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

Grafting Vinyl Monomers onto Silk Fibers. XIII. Graft Copolymerization of Methyl Methacrylate onto Silk Using Fe³ -Cysteine Redox System

Adwait K. Pradhan[a]; Gadadhar Panda[a]; Nrusingha C. Patl[a]; Padma L. Nayak[a]
[a] Laboratory of Polymers and Fibers Department of Chemistry, Ravenshaw College, Cuttack, Orissa, India

To cite this Article Pradhan, Adwait K. , Panda, Gadadhar , Patl, Nrusingha C. and Nayak, Padma L.(1981) 'Grafting Vinyl Monomers onto Silk Fibers. XIII. Graft Copolymerization of Methyl Methacrylate onto Silk Using Fe³ -Cysteine Redox System', Journal of Macromolecular Science, Part A, 16: 2, 501 — 512

To link to this Article: DOI: 10.1080/00222338108058487

URL: http://dx.doi.org/10.1080/00222338108058487

J. MACROMOL. SCI.–CHEM., A16(2), pp. 501-512 (1981)

Grafting Vinyl Monomers onto Silk Fibers. XIII. Graft Copolymerization of Methyl Methacrylate onto Silk Using Fe^{3+}-Cysteine Redox System

ADWAIT K. PRADHAN, GADADHAR PANDA, NRUSINGHA C. PATI, and PADMA L. NAYAK

Laboratory of Polymers and Fibers
Department of Chemistry
Ravenshaw College
Cuttack 753003, Orissa, India

ABSTRACT

The graft copolymerization of methyl methacrylate onto silk fibers initiated by the ferric chloride-cysteine redox system has been investigated in aqueous medium. The rate of grafting was calculated by varying the concentrations of monomer, initiator, acidity of the medium, cysteine, and temperature. The percentage of grafting increases with an increase of Fe^{3+} concentration up to 2.5×10^{-3} mol/L and thereafter it decreases. The graft yield increases steadily upon increasing the monomer concentration. The graft yield also increases with increasing cysteine concentration up to 0.5×10^{-3} mol/L and then decreases. The effect of the perchloric acid concentration, temperature, solvents, and certain neutral salts on graft yield has also been investigated and a suitable reaction scheme has been proposed.

INTRODUCTION

Grafting is a fascinating field of research with unlimited future prospects. It adds new properties to a fiber without drastically destroying the basic fiber properties. The literature abounds with examples of the successful formation of copolymers from natural and synthetic fibers [1-4]. Bendak and co-workers [5-9] have reported graft copolymerization onto wool and cellulose using a multitude of redox systems. Nayak and co-workers [10-15] have reported successful graft copolymerization onto silk fibers using a number of metal and nonmetal ions.

This paper presents the results of graft copolymerization of methyl methacrylate onto silk using the ferric chloride-cysteine redox system.

EXPERIMENTAL

Mulberry silk fibroin was collected from the Government Silk Factory, Jabalpur, India. The raw silk fibers were purified by the method mentioned in our earlier communication [11]. Methyl methacrylate (MMA) was washed with 5% sodium hydroxide solution, dried with sodium sulfate (anhydrous), and distilled under nitrogen before use.

Ferric chloride (anhydrous, Analar), cysteine hydrochloride (Eastman Kodak), and $HClO_4$ (60%, GR) were used. Water distilled twice over alkaline permanganate and deionized by passing through a Biodeminrolit resin (Permutit Co.) was used to prepare all solutions. A stock solution of ferric chloride (0.1 $\underline{M}$ in distilled water) was used throughout the experiment. The concentration of ferric(III) in the experimental system was determined by iodometry.

The grafting reaction was carried out according to our previous communications [11].

