Grafting Vinyl Monomers onto Silk Fibers. II. Graft Copolymerization of Methyl Methacrylate onto Silk by Hexavalent Chromium Ion

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Synopsis

The feasibility of chromium(VI) to induce graft polymerization of methyl methacrylate onto silk was investigated. The rate of grafting was determined by varying monomer concentration, chromium(VI) concentration, temperature, acidity of the medium, nature of the silk, reaction medium, and redox system. The graft yield increased with increasing monomer concentration up to $0.65M$, and with further increase of monomer the graft yield decreased. The graft yield increased with increasing chromium(VI) concentration. The grafting is considerably influenced by chemical modification of silk prior to grafting. The graft yield is influenced by thiourea concentration, decreasing with increasing thiourea concentration. The effect of certain inorganic salts and anionic surfactants on the rate of grafting was investigated.

INTRODUCTION

Modification of the properties of some natural macromolecules such as wool, cotton, silk, cellulose, and collagen through graft copolymerization has attracted attention in recent years. Several reviews are available in this general subject.[1-6] Grafting provides a method of adding certain properties to a fiber without greatly disturbing the strength and other mechanical behavior features. The attainment of high grafting efficiencies in graft copolymerization is a problem of paramount importance. Grafting of vinyl monomers onto cotton,[7-9] starch,[10-13] cellulose,[14-21] wool,[1] etc., has been the subject of extensive investigations during the last several years. It is surprising that comparatively little attention has been paid toward grafting vinyl monomers onto silk fibers.[22,23] Synthetic polymers are applied to silk to obtain improved textile performance and to overcome water straining which seriously impedes the general use of silk.

Graft copolymerization of vinyl monomers onto substrate polymers is generally considered to involve the generation of reactive sites on the polymer, followed by the addition of monomer which propagates in a conventional manner. This can be achieved by several methods, i.e., high-energy radiation,[22,24] low-energy radiation in the presence and absence of sensitizers,[25,26] and chemical methods.[27-30] The last method has attracted attention in recent years because it provides a direct experimental evidence of the existence of a transient radical intermediate generated by chemical reactions.

In the recent past, metal ions in their higher valency states have been extensively used for polymerization of a number of vinyl monomers in aqueous me-

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dium.[31–38] Chromium(VI) has been used by Nayak and co-workers[34,37,38] as a redox initiator for homopolymerization of vinyl monomers. Recently, we have reported graft copolymerization of methyl methacrylate onto silk by quinquevalent vanadium ion.[30] This communication presents the results of studies of grafting methyl methacrylate onto silk fibers using hexavalent chromium ion.

EXPERIMENTAL

Mulberry silk fibroin was collected from the Government Silk Factory, Jabalpur, India. The raw silk fibers were purified by scouring in an aqueous solution containing 0.4% soap for 2 hr and washing with 0.05% sodium carbonate solution followed by boiling water. Methyl methacrylate (MMA) was washed with 5% sodium hydroxide solution, dried with anhydrous sodium sulfate, and distilled under reduced pressure in nitrogen before use.

Chromic acid solutions were prepared by dissolving chromium trioxide [from BDH, Analar (AR)] in distilled water. Perchloric acid (from E. Merk, G.R. 60%) was used. Water, distilled twice over alkaline permanganate and deionized by passing through a column of Biodeminrolit resin (Permutit Co., U.K.) was used to prepare all solutions. Cr(VI) concentration was estimated either by titrimetry (for $Cr(VI) > 5 \times 10^{-4}$ mole/l) or spectrophotometry[34] (for $Cr(VI) < 5 \times 10^{-5}$ mole/l).

The reaction was carried out in Pyrex flasks equipped with gas inlet and outlet tubes. Dried and purified silk fibers were immersed in a solution of Cr(VI) (0.005–0.04M) in $HClO_4$ (0.2–1.2N) at temperatures from 40° to 55°C. The required concentration of monomer was added to the reaction mixture. The reaction time was varied from 1 to 6 hr, and the material-to-liquor ratio was 1:100. After the desired reaction time, silk fibers were taken out and washed thoroughly with water and acetone. Finally, the fibers were Soxhlet extracted with benzene or acetone until the homopolymer was completely removed. They were then dried in an oven, cooled to room temperature, and weighed. The graft yield was calculated as the percentage increase in weight over the original weight of the sample.

