Graft Copolymerization of Poly(methyl Methacrylate) onto Wool by Potassium Persulfate–Thiourea Redox Couple in the Presence of Air. V

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Synopsis

Potassium persulfate–thiourea redox couple has been employed to graft poly(methyl methacrylate) onto wool in the presence of air under different reaction conditions. Graft copolymers were characterized by scanning electron micrographs, thermogravimetry, etc. The effect of additives on graft copolymerization has been studied, and a suitable reaction mechanism has been proposed.

INTRODUCTION

Physicochemical properties of graft copolymers have been found to depend largely on different radical initiating systems.[1-7] This work is engaging attraction of a large number of scientists to investigate initiating systems to graft different polymers onto wool,[8-15] silk,[16,17] starch,[18], jute,[19] etc., for imparting better and desirable properties. In our previous work, different redox systems comprised of potassium persulfate–thiomalic acid,[20] potassium bromate–thiomalic acid,[21] potassium permanganate–thiolactic acid,[22] and ceric ammonium nitrate–thioglycolic acid[23] have been utilized to graft poly(methyl methacrylate) (PMMA) onto wool in the presence of air in order to exclude the necessity of inert atmosphere during the course of polymerization. The results were interesting, so that we have made a further attempt in this direction. Potassium persulfate (KPS)–thiourea (TU) redox pair has been employed to graft PMMA onto wool, and results are summarized here.

EXPERIMENTAL

Materials

Wool obtained from Utter Pradesh (U.P.) has been purified and characterized by the method described earlier.[21] Methylmethacrylate was washed with 10% NaOH, and distilled water to remove inhibitor and alkali respectively. The middle fraction distilled under reduced pressure was collected. Other chemicals were of analytical grade.

Graft Copolymerization

A requisite amount of thiourea (TU) and hydrochloric acid (HCl) was introduced followed by initiator (KPS) to a well-dispersed purified wool in 100

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mL of water under continuous stirring at 45 ± 0.2°C. A known amount of monomer (MMA) was added dropwise to the reaction mixture. At the end of the reaction, excess of methanol was added to quench it. Isolation, separation, and estimation of graft copolymer has been done according to the method reported earlier.[20]

Percent grafting and percent efficiency were determined from the following formula:

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

$$\%\ \text{efficiency} = \frac{W_2 - W_1}{W_3} \times 100$$

where W_1, W_2, and W_3 are the weights of wool, grafted wool, and monomer used, respectively.

EVIDENCE OF GRAFTING

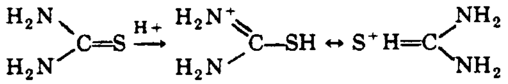
1. The IR band of grafted PMMA showed absorption at 1728 cm^{-1} attributed to $>C{=}O$ of grafted polymer. No such band was observed in the spectrum of wool.[20]

2. The residues obtained after complete hydrolysis of grafted wool, and physical mixture of wool and homopolymer were treated with ninhydrin reagent. The characteristic violet color obtained in the case of grafted wool sample only. This clearly indicated that the actual grafting of amino acid residues had taken place onto wool.[21]

3. The comparative study of scanning electron micrographs of wool and grafted wool gave another strong evidence for true grafting of PMMA onto wool.[22,23]

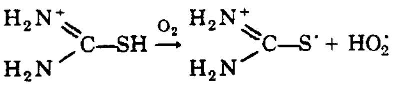
RESULTS AND DISCUSSION

In the presence of acid (HCl), thiourea is converted to the isothiourea cation which exists in tautomeric form:

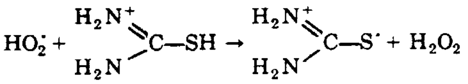


$$(H_2N)_2C{=}S \xrightarrow{H^+} (H_2N^+)(H_2N)C{-}SH \leftrightarrow S^+H{=}C(NH_2)_2 \qquad (1)$$