RESULTS AND DISCUSSION

Effect of Monomer Concentration

Figure 1 shows the results of the effect of monomer concentration on graft yield. The monomer concentration was varied from 27.56×10^{-2} to 122.044×10^{-2} mol/L. The data indicate that the percentage of grafting increases steadily with an increase of monomer concentration. A probable explanation to these observations might be: (1) complexation of silk with monomer which is required for enhancing monomer activity, and (2) the gel effect [16], i.e., the increase in viscosity of the medium due to the solubility of poly(methyl

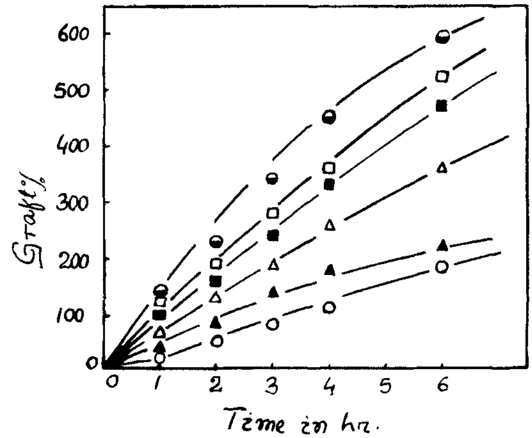


FIG. 1. Effect of [MMA] on graft yield: [$FeCl_3$] = 2.5 × 10^{-3} mol/L, [cysteine] = 1.0 × 10^{-3} mol/L, [$HClO_4$] = 37.315 × 10^{-2} mol/L, temperature = 50°C, M:L = 1:100, (○) [MMA] = 27.56 × 10^{-2} mol/L, (▲) [MMA] = 46.94 × 10^{-2} mol/L, (△) [MMA] = 65.71 × 10^{-2} mol/L, (■) [MMA] = 84.592 × 10^{-2} mol/L, (□) [MMA] = 103.268 × 10^{-2} mol/L, (◒) [MMA] = 122.044 × 10^{-2} mol/L.

methacrylate) in its own monomer which would be more pronounced at higher monomer concentrations. This causes hindrance in termination, particularly by coupling of growing polymer chains. The gel effect also causes swelling of silk, thus facilitating diffusion of monomer to growing chains and active sites on the silk backbone, thereby enhancing grafting.

Effect of Initiator Concentration

The graft copolymerization of methyl methacrylate onto silk was studied by varying the ferric chloride concentration from 1.25 × 10^{-3} to 30.0 × 10^{-3} mol/L. The graft yield increases with an increase of ferric chloride concentration up to 2.5 × 10^{-3} mol/L and thereafter it decreases with a further increase of the initiator concentration (Fig. 2).

In an initiating system consisting of Fe^{3+}, cysteine, perchloric acid, and silk, free radical formation might take place in the following way.

First, the oxidant (Fe^{3+}) might form a complex with the activator (cysteine), which subsequently breaks up, giving rise to either thiol radicals (I) or carboxyllic radicals (II).

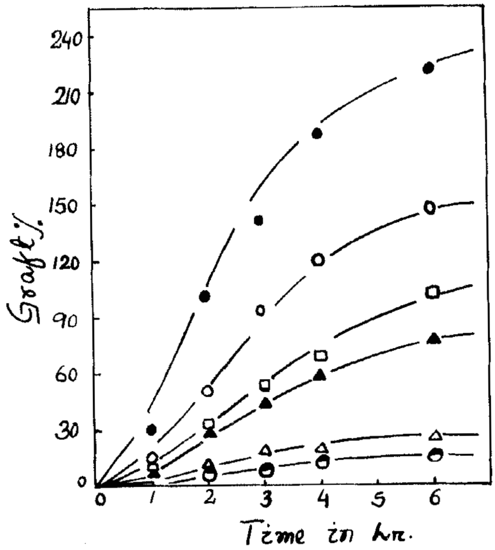
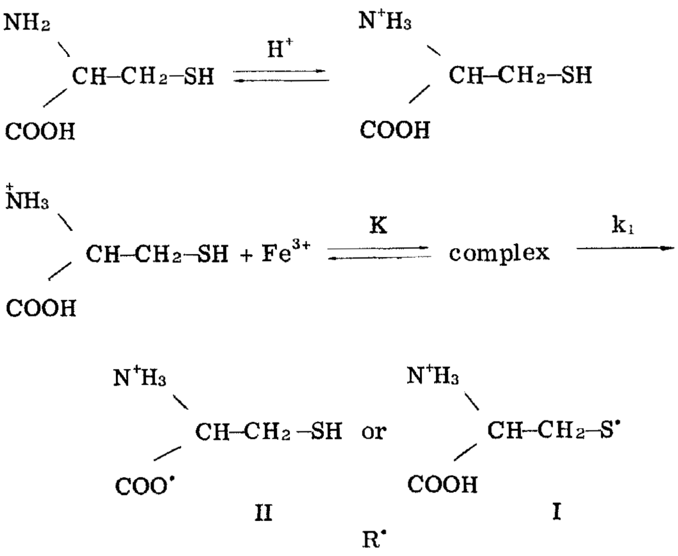