RESULTS AND DISCUSSION

The factors affecting chromium(VI)-induced grafting of MMA onto silk fibers were investigated. Variables studied included monomer concentrations, chromium(VI) concentrations, temperature, acid, substrate, reaction medium, inorganic salts, surfactants, and redox systems.

Effect of Monomer Concentration

From Figure 1 it can be seen that as the monomer concentration increases, there is an increase in percentage of grafting in the lower concentration range, which reaches a maximum value and then decreases with increasing monomer concentration. At higher monomer concentration, reactions that are competitive with the grafting probably take place in the solution, i.e., combination and disproportionation of PMMA macroradicals.[39,40] When the concentration of PMMA macroradicals increases, the rate of their combination and dispropor-
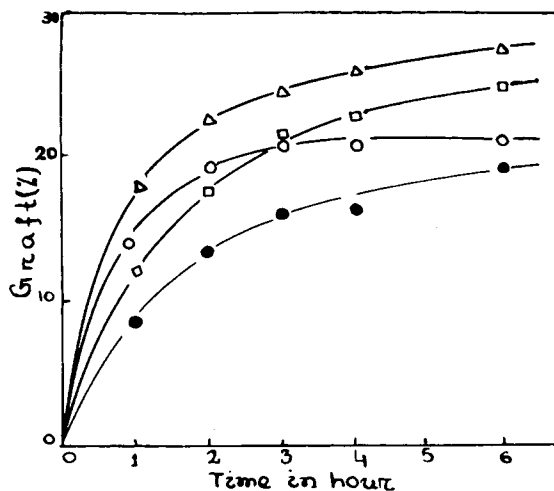
Fig. 1. Effect of [monomer] on graft yield: $[Cr^{6+}] = 0.025M$; $[HClO_4] = 0.396M$; temp. $= 50°C$; (O) $[MMA] = 2.80 \times 10^{-1}M$; ($\triangle$) $[MMA] = 6.51 \times 10^{-1}M$; ($\square$ $[MMA] = 8.37 \times 10^{-1}M$; ($\bullet$) $[MMA] = 12.10 \times 10^{-1}M$.

tionation increases faster than the rate of their combination with silk molecules. On the other hand, the rate of monomer diffusion is bound to be progressively affected by the polymer deposit formed, which of course, grows most rapidly when high concentrations of monomer are used. Similar observations have been noted by Haworth and Holker[41] in the case of grafting of acrylic acid onto nylon by the ceric ion method.

Effect of Chromium(VI) Concentration

The effect of concentration of chromium(VI) ion on grafting methyl methacrylate onto silk is shown in Figure 2. The rate of grafting has been investigated
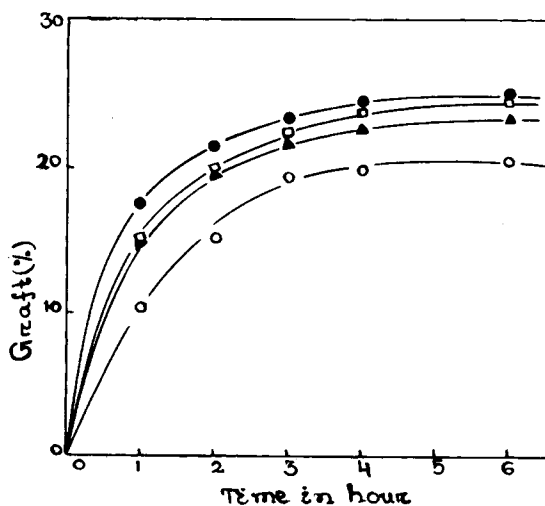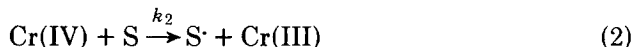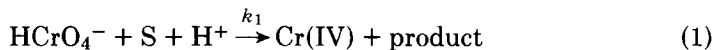

Fig. 2. Effect of [chromium(VI)] on graft yield: $[MMA] = 0.4650M$; $[HClO_4] = 0.396M$; temp. $= 50°C$; (O) $[Cr^{6+}] = 0.005M$; ($\blacktriangle$) $[Cr^{6+}] = 0.01M$; ($\square$) $[Cr^{6+}] = 0.025M$; ($\bullet$) $[Cr^{6+}] = 0.035M$.

by changing the Cr^{6+} concentration within the range of 0.005 to 0.035M. The data indicate that with increasing Cr(VI) concentration, the rate of grafting increases.

