Graft Copolymerization of Methyl Methacrylate onto Natural Polypeptides (Wool and Silk) in the Presence of Potassium Peroxydiphosphate-2-Amino Ethane Thiol System as Redox Initiator

Munmaya K. Mishra[a]; Bidu L. Sar[ab]

[a] Gaylord Research Institute Whippany, New Jersey [b] Department of Chemistry, Ravenshaw College, Orissa, India

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MUNMAYA K. MISHRA* and BIDU L. SAR†

Gaylord Research Institute
Whippany, New Jersey 07981

ABSTRACT

In an attempt to initiate grafting, methyl methacrylate (MMA) has been grafted separately to Chokla wool and Mulberry silk in aqueous medium by using the potassium peroxydiphosphate-2-amino ethane thiol (PP-AET) system as redox initiator. Percent grafting is determined as a function of concentration of MMA, concentration of PP, concentration of AET, concentration of sulfuric acid, time, and temperature. Sulfuric acid is found to catalyze the reaction to a certain extent. The rate of grafting (R_p) and the induction period (I_p) of MMA are determined as a function of the total initial monomer concentration. The moisture regain properties and infrared spectra are studied. The reaction scheme is pictured.

*To whom correspondence should be addressed at 78-A, Kalpana Area, Bhubaneswar 751014, Orissa, India.
†Present address: Department of Chemistry, Ravenshaw College, Cuttack 3, Orissa, India.

INTRODUCTION

Graft copolymerization of vinyl monomers onto natural and synthetic macromolecules is a fascinating field of research [1-4] with unlimited potential applications. With the wide variety of vinyl monomers available today, grafting promises to be a potentially powerful method for producing substantial modification of such fiber properties as stereoregularity, hygroscopicity, thermal stability, antistatic properties, and soil resistance without drastically changing the basic properties of the fiber matrix [5].

One of the major problems in grafting is the formation of homopolymers which pose enormous difficulties in the purification of the graft. In addition, the formation of homopolymers leads to considerable waste of expensive monomer. In order to overcome this difficulty, attempts have been made to find new initiating systems that will selectively cause grafting or at least minimize the formation of homopolymers. Various initiating systems have been tried with varying degrees of success.

During the last three decades, peroxydisulfate has been extensively used as a water-soluble initiator for polymerization. Peroxydiphosphate, $P_2O_8^{4-}$, which is isoelectronic and isostructural [6-9] with peroxydisulfate, received relatively little attention till Edwards et al. [10-14] recognized this ion as a free radical initiator.

Wool and silk are natural polypeptides and contain various functional groups such as –OH, –NH$_2$, –SH, –CO$_2$H, and =NH. All these groups are also capable of forming a complex with peroxydiphosphate to give free radical sites by abstraction of hydrogen. The sites are directly on the fiber backbone where grafting of the appropriate vinyl monomer can occur. With this idea in mind, a systematic study on grafting onto wool [15-18] and silk [19, 20] by peroxydiphosphate alone or as part of a redox system has been reported. In this paper we report on grafting of methyl methacrylate (MMA) onto wool and silk as a function of various reaction parameters along with a study of moisture regain properties and infrared analysis of the grafted polymer.

MATERIALS AND METHODS

The purification of wool, silk, monomer, and the grafting reaction and the separation of homopolymer from the grafted fiber were carried out according to our previous procedure [15, 19]. All other reagent used were of BDH, A.R. grade. Peroxydiphosphate was a gift sample from FMC Corp., U.S.A. The graft polymers were separated from the fiber backbone by the procedure described elsewhere [4]. The moisture regain of all the grafted and parent fibers was determined by vacuum desiccator as described by Urquart and Williams

[21]. The graft percentage is calculated as the percent increase in weight over the original weight of the fiber. R_p, the rate of polymerization, is calculated as the percentage graft per second.

Evidence of Grafting and IR Spectra

A physical mixture of poly(methyl methacrylate) (PMMA) and wool after extraction with benzene is subjected to HCl treatment. No residue is obtained, indicating that homopolymer is completely removed by benzene extraction. Isolation of polymer after treatment with HCl from the grafted material constituted evidence for grafting.

The IR spectra of grafted PMMA showed a strong absorption at 1730 cm^{-1} which is attributed to C=O of PMMA. No such band is observed in the IR spectrum of wool.