FIG. 2. Effect of [$FeCl_3$] on graft yield: [cysteine] = 2.5×10^{-3} mol/L, [$HClO_4$] = 23.32×10^{-2} mol/L, [MMA] = 46.94×10^{-2} mol/L, temperature = 50°C, M:L = 1:100, (○) [$FeCl_3$] = 1.25×10^{-3} mol/L, (●) [$FeCl_3$] = 2.5×10^{-3} mol/L, (□) [$FeCl_3$] = 5.0×10^{-3} mol/L, (▲) [$FeCl_3$] = 10.0×10^{-3} mol/L, (△) [$FeCl_3$] = 20.0×10^{-3} mol/L, (◒) [$FeCl_3$] = 30.0×10^{-3} mol/L.



$$\mathrm{(NH_2)(COOH)CH{-}CH_2{-}SH} \overset{H^+}{\rightleftharpoons} \mathrm{(N^+H_3)(COOH)CH{-}CH_2{-}SH}$$

$$\mathrm{(\overset{+}{N}H_3)(COOH)CH{-}CH_2{-}SH} + \mathrm{Fe^{3+}} \overset{K}{\rightleftharpoons} \text{complex} \xrightarrow{k_1}$$

$$\underset{\text{II}}{\mathrm{(N^+H_3)(COO^\bullet)CH{-}CH_2{-}SH}} \text{ or } \underset{\text{I}}{\mathrm{(N^+H_3)(COOH)CH{-}CH_2{-}S^\bullet}}$$

$$\mathrm{R^\bullet}$$

The free radicals (I or II = R$^\bullet$) might abstract hydrogen from the amino or carboxyl groups present in the silk backbone to form silk macroradicals which might interact with the monomer to initiate grafting.

$$\sim\sim\sim S + R^\bullet \xrightarrow{k_2} \sim\sim S^\bullet + \text{cysteine}$$

(i) Initiation:

$$\sim\sim\sim S^\bullet + M \xrightarrow{k_i} \sim\sim\sim SM^\bullet$$

(ii) Propagation:

$$\sim\sim\sim SM^\bullet + M \xrightarrow{k_p} \sim\sim\sim SM_2^\bullet$$

$$\vdots$$

$$\sim\sim\sim SM_{n-1}^\bullet + M \xrightarrow{k_p} \sim\sim\sim SM_n^\bullet$$

(iii) Termination:

$$\sim\sim\sim SM_n^\bullet + Fe^{3+} \xrightarrow{k_t} \text{grafted polymer}$$

(iv) Oxidation:

$$\sim\sim\sim S^\bullet + Fe^{3+} \xrightarrow{k_0} \text{oxidation products} + Fe^{2+} + H^+$$

Applying the steady-state assumptions to both [R$^\bullet$] and [SM$^\bullet$] separately, the following expressions have been derived.

$$\frac{d[R^\bullet]}{dt} = k_1K[Cy][Fe^{3+}] - k_2[R^\bullet][S] = 0$$

Therefore

$$[R^\bullet] = \frac{k_1K[Cy][Fe^{3+}]}{k_2[S]}$$

$$\frac{d[S^\bullet]}{dt} = k_2[R^\bullet][S] - k_i[S^\bullet][M] - k_0[S^\bullet][Fe^{3+}] = 0$$