In a system consisting of Cr^{6+}, perchloric acid, MMA, and silk, Cr^{6+} reacts with silk forming silk macroradical, which reacts with the vinyl monomer resulting in the formation of the graft copolymer on the backbone of the fiber:
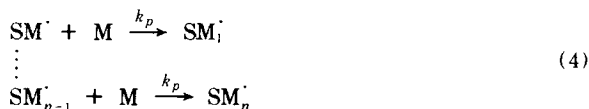
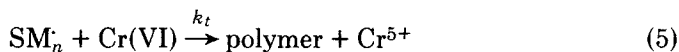$$HCrO_4^- + S + H^+ \xrightarrow{k_1} Cr(IV) + product \tag{1}$$

$$Cr(IV) + S \xrightarrow{k_2} S^\cdot + Cr(III) \tag{2}$$

where S = silk, M = monomer.
Initiation

$$S^\cdot + M \xrightarrow{k_1} SM^\cdot \tag{3}$$

Propagation

$$SM^\cdot + M \xrightarrow{k_p} SM_1^\cdot$$
$$\vdots \tag{4}$$
$$SM_{n-1}^\cdot + M \xrightarrow{k_p} SM_n^\cdot$$

Termination

$$SM_n^\cdot + Cr(VI) \xrightarrow{k_t} polymer + Cr^{5+} \tag{5}$$

With increasing Cr^{6+} concentration, more silk macroradicals are formed, and hence the rate of grafting increases. A similar mechanism has been reported by us in case of aqueous polymerization of acrylonitrile initiated by Cr^{6+}–propane–1,2-diol,[34] Cr^{6+}–1-propanol,[37] and Cr^{6+}–thiourea redox systems.

Effect of Temperature

The graft copolymerization was carried out at four different temperatures ranging from 40° to 55°C, keeping the concentrations of all other reagents constant (Fig. 3). A perusal of result indicates that with increasing temperature, the percentage of graft-on increases up to 50°C and then decreases. The dependence of the rate of grafting on temperatures between 40° and 50°C could be ascribed to the greater activation energy. The swellability of silk, solubility of monomer, and its diffusion rates are enhanced by increasing the reaction temperature. But beyond 50°C, the percent graft-on decreases probably because of the fact that at higher temperatures there is a possibility of higher combination rates of monomer which results in a decrease in rate of grafting. Similar ob-
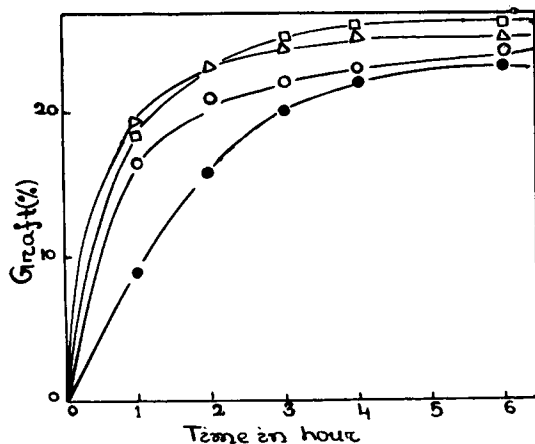
Fig. 3. Effect of temperature on graft yield: $[Cr^{6+}] = 0.025M$; $[HClO_4] = 0.396M$; [MMA] = $0.4650M$; (O) 40°C; (△) 45°C; (□) 50°C; (●) 55°C.

servations have been noted by Nayak and co-workers while grafting MMA onto wool using the V^{5+}/thiourea redox system.[42]