The presence of oxygen in the system is capable of creating free radicals as follows:



$$(H_2N^+)(H_2N)C{-}SH \xrightarrow{O_2} (H_2N^+)(H_2N)C{-}S^{\cdot} + HO_2^{\cdot} \qquad (2)$$



$$HO_2^{\cdot} + (H_2N^+)(H_2N)C{-}SH \rightarrow (H_2N^+)(H_2N)C{-}S^{\cdot} + H_2O_2 \qquad (3)$$

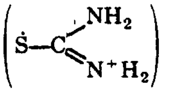
$$H_2O_2 \rightarrow 2\dot{O}H \rightarrow H_2O + \tfrac{1}{2}O_2 \qquad (4)$$

TABLE I
Effect of Initiator Concentration onto % Grafting and Efficiency[a]

Sample no.	$[K_2S_2O_8]$ (mmol/L)	% Grafting	% Efficiency
1	15.0	17.08	4.58
2	20.0	28.98	7.77
3	25.0	35.02	9.39
4	35.0	42.12	11.30
5	40.0	58.76	15.76
6	50.0	51.23	13.74

[a] Reaction conditions: [TU] = 20.0 mmol/L; [HCl] = 20.0×10^{-2} mol/L; [MMA] = 18.64×10^{-2} mol/L; time = 150 min; temp = 45°C; wool = 0.5 g; H_2O = 100 mL.

The oxidant, $S_2O_8^{2-}$ produced isothiocarbamido radicals

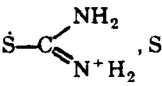


and $SO_4^{\cdot -}$ radicals on interaction with isothiourea cation.[23] The $SO_4^{\cdot -}$ radicals interact with water and give rise to $\dot{O}H$ radicals. These free radicals abstract hydrogen from the reactive functional groups of wool. Thus wool macroradicals came in existence which initiate graft copolymerization according to the reaction mechanism discussed earlier.[20]

Effect of Initiator Concentration

Table I shows the effect of variation of initiator $K_2S_2O_8$, concentration (15.0–50.0 mmol/L) onto percentage grafting, and efficiency at the fixed values of other parameters. The percentage grafting and efficiency increase up to 40.0 mmol/L concentration of $S_2O_8^{2-}$ and then both decrease.

A large number of



$, \dot{S}O_4^{-}$, and $\dot{O}H$

radicals are created due to the increased oxidation of isothiourea cation with the rise of $S_2O_8^{2-}$ concentration. On the other hand, atmospheric oxygen also oxidizes isothiourea cation to isothiocarbamido radicals. Consequently, graft yield is found to enhance up to 40.0 mmol/L concentration of oxidant. At a higher concentration than 40.0 mmol/L, the marked fall in graft yield is due to the abundance of free radicals which terminate the grafted chain, formation of large amount of homopolymer, inhibitory action of oxygen, and a large number of K^+ ions in the system which hinder the normal course of graft copolymerization.

Effect of Activator Concentration

With the increase in thiourea concentration in the range of 5.0–50.0 mmol/L, the percentage grafting and efficiency were found to pass a maximum value and then decreased (Table II).

TABLE II
Effect of Activator Concentration onto % Grafting and Efficiency[a]

Sample no.	[TU] (mmol/L)	% Grafting	% Efficiency
1	5.0	19.26	5.17
2	10.0	38.14	10.23
3	30.0	66.98	17.96
4	35.0	52.62	14.12
5	50.0	30.88	8.28

[a] Reaction conditions: $[K_2S_2O_8] = 40.0$ mmol/L; $[HCl] = 20.0 \times 10^{-2}$ mol/L; $[MMA] = 18.64 \times 10^{-2}$ mol/L; time = 150 min; temp = 45°C; wool = 0.5 g; H_2O = 100 mL.