Therefore:

$$[S^\bullet] = \frac{k_2[R^\bullet][S]}{k_i[M] + k_0[Fe^{3+}]}$$

$$\frac{d[SM^\bullet]}{dt} = k_i[S^\bullet][M] - k_t[SM^\bullet][Fe^{3+}] = 0$$

Therefore

$$[SM^\bullet] = \frac{k_i[S^\bullet][M]}{k_t[Fe^{3+}]}$$

$$= \frac{k_ik_1K[Cy][M]}{k_t\{k_i[M] + k_0[Fe^{3+}]\}}$$

$$R_p = k_p[SM^\bullet][M]$$

$$= \frac{k_pk_ik_1K[Cy][M]^2}{k_t\{k_i[M] + k_0[Fe^{3+}]\}}$$

The initial increase in graft yield with the increase of Fe^{3+} concentration might be due to the increase in the number of free radicals ($R^\bullet$) which initiate the formation of graft copolymer.

But beyond 2.5×10^{-3} mol/L of ferric chloride concentration, the decrease in graft yield could be due to (1) the oxidation of free radicals produced on the backbone of the silk fiber to give rise to oxidation products at a higher initiator concentration, (2) the formation of a larger amount of homopolymer, or (3) termination of the graft macroradicals by the metal ions at high initiator concentrations.

Effect of Cysteine Concentration

The effect of cysteine concentration on the graft copolymerization of methyl methacrylate onto silk was studied by varying the cysteine concentration from 0.25×10^{-3} to 10.0×10^{-3} mol/L. The results show that the graft yield increases significantly with an increase of cysteine concentration up to 0.50×10^{-3} mol/L and thereafter it decreases (Fig. 3).

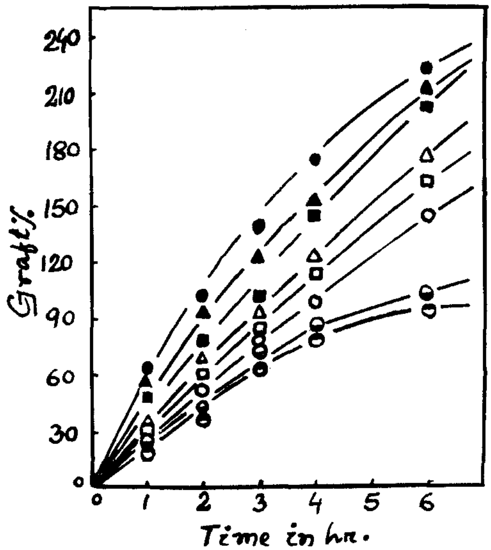
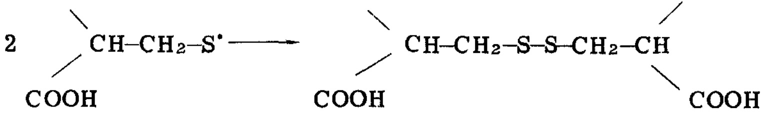


FIG. 3. Effect of [cysteine] on graft yield: [$FeCl_3$] = 2.5 × 10^{-3} mol/L, [$HClO_4$] = 23.32 × 10^{-2} mol/L, [MMA] = 46.94 × 10^{-2} mol/L, temperature = 50°C, M:L = 1:100, (◒) [cysteine] = 0.25 × 10^{-3} mol/L, (●) [cysteine] = 0.5 × 10^{-3} mol/L, (▲) [cysteine] = 1.0 × 10^{-3} mol/L, (■) [cysteine] = 1.25 × 10^{-3} mol/L, (△) [cysteine] = 2.5 × 10^{-3} mol/L, (□) [cysteine] = 3.75 × 10^{-3} mol/L, (○) [cysteine] = 5.0 × 10^{-3} mol/L, (◓) [cysteine] = 10.0 × 10^{-3} mol/L.