Physical Characterization of Graft Copolymer

The treatment of wool and silk with the methyl methacrylate-potassium peroxydiphosphate-2-amino ethane thiol (MMA-PP-AET) system results in a decrease in the moisture regain of the grafted samples compared to the parent fiber (Table 1). This could be ascribed to the deposition of the PMMA in the amorphous regions of the samples and to the hydrophobic nature of this polymer.

RESULTS AND DISCUSSION

Effect of Monomer Concentration

In accordance with the mechanism an increase in the concentration of vinyl monomer should enhance grafting. It is observed from Table 2 that with an increase in concentration of MMA, the percentage of grafting increases in the case of wool and silk. The increase in graft yield might be attributed to a couple of reasons. (1) Complexation of the fiber with monomer enhances its reactivity, thereby increasing the graft yield. (2) The other reason may be the gel effect [22], i.e., an increase in viscosity of medium due to the solubility of the PMMA in its own monomer would be more pronounced at higher monomer concentrations. This causes hindrance in termination, particularly by coupling of growing polymer chains. This gel effect also causes swelling of the fiber, thus facilitating diffusion of monomer to the growing chain and active sites on the fiber backbone, thereby enhancing grafting.

TABLE 1. Moisture Regain Behavior of Grafted Samples

Graft (%)		Moisture regain (%)	
Wool	Silk	Wool	Silk
0	0	7.35	8.25
50.1	41.2	3.21	2.87
100.0	78.8	1.98	2.68
145.1	118.3	1.23	2.13
258.6	187.4	1.01	1.86

Effect of Peroxydiphosphate Concentration

Table 2 shows that the maximum graft yield of both wool and silk occurs at a concentration of PP = 66×10^{-4} mol/L. When the concentration exceeds this value, percent grafting decreases. When the concentration of peroxydiphosphate is increased, a large number of $H_2PO_4^{\cdot}$, $^{\cdot}OH$, and $HPO_4^{\cdot -}$ radicals are formed. These radicals interact with the sites which initiate grafting, thereby increasing the graft yield. As the concentration of PP increases beyond 60×10^{-4} mol/L, 1) there will be an abundance of free radicals in solution due to the increase of concentration of oxidant which may terminate the growing chain, 2) at higher concentrations of oxidant the fiber macroradicals may be oxidized to give rise to the oxidation product, and 3) graft formation and homopolymerization depend upon the direct attack of PP on the fiber and monomer. At higher concentrations of PP this may interact with the monomer to give rise to homopolymer, thereby decreasing grafting. All these factors are responsible for the low graft yield at higher PP concentrations.

Effect of H_2SO_4 Concentration

It is apparent from Table 2 that the percentage grafting in the cases of wool and silk increases up to 14.8×10^{-2} mol/L, and with a further increase of acid concentration the grafting decreases. It is evident that the reactions of peroxydiphosphate are subject to acid catalysis [23, 24]. Hence it is possible that the reactions of peroxydiphosphate, which is both a peroxide and an oxyanion, i.e., an oxyanion derivative of H–O–O–H are strongly subject to acid catalyst. Peroxydiphosphate is protonated due to its high negative charge, giving rise to various species like $HP_2O_8^{3-}$, $H_2P_2O_8^{2-}$, $H_3P_2O_8^{-}$, $H_4P_2O_8$, $H_5P_2P_8^{+}$, and $H_6P_2O_8^{2-}$. It is stated by Santappa et al. [25] that the reaction rate

TABLE 2. Effect of Variables on Graft Copolymerization onto Wool and Silk[a]

Sample no.	$[PP] \times 10^4$ mol/L	$[MMA] \times 10^2$ mol/L	$[AET] \times 10^4$ mol/L	$[H_2SO_4] \times 10^2$ mol/L	Temperature (°C)	Graft (%) Wool	Graft (%) Silk
1	50	46.94	6.25	9.8	50	187.8	100.2
2	60	46.94	6.25	9.8	50	214.7	123.1
3	80	46.94	6.25	9.8	50	200.2	105.6
4	100	46.94	6.25	9.8	50	175.3	87.3
5	60	27.98	6.25	9.8	50	114.6	62.6
6	60	65.72	6.25	9.8	50	258.6	145.0
7	60	84.50	6.25	9.8	50	341.5	187.3
8	60	46.94	6.25	4.8	50	199.1	100.1
9	60	46.94	6.25	14.8	50	224.3	118.3
10	60	46.94	6.25	24.8	50	200.7	101.6
11	60	46.94	6.25	32.5	50	165.8	78.8
12	60	46.94	3.75	14.8	50	197.3	100.5
13	60	46.94	5.00	14.8	50	218.2	111.6
14	60	46.94	7.50	14.8	50	187.7	87.3
15	60	46.94	10.00	14.8	50	148.7	82.6
16	60	46.94	6.25	9.8	45	188.1	61.1
17	60	46.94	6.25	9.8	55	254.9	290.4