Effect of Acid Concentration

It is evident that the presence of an acid in a graft copolymerization system initiated by chromium(VI) is essential. It is therefore interesting to study the effect of acid concentration on graft yield. The grafting reaction was conducted by varying perchloric acid concentrations from 0.2 to 0.9M (Fig. 4). It is observed that the percentage graft-on increases with increase in acid concentration in the initial stages; and with further increase in acid, the percentage graft-on decreases. With increasing acid concentrations, the acid anions probably complex with monochromate ion, reducing the oxidizing power of the latter, as pointed out by Stewart and Lee[43] for the variation of oxidation rates of isopropyl alcohol.
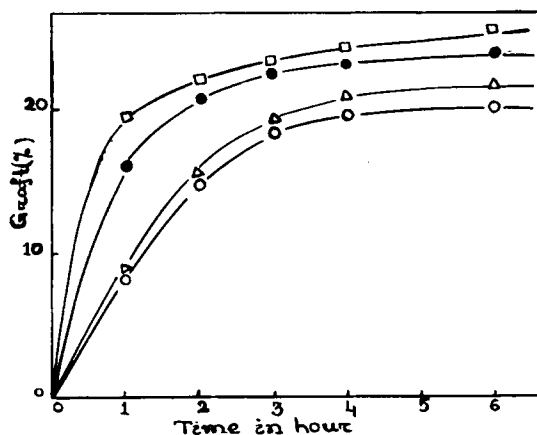

Fig. 4. Effect of acid concentration on graft yield: $[Cr^{6+}] = 0.025M$; [MMA] = $0.4650M$; temp. = 50°C; (O) $[H^+] = 0.233M$; (△) $[H^+] = 035M$; (□) $[H^+] = 0.513M$; (●) $[H^+] = 0.90M$.

Nature of Substrate

The effect of the changes in the physical or chemical structure of silk brought about by esterification or trinitrophenylation on its behavior toward grafting has been investigated. The order of the effect is unmodified silk > esterified silk > trinitrophenylated silk. Acetylation and trinitrophenylation of silk reduce significantly its ability toward grafting. When silk fiber is subjected to acetylation or trinitrophenylation, the amino and the carboxyl groups will be blocked. Free radicals cannot be created at the silk backbone by the interaction of the metal ions as a result of which the graft yield decreases. The other reasons for the low graft yield might be due to (1) lowering of the swellability of the fiber, and (2) hindrance of adsorption of MMA owing to low fiber swellability and repulsion of MMA molecules by the negatively charged substituted nitro groups in the case of TNP silk. The net effect of all these factors is a decrease of grafting.

Effect of Polymerization Medium

The reaction medium plays an important role in grafting vinyl monomers onto silk fibers. The graft yield follows the order formic acid > acetic acid > dimethylformamide > ethanol > n-propanol > n-butanol > $tert$-butanol.

The dependence of grafting upon the nature of the solvent suggests that the solvents examined differ considerably in their (a) capability of swelling of silk, (b) miscibility with monomer, (c) formation of solvent radical from the primary radical species of the initiating system, (d) contribution of the solvent radical in activation of silk, and (e) termination of the graft radical and silk macroradical via chain transfer. While the first four factors favor grafting by simplifying access and diffusion of monomer, the last factor adversely affects grafting by lowering the molecular size of the graft.[44,45]

Increasing the molecular weight of alcohol, the graft yield decreases from ethanol to $tert$-butanol. The lower graft yields could be ascribed to its adverse effect on the swelling of silk by water. Associated with this factor is the hydrophobic character of the alcohols, which decreases from butanol to ethanol. These effects seriously hinder monomer access to reactive sites on silk.[30]

Effect of Inorganic Salts and Surfactants

The addition of neutral salts such as KCl, NaF, Na_2SO_4, and $MgSO_4$ increases the graft yield. This might be due to the fact that these salts catalyze the propagation step, thereby increasing the grafting efficiency.