The increase in the graft yield with the activator concentration could be ascribed to the formation of a large amount of cysteine radicals which initiate the graft copolymerization. The decrease in graft yield beyond 0.50 × 10^{-3} mol/L of cysteine could be due to the following reasons: (a) The concentration of cysteine radicals might be decreasing due to the formation of cystine molecules in the following manner:



(b) At higher cysteine concentrations the cysteine free radicals formed might interact with the monomer to form a large amount of homopolymer. (c) The diffusion of cysteine molecules might be hindered due to the increase in the viscosity of the medium.

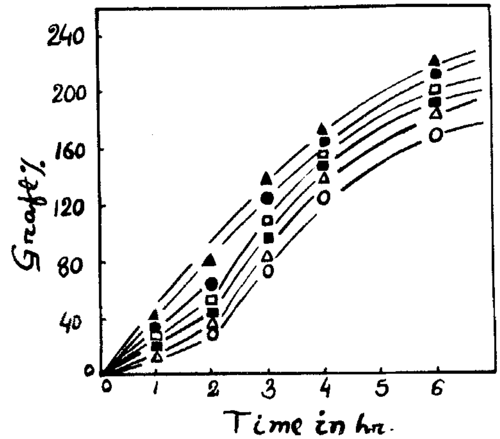


FIG. 4. Effect of [$HClO_4$] on graft yield: [$FeCl_3$] = 2.5×10^{-3} mol/L, [cysteine] = 1.0×10^{-3} mol/L, [MMA] = 46.94×10^{-2} mol/L, temperature = 50°C, M:L = 1:100, (○) [$HClO_4$] = 4.665×10^{-2} mol/L, (△) [$HClO_4$] = 9.33×10^{-2} mol/L, (□) [$HClO_4$] = 13.99×10^{-2} mol/L, (●) [$HClO_4$] = 23.32×10^{-2} mol/L, (▲) [$HClO_4$] = 37.315×10^{-2} mol/L, (■) [$HClO_4$] = 46.65×10^{-2} mol/L.

(d) Some species might be forming which might act as radical scavengers, as a result of which the graft yield would decrease.

Effect of Acid Concentration

Graft copolymerization onto silk fibers was carried out in the presence of perchloric acid. The effect of the acid concentration was studied by varying the concentration of perchloric acid from 4.66×10^{-2} to 46.65×10^{-2} mol/L. The results show that the graft yield increases significantly with an increase of the acid concentration up to 37.31×10^{-2} mol/L and then decreases (Fig. 4). These observations could be attributed to a variety of reasons.

The cation binding capacity of silk is high in acidic medium. This is due to the fact that besides the free carboxyl groups at the ends of the polypeptide chains of silk, free carboxyl groups are created in the presence of acid as a result of the breakage of the salt linkages:

$$R-\overset{|}{\underset{|}{C}}-COO^{-}\ldots\overset{+}{H_3N}-\overset{|}{\underset{|}{C}}-R \xrightarrow{\text{acid}} R-\overset{|}{\underset{|}{C}}-COOH + H_2N-\overset{|}{\underset{|}{C}}-R$$

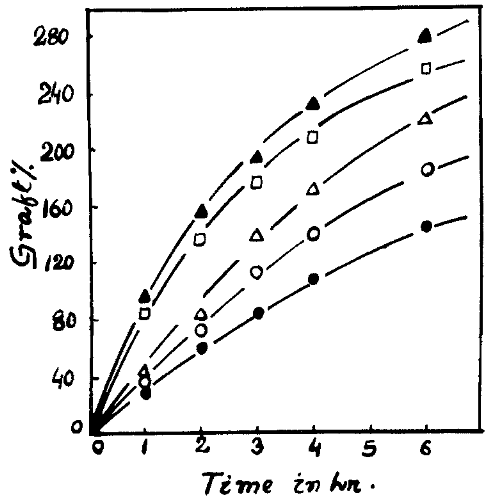


FIG. 5. Effect of temperature of graft yield: $[FeCl_3] = 2.5 \times 10^{-3}$ mol/L, [cysteine] $= 1.0 \times 10^{-3}$ mol/L, $[HClO_4] = 37.315 \times 10^{-2}$ mol/L, [MMA] $= 46.94 \times 10^{-2}$ mol/L, M:L = 1:100, (●) temperature = 40°C, (○) temperature = 45°C, (△) temperature = 50°C, (□) temperature = 55°C, (▲) temperature = 60°C.

