ceric ion and the functional groups of gelatin. A similar behavior was observed during grafting of methyl acrylate onto wool fiber in ceric ion initiated grafting [9]. Odian and Kho [22] have also observed that during grafting of a mixture of monomers (VAc and AN) on poly(vinyl alcohol) by ceric ion, the percentage of grafting was dependent upon the nitric acid concentration. In the absence of nitric acid, grafting did not occur. Odian and Kho explained the mechanism of grafting by assuming a prior complex formation between ceric ion and poly(vinyl alcohol).

Effect of Monomer Concentration

It is observed from Table 1 that zero grafting is obtained when the monomer concentration of 11.0×10^{-2} mol/L was used. With a further increase in the monomer concentration, grafting increases steadily and reaches a maximum value of 802.53% at a monomer concentration of 110.4×10^{-2} mol/L. The zero grafting at low monomer concentration indicates that for grafting there exists an optimum monomer concentration. Below this concentration, monomer preferentially undergoes homopolymerization, and hence no grafting is observed. With a further increase in monomer concentration, the percent grafting increases tremendously. This may indicate that at higher monomer concentration, a larger amount of the growing polymeric chains that are formed are involved in generating additional active sites onto gelatin by the chain transfer reaction.

Effect of Temperature

The grafting reactions were carried out at temperatures ranging from 35-55°C for different time periods. It is observed from Table 1 that maximum grafting occurred at 45°C. The same temperature was found to be optimum when grafting of poly(methyl acrylate) was carried out onto wool using CAN as the redox initiator [9]. At higher temperatures, homopolymerization was found to be predominant.

Effect of Time

The effect of reaction period on percent grafting was studied. Maximum grafting was obtained at a time period of only 60 min. With

a further increase in time, grafting increases slowly and then decreases. This may indicate that with an increase in reaction time, mutual annihilation of growing grafted chains occurs and leads to a decrease in graft yield. A similar behavior has been reported by Santappa et al. [19] during grafting of ethyl acrylate onto gelatin in the presence of persulfate initiator.

Thus, from the foregoing discussion, it is concluded that grafting of methyl acrylate onto the globular protein gelatin can be carried out successfully by the ceric ion technique. It has not been possible to ascertain precisely the nature of the complex formed between ceric ion and gelatin. Work along this line is in progress. Since gelatin contains –OH and $-NH_2$ as major functional groups in the side chain, it is believed that both these groups are involved in the formation of a chelate-type structure with the ceric ion. The temperature dependence of percent grafting supports the chelate formation between Ce^{4+} and –OH and $-NH_2$ groups of gelatin. Attempts are being made to ascertain the relative contribution of each of these functional groups in the production of graft copolymerization. The results will be communicated in due course.

ACKNOWLEDGMENTS

The authors (I.K.M. and D.S.S.) are grateful to the department of Atomic Energy, Government of India, for the award of a Senior Research fellowship and to UGC for the award of a Junior Research fellowship, respectively.

REFERENCES

[1] P. Flory, J. Am. Chem. Soc., 59, 241 (1937).
[2] K. P. Rao, K. T. Joseph, and N. Nayudamma, J. Polym. Sci., Part A-1, 9, 319 (1971).
[3] J. Le Bras and P. Compagnon, C. R. Hebd. Seances Acad. Sci., 212, 616 (1941).
[4] B. N. Misra, C. S. Pande, and B. K. Srivastava, Indian J. Chem., 14A(4), 274 (1976).
[5] B. N. Misra, R. Dogra, and I. K. Mehta, J. Polym. Sci., Polym. Chem. Ed., 18, 341 (1980).
[6] B. N. Misra, R. Dogra, and I. K. Mehta, Indian J. Chem., 17A, 390 (1979).
[7] B. N. Misra and C. S. Pande, J. Polym. Sci., Polym. Chem. Ed., 11, 2369 (1973).
[8] B. N. Misra, J. K. Jassal, and C. S. Pande, Ibid., 16, 295 (1978).
[9] B. N. Misra and P. S. Chandel, Ibid., 15, 1545 (1977).
[10] B. N. Misra and P. S. Chandel, Ibid., 15, 1554 (1977).
[11] B. N. Misra, P. S. Chandel, and R. Dogra, Ibid., 16, 1801 (1978).

[12] B. N. Misra and P. S. Chandel, Ibid., 18, 1171 (1980).
[13] B. N. Misra, I. K. Mehta, and R. Dogra, J. Macromol., Sci.–Chem., A12(10), 1513 (1978).
[14] B. N. Misra, I. K. Mehta, and R. Dogra, J. Appl. Polym. Sci., 25, 235 (1980).
[15] Y. Imai and Y. Iwakura, Ibid., 11, 1529 (1967).
[16] K. Kojima, S. Iwabuchi, K. Kojima, and N. Taruni, J. Polym. Sci., Part B, 9, 453 (1971).
[17] S. A. Azimov, Kh. U. Osmanov, N. V. Kordub, and S. I. Sleparkova, BCIRA J., 41(1), 23 (1961).
[18] T. Nagabhushanam and M. Santappa, J. Polym. Sci., Polym. Chem. Ed., 14, 507 (1976).
[19] T. Nagabhushanam, K. T. Joseph, and M. Santappa, Ibid., 16, 3287 (1978).
[20] C. H. Bamford, A. D. Jenkins, and R. Johnson, Nature, 177, 992 (1956); Proc. R. Soc., London, A239, 214 (1957).
[21] E. Collision and F. S. Daiton, Nature, 177, 1224 (1956).
[22] G. Odian and J. H. J. Kho, Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 9(1), 675 (1968).
[23] T. Kuwajima, H. Yoshida, and K. Hayashi, J. Appl. Polym. Sci., 20, 967 (1976).

Accepted by editor September 20, 1979
Received for publication November 13, 1979