[a]Reaction conditions: Total volume including water = 20 cm^3; fiber = 0.2 g, time = 6 h, dioxane = 0.5 cm^3.

as well as the concentration of $H_3P_2O_8^-$ and $H_4P_2O_8$ increase with an increase in H^+ concentration. In the lower concentration range of the acid the most active species, $H_3P_2O_8^-$, may be formed. It interacts with various other species, giving rise to a multitude of free radicals which enhance grafting. However, the less active species like $H_5P_2O_8^+$ and $H_6P_2O_8^{2+}$ may be formed at higher acid concentrations, thereby decreasing the graft yield.

Effect of 2-Amino Ethane Thiol Concentration

It is observed in the case of wool and silk that with increasing AET concentration up to 6.25×10^{-4} mol/L the graft yield increases and beyond this concentration the graft yield decreases (Table 2). The decrease in graft yield at higher concentration may be due to 1) an increase in AET radicals which terminate the growing polymer chain, 2) higher concentrations of AET which acts as a radical scavenger, thereby decreasing grafting, and 3) an increasing amount of homopolymer.

Effect of Temperature and Time

The effect of temperature upon the percentage of grafting was investigated. From Table 2 it is observed that grafting increases in both cases with an increase of temperature. With an increase of temperature the percentage grafting increases due to the following reasons: 1) solution of the monomer in the reaction medium and its diffusion from the solution phase to the fiber phase, and 2) adsorption of monomer on the fiber and its complexation with the fiber molecules to enhance the availability and reactivity of monomer.

From the Arrhenius plot of log R_p vs $1/T$, the overall activation energy is found to be 21.9 and 27.6 kcal/mol for wool and silk, respectively (Fig. 1).

The induction period (I_p) and rate of grafting (R_p) are determined for wool and silk as functions of the total monomer concentration. Figures 2 and 3 show plots of the percentage of grafting for grafting onto wool and silk, respectively, versus time. The (R_p) as well as the I_p have been determined from the slopes. It is apparent from Figs. 3 and 4 that both R_p and I_p are affected by the total initial monomer concentration. Table 3 shows that MMA at a monomer concentration of 84.5×10^{-2} mol/L yields a maximum rate of grafting (R_p = 1.52 for wool and 0.4 for silk) with an I_p of 30 min for wool and 20 min for silk. This indicates that the rate of grafting increases and the induction period decreases with an increase of monomer concentration.
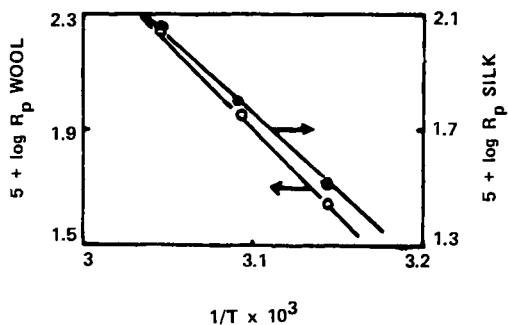
FIG. 1. 0.2 g fiber; reaction volume including water = 20 cm^3, [PP] = 60×10^{-4} mol/L, [AET] = 6.25×10^{-4} mol/L, [H$_2$SO$_4$] = 9.8×10^{-2} mol/L, [MMA] = 46.94×10^{-2} mol/L, time = 6 h, dioxane = 0.5 cm^3.
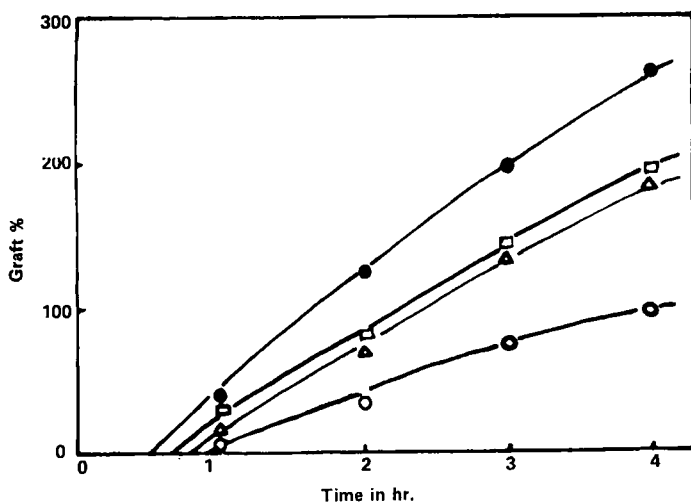