Hence more free carboxyl and amino groups, which are the active centers for the production of silk macroradicals, are formed as the concentration of the acid is increased. The decrease in graft yield beyond 37.31×10^{-2} mol/L of acid concentration could be due to the fact that at higher acid concentrations the cysteine loses its reducing properties. Further, at higher acid concentrations the acid anions might be forming some type of complex with Fe^{3+}, thereby reducing its oxidizing capacity.

Effect of Temperature on Graft Yield

The graft copolymerization reaction was studied at five different temperatures ranging from 40 to 60°C. A perusal of the results indicates that the graft yield increases steadily with an increase of temperature (Fig. 5). A probable explanation for these observations could be the greater activation energy. As the temperature is increased, the swellability of silk, the solubility of monomer, and its diffusion rates are enhanced. As a result, the graft yield increases.

From the Arrhenius plot of log R_p versus 1/T, the overall activation energy was found to be 7.830 kcal/mol (Fig. 6). Using the

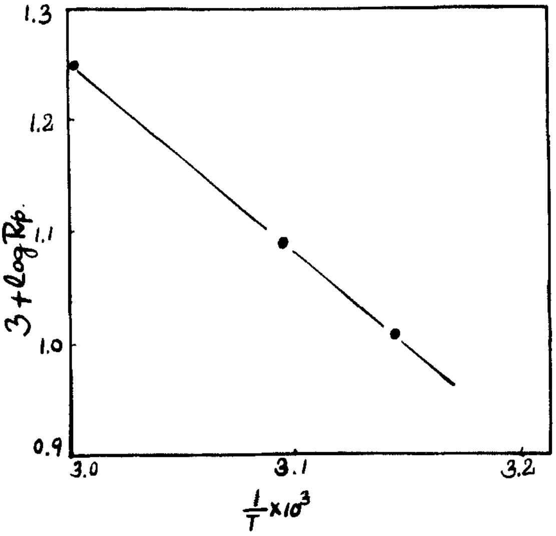


FIG. 6. Arrhenius plot of log R_p versus 1/T for grafting MMA onto silk using Fe^{3+}-cysteine redox system.

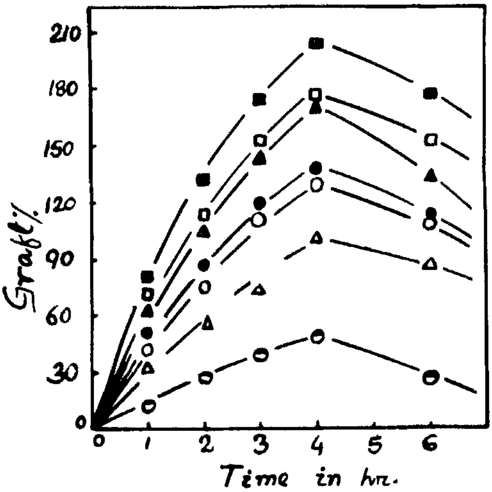


FIG. 7. Effect of solvents on graft yield: [$FeCl_3$] = 2.5×10^{-3} mol/L, [cysteine] = 1.0×10^{-3} mol/L, [$HClO_4$] = 37.315×10^{-2} mol/L, [MMA] = 46.94×10^{-2} mol/L, temperature = 50°C, M:L = 1:100, solvent = 10% v/v, (■) CH_3OH, (□) C_2H_5OH, (▲) propanol, (●) butanol, (○) HCOOH, (△) CH_3COOH, (⊖) hexane.

value of $E_p - \frac{1}{2}E_t = 4 \sim 5$ kcal/mol given by Tobolsky [17], where E_p and E_t are the energies of propagation and termination, respectively, the activation energy of initiation, E_d, can be calculated from these values as follows:

$$E_d = 2E_a - (2E_p - E_t)$$

where E_a is the overall activation energy. E_d = 6.66 kcal/mol for the total conversion of MMA to PMMA.