It was observed that TU alone is incapable of initiating graft copolymerization even after several hours. Within the range of 5.0–30.0 mmol/L of TU, there was a sharp increase in percent grafting and efficiency. The increase in graft yield may be attributed to the increase in isothiocarbamido free radicals in the system. At higher thiourea concentration than 30.0 mmol/L, the decrease in graft yield was due to termination of growing polymer chains, a large amount of formation of homopolymer, and radical scavenger behavior of thiourea.[25]

Effect of Acid Concentration

The effect of variation of acid (HCl) concentration within the range of $5.0–60.0 \times 10^{-2}$ mol/L has been recorded in Table III.

The grafting of PMMA onto wool in the absence of HCl was also carried out. It was observed that a little grafting has also taken place. The increase in graft yield up to 50.0×10^{-2} mol/L concentration of acid revealed that the increase of H^+ ion facilitates the formation of isothiourea molecules, which were ultimately converted into isothiocarbamido free radicals either by oxidant or oxygen present in the system. The decrease in graft yield was due to the large number of H^+ ions, which affect the graft yield adversely.[26]

TABLE III
Effect of Acid Concentration onto % Grafting and % Efficiency

Sample no.	[HCl] ($\times 10^2$ mol/L)	% Grafting	% Efficiency
1	5.0	11.16	2.99
2	10.0	40.92	10.98
3	20.0	67.12	18.00
4	30.0	75.96	20.38
5	50.0	88.80	23.82
6	60.0	70.06	18.79

[a] Reaction conditions: $[K_2S_2O_8] = 40.0$ mmol/L; [TU] = 30.0 mmol/L; $[MMA] = 18.64 \times 10^{-2}$ mol/L; time = 150 min; temp = 45°C; wool = 0.5 g; H_2O = 100 mL.

TABLE IV
Effect of Monomer Concentration onto % Grafting and % Efficiency[a]

Sample no.	[MMA] ($\times 10^2$ mol/L)	% Grafting	% Efficiency
1	9.32	28.12	15.08
2	18.64	67.30	18.05
3	27.96	88.02	15.74
4	37.28	102.62	13.76

[a] Reaction conditions: $[K_2S_2O_8]$ = 40.0 mmol/L; [TU] = 30.0 mmol/L; [HCl] = 20.0 × 10^{-2} mol/L; time = 150 min; temp = 45°C; wool = 0.5 g; H_2O = 100 mL.

Effect of Monomer Concentration

Wool was grafted with PMMA using concentration of $[K_2S_2O_8] = 40.0$ mmol/L, [TU] = 30.0 mmol/L, [HCl] = 20.0 × 10^{-2} mol/L at 45°C by varying the monomer concentration in the range of 9.32×10^{-2}–37.28×10^{-2} mol/L, and results are recorded in Table IV.

From the data it appears that percent grafting increases continuously whereas efficiency reaches a maximum and then falls. Shukla et al.,[20-23] Hiroshi,[27] and Varma and Ray[28] have found the similar effect on graft add-on % by increase of monomer concentration. Varma and Shanker[29] reported that the grafting efficiency was good only at low concentration of monomer by another system and sometimes it decreases with increase in monomer concentration.[30]

The increment in percent grafting by increasing MMA concentration could be interpreted in terms of gel effect due to solubility of PMMA in its own monomer whereas the decrement in grafting efficiency suggests that homopolymerization prevails over grafting at higher monomer concentrations.[31-34]

Effect of Wool

The increase in amount of backbone (wool) follows the decrease in percent grafting and a continuous increase in percent efficiency (Table V). The results are in conformity with those of Shukla et al.[20-23]

TABLE V
Effect of Amount of Wool onto % Grafting and % Efficiency[a]

Sample no.	Wool (g)	% Grafting	% Efficiency
1	0.25	94.08	12.62
2	1.00	80.22	43.04
3	2.50	38.22	51.26

[a] Reaction conditions: $[K_2S_2O_8]$ = 40.0 mmol/L; [TU] = 30.0 mmol/L; [HCl] = 20.0 × 10^{-2} mol/L; [MMA] = 18.64 × 10^{-2} mol/L; time = 150 min; temp = 45°C; H_2O = 100 mL.