The effect of $CuSO_4$ concentration on grafting is quite interesting (Fig. 5). It is observed that with increasing $CuSO_4$ concentration, the graft yield first increases and then decreases. The initial increase in graft yield might be due to the fact that the presence of Cu^{2+} ions in the vicinity of silk certainly favors grafting since the involvement of Cu^{2+} ion in the silk–monomer complex would be easier. Furthermore, the creation of free-radical species under the influence of Cu^{2+} ions would be in the proximity of silk, thus assisting formation of silk macroradicals. The drop in the graft yield with higher concentrations of cupric sulfate could be attributed to a variety of reasons. First is termination of free radicals in solution, on homopolymer, and/or on silk, the Cu^{2+} ions seeming to
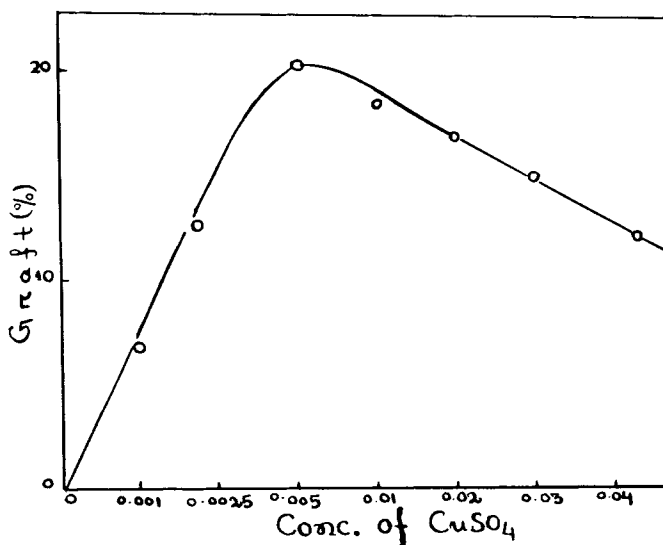
Fig. 5. Effect of [CuSO$_4$] on graft yield. [Cr^{6+}] = 0.025M; [HClO$_4$] = 0.396M; [MMA] = 0.4650M, temp. = 50°C.

act as radical traps. Second might be that a particular concentration of Cu^{2+} favors complexation of monomer with silk and that beyond this concentration the Cu^{2+} ions perturb such complexation.

The percentage graft-on has also been calculated in the presence of the anionic surfactant sodium lauryl sulfate at critical micelle concentration (CMC) (Fig. 6). At CMC, micelles are formed which are roughly spherical in size with the sulfate ions forming the Gouy–Chapman double layer.[46,47] The enhancement of graft yield by NaLS at CMC can be explained on the assumption that the micelles become entangled with the silk fiber as a result of which the chromi-
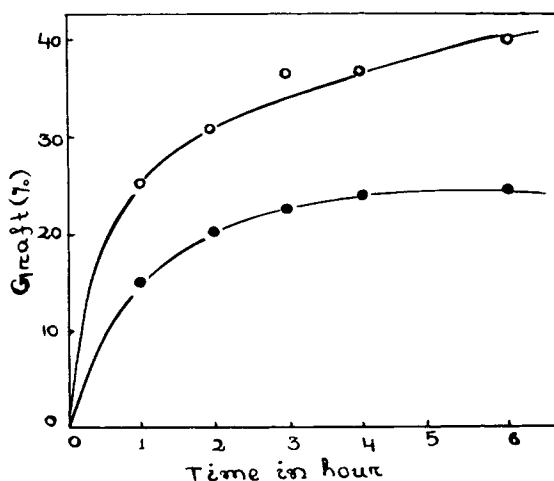

Fig. 6. Effect of surfactant, NaLS, at CMC on graft yield: [Cr^{6+}] = 0.025M; [HClO$_4$] = 0.396M; [MMA] = 0.4650M; temp. = 50°C; sodium lauryl sulfate [NaLS] = 8.1 × 10^{-3}M; (O) NaLS; (●) Nil.

um(VI) ion is electrostatically attracted toward the silk matrix. The concentration of Cr^{6+} ion will be more near the vicinity of the fiber, and free-radical formation on the silk backbone will be facilitated as a result of which the graft yield increases.