Effect of Reaction Medium

The nature of the reaction medium plays an important role in the graft copolymerization reaction. Hence it is necessary to study the effects of different solvents such as protic, dipolar protic, and nonpolar solvents on graft yield and to select the most suitable solvent for the graft copolymerization of MMA onto silk fibers. The results of various solvents affecting the graft yield follow the order (Fig. 7): methanol > ethanol > propanol > butanol > HCOOH > CH_3COOH > hexane.

The variation in graft yield upon using different solvents could be associated with differences in their (1) capability of swelling of silk, (2) miscibility with monomer, (3) formation of solvent radicals from the primary radical species of the initiating system, (4) contribution of the solvent radical in the activation of silk, and (5) termination of the graft chain radical and silk macroradical via chain transfer. While the first four factors favor grafting by simplifying the access and diffusion of monomer, the last factor adversely affects grafting by lowering the molecular size of the graft.

Effect of Different Monomers on Graft Yield

The graft copolymerization reaction was investigated with different monomers. The order of their activities as far as their graft yield is concerned is as follows: methyl methacrylate > styrene > acrylonitrile.

ACKNOWLEDGMENTS

This project is financed by C.S.I.R., New Delhi, India, by Project No. 14(12)/76-EMR-II. One of the authors (G.P.) is thankful to C.S.I.R., New Delhi, for offering a Junior Fellowship.

REFERENCES

[1] P. L. Nayak, J. Macromol. Sci.–Rev. Macromol. Chem., C14, 193 (1976).

[2] P. L. Nayak, Ibid., C17, 267 (1969).

[3] K. Arai, Block Graft Copolym., 1, 193 (1973).

[4] J. C. Watt, J. Macromol. Sci.–Rev. Macromol. Chem., C5, 176 (1970).

[5] A. Hebeish, S. H. Abdel-Fattah, and A. Bendak, Angew. Makromol. Chem., 37, 11 (1974).

[6] A. Hebeish and A. Bendak, J. Appl. Polym. Sci., 18, 1305 (1974).

[7] A. Kantouch, S. Abdel-Fattah, and A. Hebeish, Polym. J., 3, 375 (1972).

[8] A. Kantouch, A. Hebeish, and A. Bendak, Text. Res. J., 42, 7 (1972).

[9] A. Bendak and A. Hebeish, J. Appl. Polym. Sci., 17, 1953 (1973).

[10] P. L. Nayak, S. Lenka, and N. C. Pati, Angew. Makromol. Chem., 68, 117 (1978).

[11] P. L. Nayak, S. Lenka, and N. C. Pati, J. Appl. Polym. Sci., 23, 1345 (1979).

[12] P. L. Nayak, S. Lenka, and N. C. Pati, Angew. Makromol. Chem., 75, 29 (1979).

[13] N. C. Pati, S. Lenka, and P. L. Nayak, J. Macromol. Sci.–Chem., A13(8), 1157 (1979).

[14] P. L. Nayak, S. Lenka, and N. C. Pati, Angew. Makromol. Chem., 85, 29 (1980).

[15] G. Panda, N. C. Pati, and P. L. Nayak, J. Appl. Polym. Sci., Communicated.

[16] S. Dilli, J. L. Garnett, E. C. Martin, and D. H. Phvoc, J. Polym. Sci., Polym. Symp., 25, 1479 (1980).

[17] A. V. Tobolsky, J. Colloid Sci., 12, 325 (1957).

Accepted by editor January 30, 1980
Received for publication March 5, 1980