FIG. 2. Grafting onto wool. 0.2 g fiber; reaction volume including water = 20 cm^3; [PP] 60×10^{-4} mol/L; [AET] = 6.25×10^{-4} mol/L; [H$_2$SO$_4$] = 9.8×10^{-2} mol/L; temperature = 50°C; [MMA] = 27.98×10^{-2} (o), 46.94×10^{-2} (△), 65.72×10^{-2} (□), and 84.50×10^{-2} (●) mol/L; dioxane = 0.5 cm^3.
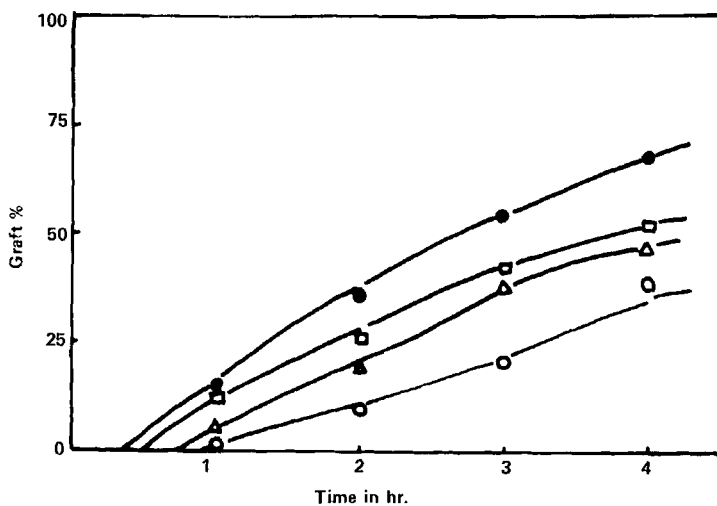
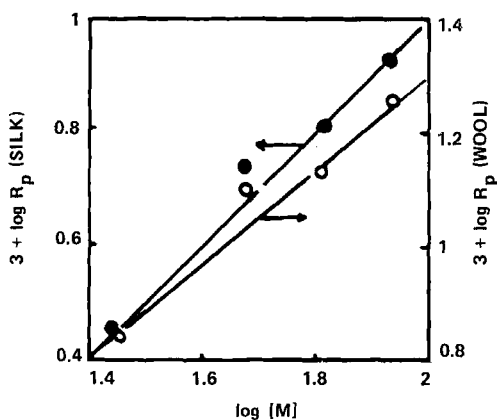FIG. 3. Grafting onto silk. Values as for Fig. 2.

FIG. 4. 0.2 g fiber, reaction volume including water = 20 cm^3, [PP] = 60 × 10^{-4} mol/L, [AET] = 6.25 × 10^{-4} mol/L, [H$_2$SO$_4$] = 9.8 × 10^{-2} mol/L, temperature = 50°C, time = 6 h, dioxane = 0.5 cm^3.
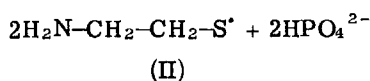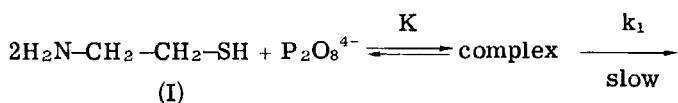
TABLE 3. Effect of Total Initial Monomer (MMA) Concentration upon Percentage of Grafting onto Wool and Silk[a]

Sample no.	Initial concentration of MMA (mol/L)	Initial rate of grafting (R_p) (%/min)		Induction period (I_p) (min)	
		Wool	Silk	Wool	Silk
1	27.98×10^{-2}	0.69	0.20	55	55
2	46.94×10^{-2}	1.04	0.25	48	42
3	65.72×10^{-2}	1.15	0.33	42	30
4	84.50×10^{-2}	1.52	0.4	30	20