TABLE VI
Effect of Temperature onto % Grafting and % Efficiency[a]

Sample no.	Temp (°C)	% Grafting	% Efficiency
1	35	21.23	5.69
2	45	67.12	18.00
3	55	62.16	16.67
4	60	42.66	11.44

[a] Reaction conditions: [$K_2S_2O_8$] = 40.0 mmol/L; [TU] = 30 mmol/L; [HCl] = 20.0×10^{-2} mol/L; [MMA] = 18.64×10^{-2} mol/L; time = 150 min; wool = 0.5 g; H_2O = 100 mL.

Effect of Temperature

It was observed that, at a higher temperature than 45°C, the homopolymer formed was more in excess than grafting (Table VI). The increase in graft yield and efficiency up to 45°C may be due to the favorable influence of temperature on wool swellability, monomer solubility, and its diffusion initiation, and propagation of the graft yield.[22] Beyond 45°C, the termination of grafted chain free radicals and a large amount of homopolymer formation may be the cause of such a decrease.

Effect of Time

The effect of time on the percent grafting of PMMA onto wool has been recorded in the Table VII, keeping the concentration of initiator 40.0 mmol/L, activator 30.0 mmol/L, acid 20×10^{-2} mol/L, and MMA 18.64×10^{-2} mol/L constant at 45°C.

The maximum graft yield and efficiency were found within 150 min and then both leveled off. These observations are in accordance to Bendak and Hebeish[35] and Shukla and Sharma.[20]

Effect of Salts

The effect of $CuSO_45H_2O$ and KCl onto the percent graft yield is recorded in Table VIII.

The decrease in graft yield by the addition of KCl is due to an increase of ionic strength of the medium which interferes with the usual polymerization reaction, resulting in the premature termination of the growing chain.

TABLE VII
Effect of Time onto % Grafting and % Efficiency[a]

Sample no.	Time	% Grafting	% Efficiency
1	30	18.66	5.00
2	60	25.88	6.94
3	90	38.12	10.22
4	120	49.34	13.24
5	150	66.88	17.94
6	180	66.54	17.84

[a] Reaction conditions: [$K_2S_2O_8$] = 40.0 mmol/L; [TU] = 30.0 mmol/L; [HCl] = 20.0×10^{-2} mol/L; [MMA] = 18.64×10^{-2} mol/L; temp = 45°C; wool = 0.5 g; H_2O = 100 mL.

TABLE VIII
Effect of Salts onto % Grafting and % Efficiency[a]

Sample no.	Concentration (mmol/L)	% Grafting
1	0.0	66.66
$CuSO_4$		
2	5.0	88.26
3	15.0	102.05
4	25.0	77.82
KCl		
5	5.0	49.00
6	15.0	37.00
7	25.0	25.00

[a] Reaction conditions: $[K_2S_2O_8] = 40.0$ mmol/L; [TU] = 30.0 mmol/L; [HCl] = 20.0×10^{-2} mol/L; [MMA] = 18.64×10^{-2} mol/L; time = 150 min; temp = 45°C; wool = 0.5 g; H_2O = 100 mL.

It was observed (Table VIII) that the increase in $CuSO_4$ concentration from 5.0 to 15.0 mmol/L enhances the graft yield.[35,36] It may be attributed to the fact that the additional Cu^{2+} ion probably favors the wool-monomer complex. The free radicals generated under the influence of Cu^{2+} ion would be in the proximity of wool, thus facilitating the formation of wool macroradicals.[37] The Cu^+ ion formed during the polymerization reaction could be oxidized back to cupric state by atmospheric oxygen, thus utilizing the oxygen:

$$O_2 + Cu^+ \rightarrow CuO_2^+$$

$$CuO_2^+ + H^+ \rightarrow Cu^{2+} + HO_2^{\cdot}$$

$HO_2^{\cdot}$ radicals thus produced underwent further reaction to produce H_2O_2, which on decomposition yielded $\dot{O}H$ radicals. These free radicals initiated the grafting.