Effect of Redox System

Although redox systems have been extensively used for homopolymerization of vinyl monomers,[31-38] the application of such systems for graft copolymerization onto natural macromolecules is rather limited. During the last few years, the use of thiourea and N-substituted thioureas for initiation of aqueous vinyl polymerization has been examined.[35,48-50] Hebeish and Bendak have reported the redox-initiated vinyl graft copolymerization onto wool fibers using hydrogen peroxide–thiourea[51] and Fe^{3+}–thiourea as cocatalyst.[52] Recently,[30] we have reported the redox-initiated vinyl graft copolymerization onto wool using V^{5+}/thiourea cocatalyst.

The graft copolymerization of silk has been investigated by using the Cr^{6+}/ thiourea redox system, changing thiourea concentration over the range of 0.005 to $0.0125M$. The percentage graft yield decreases with increasing thiourea concentration (Fig. 7).

In all initiating systems containing thiourea the redox component is isothiourea, a thiol existing in a tautomeric equilibrium with thiourea as the reductant:
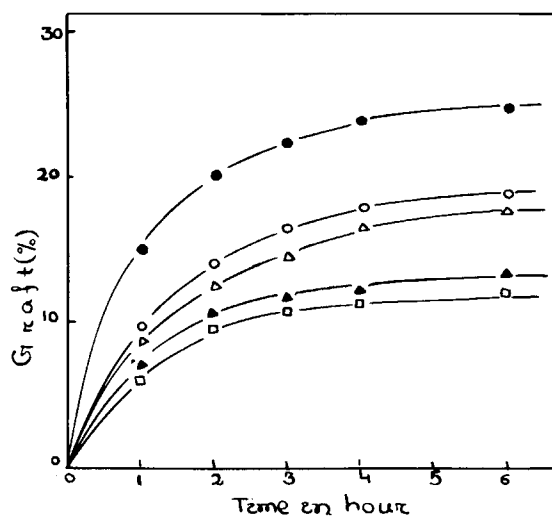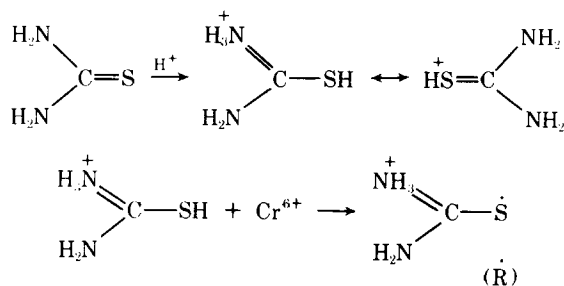

Fig. 7. Effect of [thiourea] on graft yield: $[Cr^{6+}] = 0.025M$; $[HClO_4] = 0.396M$; $[MMA] = 0.4650M$; temp. $= 50°C$; (●) Nil; (○) [TU] $= 0.005M$; (△) [TU] $= 0.0075M$; (▲) [TU] $= 0.01M$; (□) [TU] $= 0.125M$; TU $=$ thiourea.

The isothiocarbamido radicals (R·) abstract hydrogen from amino or carboxyl groups in silk to yield silk macroradicals which initiate graft copolymerization. The isothiocarbamido radical might also react with the monomer to give rise to the monomer radical which initiates the homopolymerization:

$$M + R^{\cdot} \longrightarrow RM^{\cdot}$$
$$\vdots$$
$$RM^{\cdot} + M \longrightarrow RM_n^{\cdot}$$
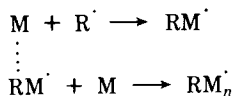
The decrease in percentage grafting with increasing thiourea concentration could possible be associated with a faster rate of termination probably owing to the abundance of free-radical species in the polymerization system.