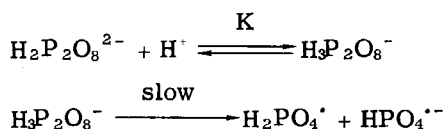[a]0.2 g fiber, reaction volume including water = 20 cm^3, $[PP] = 60 \times 10^{-4}$ mol/L, $[AET] = 6.25 \times 10^{-4}$ mol/L, $[H_2SO_4] = 9.8 \times 10^{-2}$ mol/L, temperature = 50°C.
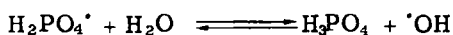
Reaction Mechanism

The following plausible mechanism has been suggested for grafting MMA onto natural polypeptides using the PP-AET redox system. In this initiating system the redox component is AET (I). The free radical (II) is generated by abstraction of the reactive hydrogen from the thiol groups. It is likely that the peroxydiphosphate, $P_2O_8^{4-}$, first forms a complex with AET, and the complex breaks down slowly to give rise to AET radicals which are the active species:

$$2H_2N-CH_2-CH_2-SH + P_2O_8^{4-} \xrightarrow{K} \text{complex} \xrightarrow[\text{slow}]{k_1}$$

$$\text{(I)}$$

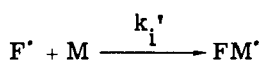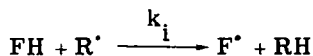$$2H_2N-CH_2-CH_2-S^\bullet + 2HPO_4^{2-}$$

$$\text{(II)}$$

The second possibility of formation of free radicals is due to the decomposition of PP during the grafting reaction [15]. The reaction scheme is
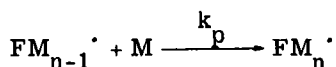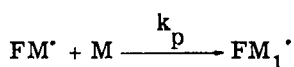
$$H_2P_2O_8^{2-} + H^+ \xrightarrow{K} H_3P_2O_8^-$$

$$H_3P_2O_8^- \xrightarrow[]{\text{slow}} H_2PO_4^\bullet + HPO_4^{\bullet-}$$

$$H_2PO_4^{\cdot} + H_2O \rightleftharpoons H_3PO_4 + {}^{\cdot}OH$$

$$HPO_4^{\cdot-} + H_2O \rightleftharpoons H_2PO_4^{-} + {}^{\cdot}OH$$

The above free radicals are represented by $R^{\cdot}$. This $R^{\cdot}$ abstracts hydrogen from the fiber backbone to yield fiber macroradicals.
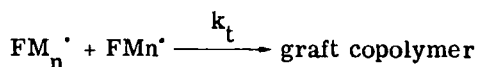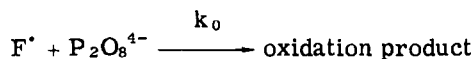
Initiation:

$$FH + R^{\cdot} \xrightarrow{k_i} F^{\cdot} + RH$$

$$F^{\cdot} + M \xrightarrow{k_i'} FM^{\cdot}$$

Propagation:

$$FM^{\cdot} + M \xrightarrow{k_p} FM_1^{\cdot}$$

$$FM_{n-1}^{\cdot} + M \xrightarrow{k_p} FM_n^{\cdot}$$

Termination:

$$FM_n^{\cdot} + FMn^{\cdot} \xrightarrow{k_t} \text{graft copolymer}$$

Oxidation:

$$F^{\cdot} + P_2O_8^{4-} \xrightarrow{k_0} \text{oxidation product}$$

where FH is the fiber, M is the monomer, and $F^{\cdot}$ and $FM^{\cdot}$ are the corresponding radicals. By applying the steady-state assumption to both $[R^{\cdot}]$ and $[FM^{\cdot}]$ separately, the following expressions have been derived:

$$\frac{d[R^{\cdot}]}{dt} = Kk_1[AET]^2[P_2O_8^{4-}] - k_i[FH][R^{\cdot}] = 0$$

$$[R^{\cdot}] = \frac{Kk_1[AET]^2[P_2O_8^{4-}]}{k_i[FH]}$$

$$\frac{d[FM^\cdot]}{dt} = k_i^1[F^\cdot][M] - k_t[FM^\cdot]^2 = 0$$

$$[FM^\cdot] = (\frac{k_i^1[F^\cdot][M]}{k_t})^{1/2}$$

$$\frac{d[F^\cdot]}{dt} = k_i[FH][R^\cdot] - k_i^1[F^\cdot][M] = 0$$

$$[F^\cdot] = \frac{k_i[FH][R^\cdot]}{k_i^1[M]}$$

Putting the value of

$$[R^\cdot], [F^\cdot] = \frac{Kk_1[AET]^2[P_2O_8^{4-}]}{k_i^1[M]}$$

and putting the value of

$$[F^\cdot], [FM^\cdot] = \frac{K^{1/2}k_1^{1/2}[AET][P_2O_8^{4-}]^{1/2}}{k_t^{1/2}}$$

then

$$R_p = k_p[FM^\cdot][M] = k_p(\frac{Kk_1}{k_t})^{1/2}[AET][P_2O_8^{4-}]^{1/2}[M]$$