All the above factors were responsible for the increase in graft yield. The decrease in graft yield at higher $CuSO_4$ concentration (> 15.0 mmol/L) might be due to the radical trap action of Cu^{2+} ion.

Effect of Alcohols

The effect of addition of aliphatic alcohols (10% w/v) onto percent grafting has been determined (Table IX). It is obvious from the data that the addition

TABLE IX
Effect of Alcohols onto % Grafting and % Efficiency[a]

Sample no.	Alcohols	% Grafting
1	OO	66.66
2	CH_3OH	52.52
3	C_2H_5OH	50.02
4	n-C_4H_9OH	40.96

[a] Reaction conditions: $[K_2S_2O_8] = 40.0$ mmol/L; [TU] = 30.0 mmol/L; [HCl] = 20.0×10^{-2} mol/L; [MMA] = 18.64×10^{-2} mol/L; [alcohols] = 10% w/v; time = 150 min; temp = 45°C; wool = 0.5 g; H_2O = 100 mL.

of each alcohol, i.e., methanol, ethanol, *n*-butanol, depress the graft yield in the following order:

$$n - C_4H_9OH > C_2H_5OH > CH_3OH$$

Thus the order of depression is dependent on the number of carbon atoms per alcohol molecule.

Thermal Behavior of Grafted and Ungrafted Wool

Thermogravimetric analysis (TGA) has been employed to determine the thermal stability of pure wool, and grafted samples (49 and 66%) with poly(methyl methacrylate) at the heating rate of 6°C/min within the temperature range of 50–600°C in air (Fig. 1).

It is observed from the figure that mass loss at the initial stage due to moisture improves after graft add on percent approximately up to 135°C for the grafted sample compared to pure wool (160°C). Graft copolymerization of poly(methyl methacrylate) onto wool leads to the formation of new crosslinkages and the simple molecules like H_2O, NH_3, H_2S, CO_2, and CH_3SH are eliminated to a lesser extent. That is why the decomposition temperature of grafted wool increases up to 320°C. Above this temperature (> 320°C) the loss of mass of grafted wool increases compared to pure wool. The decrease in decomposition temperature with the increase in graft yield may be attributed to the early decomposition of PMMA as compared to the polypeptide chain. These results are in accordance with Varma and Sarkar.[38]

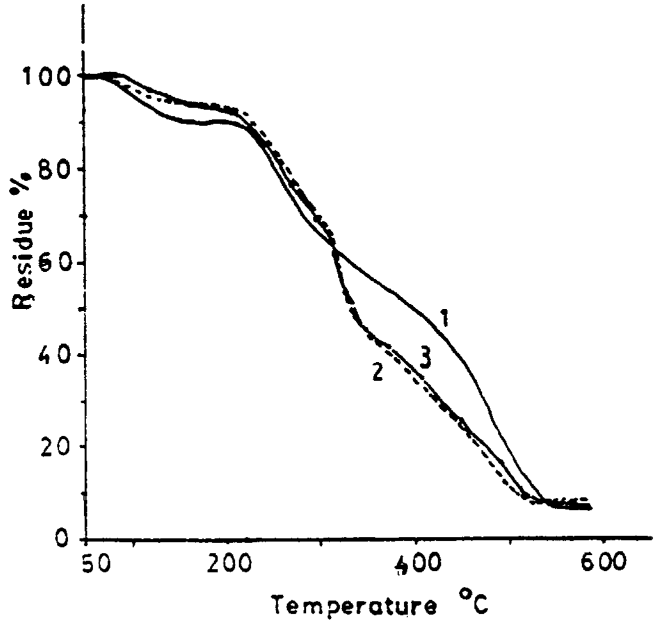


Fig. 1. TGA curve of: (1) pure wool; (2) 49% grafted wool; (3) 66% grafted wool.

TABLE X
Effect of Acid, Alkali, Reducing, and Oxidizing Agents onto Grafted and Ungrafted Wool[a]

Solvent	Weight loss (%)	
	Ungrafted wool	Grafted wool
6.0*N* HCl	15.81	19.20
0.1*N* NaOH	12.09	7.91
Urea bisulphite (3%)	11.72	4.26
Peracetic acid	12.96	8.2

[a] Exposure time = 60 min; temp = 70°C; [urea] = 50%; pH = 7.0.

Effect of Acid, Alkali, Reducing, and Oxidizing Solvents

The effect of 6.0*N* HCl, 0.1*N* NaOH, metabisulfite–urea and peracetic acid onto the grafted wool and control samples has been determined. The observations are recorded in Table X. The results are in accordance to our previous study.[20-24] The grafted samples were found more resistant in 0.1*N* NaOH, urea–bisulphate solution, and peracetic acid. The decrease in alkaline solubility of grafted wool might be due to the formation of stable new crosslinkages in the wool backbone, retarding the action of alkali.[36] The grafted sample degraded more than the control sample in 6*N* HCl. It reveals that crosslinkage due to the —SS— bond is affected during grafting of poly(methyl methacrylate) in the presence of hydrochloric acid. Solubility in reducing solvent for grafted sample was found less than the control sample.

Oxidizing solvent swells ungrafted samples much more than the grafted one. Grafted wool was found less soluble in oxidizing solvent. This may be due to the greater stiffness in wool due to grafting of MMA.[39]

Viscosity Average Molecular Weight

The viscosity average molecular weight of grafted poly(methyl methaceylate) and homopolymer formed during the graft copolymerization has been determined by using the Mark–Howwink equation.[40]

The data (Table XI) reflected that the increase in graft yield leads to the decrease in the molecular weight of grafted poly(methyl methacrylate) onto

TABLE XI
Viscosity Average Molecular Weight[a]

$K_2S_2O_8$ (mmol/L)	Add-on % (% Grafting)	Viscosity average molecular weight of	
		Grafted PMMA	Homopolymer of PMMA
20	28	22,000	24,200
25	35	21,006	23,120
35	42	20,000	21,926

[a] Reaction conditions, for grafted samples, other than $K_2S_2O_8$: TU = 20 mmol/L, HCl = 20.0 × 10^{-2} mol/L, MMA = 18.64 × 10^{-2} mol/L, time = 150 min, temp = 45°C, wool = 0.5 g, H_2O = 100 mL.

wool. A little difference in low molecular weight of grafted polymer was observed as compared to the molecular weight of homopolymer. It suggests that during hydrolysis the grafted poly(methyl methacrylate) onto wool undergoes degradation. Low molecular weight of polymer may be due to the chain ender reaction of oxygen.[3,20-23]