The dependence of R_p on $[M]$, $[AET]$, and $[P_2O_8^{4-}]^{1/2}$, which are experimentally observed, favors the above rate expression.

Thus the plot of log R_p vs log $[M]$ should be linear (Fig. 4). From the slope the monomer exponents for silk and wool are calculated to be 1.0 and 0.9, respectively. This nearness to unity shows the validity of the above rate expression. Taking into account of oxidation step, the value of R_p will be

$$R_p = \frac{k_p K^{1/2} k_i^{'1/2} k_1^{1/2} [AET][P_2O_8^{4-}]^{1/2}[M]^{3/2}}{k_t^{1/2} \{k_i^1[M] + k_0[P_2O_8^{4-}]\}^{1/2}}$$

REFERENCES

[1] M. K. Mishra, J. Macromol. Sci.–Rev. Macromol. Chem., C19(2), 193 (1980).

[2] M. K. Mishra, Ibid., C20(1), 149 (1981).

[3] P. L. Nayak, Ibid., C14(2), 193 (1976); C17(2), 267 (1979).

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

[5] W. L. Wasley, Ibid., 1, 311 (1973).

[6] J. W. Vanaderhoff, in Vinyl Polymerization, Part II (G. E. Ham, ed.), Dekker, New York, 1969, Chap. I.

[7] W. K. Wilmarth and A. Haim, in Peroxide Reaction Mechanisms (J. O. Edwards, ed.), Wiley-Interscience, New York, 1962, p. 175.

[8] A. A. Green, J. O. Edwards, and P. Jones, Inorg. Chem., 5, 1858 (1966).

[9] A. Indelli and P. Bonora, J. Am. Chem. Soc., 88, 924 (1966).

[10] M. Anderson, J. O. Edwards, A. A. Green, and M. D. Wiswell, Inorg. Chem. Acta, 3, 655 (1969).

[11] R. J. Lussier, W. M. Risen, and J. O. Edwards, J. Phys. Chem., 74, 4039 (1970).

[12] E. Chaffee, I. I. Creaser, and J. O. Edwards, Inorg. Nucl. Chem. Lett., 7, 1 (1971).

[13] J. O. Edwards, Coord. Chem. Rev., 8, 87 (1972).

[14] I. I. Creaser and J. O. Edwards, in Topics in Phosphorus Chemistry, Vol. 7 (E. J. Griffith and M. Grayson, eds.), Wiley-Interscience, New York, 1972, p. 379.

[15] P. L. Nayak, S. Lenka, and M. K. Mishra, J. Appl. Polym. Sci., 25, 63 (1980).

[16] P. L. Nayak, S. Lenka, and M. K. Mishra, Ibid., 26, 733 (1981).

[17] P. L. Nayak, S. Lenka, and M. K. Mishra, Angew. Makromol. Chem., 90, 155 (1980).

[18] P. L. Nayak, S. Lenka, and M. K. Mishra, J. Macromol. Sci.– Chem., 16(4), 843 (1981).

[19] S. Lenka, P. L. Nayak, and M. K. Mishra, Angew. Makromol. Chem., 84, 183 (1980).

[20] P. L. Nayak, S. Lenka, and M. K. Mishra, J. Polym. Sci., Polym. Chem. Ed., 18, 2247 (1980).

[21] A. R. Urquart and A. M. Williams, J. Text. Inst., T15, 138 (1924).

[22] S. Dilli, J. L. Garnett, E. C. Martin, and D. H. Phvoc, J. Polym. Sci., C, 37, 57 (1972).

[23] J. O. Edwards, J. Chem. Educ., 31, 270 (1959); Chem. Rev., 50, 455 (1952).

[24] J. Sigalla, J. Chim. Phys., p. 758 (1958).
[25] P. Maruthamuthu and M. Santappa, Indian J. Chem., 14A, 35 (1976); J. Inorg. Nucl. Chem., 37, 1305 (1975).