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References

1. E. E. Magat and D. Tanner, U.S. Pat. 3,338,985 (1967).
2. P. L. Nayak, *J. Macromol. Sci., Rev. Macromal. Chem.*, **C17**, 267 (1979).
3. J. H. Bexendale, *Trans Faraday Soc.*, **42**, 155 (1946).
4. S. B. Dash, A. K. Pradhan, and N. C. Pati, *J. Appl. Polym. Sci.*, **28**, 2673 (1983).
5. S. B. Dash, A. K. Pradhan, N. C. Pati, and S. L. Nayak, *J. Macromol. Sci. Chem.*, **A19**, 343 (1983).
6. S. Howarth and J. R. Holker, *J. Soc. Dyers Colour.*, **82**, 257 (1966).
7. M. K. Misra, B. G. Sar, and G. Norman, *Polym. Bull.*, **9**, 106 (1983).
8. T. Barr, C. W. Capp, and J. B. Speakman, *J. Soc. Dyers, Colour.*, **62**, 338 (1946).
9. R. E. Whitfield, L. A. Miller, and W. L. Wasley, *J. Appl. Polym. Sci.*, **8**, 1607 (1964).
10. T. N. Aleksandrova, L. S. Sletkenov, and Z. A. Rogovin, *Nauch. Issled Tr. Tsentr. Nanch-Isslad Inst. Sherst Prom Sti*, **26**, 67 (1973).
11. I. P. Brensova, B. P. Noren and Z. A. Rogovin, *Faserforsch. Textil.*, **29**, 697 (1978).
12. A. J. McKinnen, *J. Appl. Polym. Sci.*, **14**, 3033 (1970).
13. B. N. Misra, A. S. Singha, and R. K. Sharma, *J. Appl. Polym. Sci.*, **27**, 1321 (1982).
14. E. P. Clay, Jr., and P. L. Harold, U.S. Pat. Appl. 3,005 (1954).
15. A. Bendak, A. Kutouch, and A. Hebeish, *Kolov. Est.*, **13**, 106 (1971).
16. L. I. Butina, L. F. Zhukova, S. F. Poleskaya, and M. V. Kordiagin, *Izv. Vyssh. Ucheb. Zaved. Technol. Tekst Prom*, **287** (1974).
17. L. I. Butina, M. V. Shisukina, S. F. Sadova, and M. V. Karchagin, *Vysokemel. Soedin. Ser. A*, **17**, 1150 (1975).
18. B. K. Srivastava and P. S. Chandel, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 1545 (1977).
19. N. Y. Abou-Zeid, A. Kigazy, and A. Hebeish, *Angew. Macromol. Chem.*, **121**, 69 (1984).
20. J. S. Shukla, G. K. Sharma, R. K. Tewari, and S. K. Shukla, *J. Macromol. Sci. Chem.*, **A21**, 225 (1984).
21. J. S. Shukla and G. K. Sharma, *Indian J. Chem.*, **24A**, 467 (1985).
22. J. S. Shukla and G. K. Sharma, *Indian J. Chem.*, **25A**, 463 (1986).
23. J. S. Shukla and G. K. Sharma, *J. Polym. Sci.*, to appear.
24. A. R. Mukherjee, R. P. Mitra, A. M. Biswas, and S. Maity, *J. Polym. Sci., Part A-1*, **5**, 135 (1967).
25. A. Hebeish, M. H. El-Rafie, and A. I. Waly, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2895 (1976).
26. P. L. Nayak, S. Lenka, and N. C. Pati, *Angew. Makromol. Chem.*, **85**, 29 (1980).
27. I. Hiroshi, *Kobunshi Kagaku*, **23**, 256 (1966).
28. D. S. Varma and N. D. Ray, *Angew. Makromol. Chem.*, **32**, 81 (1973).
29. D. S. Varma and R. Shanker, *Angew. Makromol. Chem.*, **28**, 191 (1973).
30. K. Howard and J. Peters, *J. Polym. Sci.*, **85**, 468 (1969).
31. J. Toda, *J. Polym. Sci., Polym. Chem. Ed.*, **58**, 441 (1962).
32. A. K. Mukherjee and S. Sanyal, *Cell. Chem. Technol.*, **3**, 13 (1979).
33. P. L. Nayak, S. Lenka and M. K. Misra, *J. Appl. Polym. Sci.*, **25**, 63 (1980).
34. K. S. Basu, K. P. Rao, K. T. Joseph, M. Santappa, and Y. N. Nayudamma, *Leather Sci.*, **28**, 355 (1981).
35. A. Bendak and A. Hebeish, *J. Appl. Polym. Sci.*, **17**, 1953 (1973).

36. A. Bendak, M. I. Khalil, M. H. El-Rafie, and A. Hebeish, *J. Appl. Polym. Sci.*, **19**, 335 (1975).

37. M. H. El-Rafie and A. Hebeish, *J. Appl. Polym. Sci.*, **19**, 1815 (1975).

38. D. S. Varma and R. K. Sarkar, *J. Appl. Polym. Sci.*, **15**, 2173 (1971).

39. B. N. Misra, I. K. Mehta, and R. Dogra, *J. Macromol. Sci. Chem.*, **A12**, 1513 (1978).

40. *Polymer Handbook*, Brandrup and E. H. Inomergul, Wiley-Interscience, New York, 1965.

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