References

1. P. L. Nayak, *J. Macromol. Sci., Rev. Macromol. Chem.,* C14, 192 (1976).
2. K. Arai, *Block Graft Copolym.,* 1, 193 (1973).
3. I. C. Watt, *J. Macromol. Sci., Rev. Macromol. Chem.,* C5, 176 (1970).
4. H. A. Krassig and V. Stannett, *Adv. Polym. Sci,* 4, 11 (1965).
5. J. C. Arthur, Jr., *Adv. Macromol. Chem.,* 2, 1 (1970).
6. V. T. Stannett, J. Burke, and V. Weiss, Eds., *Block and Graft Copolymerization,* Syracuse University Press, Syracuse, New York, 1973.
7. A. Hebeish, A. Kantoch, and M. H. El-Rafie, *J. Appl. Polym. Sci.,* 15, 11 (1971).
8. A. Kantouch, A. Hebeish, and M. H. El-Rafie, *J. Appl. Polym. Sci.,* 15, 1007 (1971).
9. A. Hebeish, A. Kantouch, and M. H. El-Rafie, *J. Appl. Polym. Sci.,* 15, 1921 (1971).
10. N. Gaylord, *Interchem. Rev.,* 15, 91 (1956–57).
11. S. H. Pinner and W. Wycherley, *Plastics (London),* 22, 456 (1957).
12. E. Schwab, V. Stannett, and J. J. Hermans, *Tappi,* 44, 251 (1961).
13. V. Stannett, *Tappi,* 47, 584 (1964).
14. Y. Iwakura, T. Kurosaki, and Y. Imai, *J. Polym. Sci. A,* 3, 1185 (1965).
15. A. Hebeish and P. C. Mehta, *J. Appl. Polym. Sci.,* 12, 1625 (1968).
16. A. Hebeish and P. C. Mehta, *Text. Res. J.,* 39, 99 (1969).
17. Y. Ogiwara, Y. Ogiwara, and H. Kubota, *J. Polym. Sci. A-1,* 6, 1489 (1968).
18. Y. Ogiwara, K. Igeta, and H. Kubota, *J. Appl. Polym. Sci.,* 15, 1119 (1971).
19. H. Kubota and Y. Ogiwara, *J. Appl. Polym. Sci.,* 16, 337 (1972).
20. H. Kubota, Y. Murata, and Y. Ogiwara, *J. Polym. Sci. A,* 11, 485 (1973).
21. T. O. Song, Y. D. Kim, and I. S. Noh, *Kungnip Kongop Yonguso Pago,* 16, 7 (1966).
22. K. Arai, M. Negishi, S. Komino, and K. Takada, *Appl. Polym. Symp.,* 18, 545 (1971).
23. K. Kojima, S. Iwabuchi, and K. Kojima, *J. Polym. Sci. B,* 9, 25 (1971).
24. J. L. Williams and V. Stannett, *Teintex,* 10, 719 (1971).
25. H. Ishibashi and M. Oku, Proc. Int. Wool. Text, Res. Conf. Paris, Sec. III, 1965.
26. H. L. Needles and W. L. Wasley, *Text. Res. J.,* 39, 97 (1969).
27. M. Negishi, K. Arai, and S. Okada, *J. Appl. Polym. Sci.,* 11, 115 (1967).
28. A. Kantouch, A. Hebeish, and A. Bendak, *Eur. Polym. J.,* 7, 153 (1971).
29. A. Bendak, A. Kantouch, and A. Hebeish, *Kolorisztikai Ertesite,* 13, 106 (1971).
30. P. L. Nayak, S. Lenka, and N. C. Pati, *Angew. Makromol. Chem.,* 67, (1977).
31. T. R. Mohanty, B. C. Singh, and P. L. Nayak, *Makromol. Chem.,* 175, 2345 (1974).
32. P. L. Nayak, T. R. Mohanty, and B. C. Singh, *Makromol. Chem.,* 176, 873 (1975).
33. T. R. Mohanty, B. C. Singh, and P. L. Nayak, *J. Polym. Sci. A-1,* 13, 2075 (1975).
34. R. K. Samal, B. C. Singh, T. R. Mohanty, and P. L. Nayak, *Makromol. Chem.* 176, 2989 (1976).
35. B. C. Singh, T. R. Mohanty, and P. L. Nayak, *Eur. Polym. J.,* 12, 371 (1976).
36. R. K. Samal, T. R. Mohanty, and P. L. Nayak, *Macromolecules,* 10, 489 (1977).
37. R. K. Samal, T. R. Mohanty, and P. L. Nayak, *J. Macromol. Sci., Chem.,* A10, 1239 (1976).
38. R. K. Samal and P. L. Nayak, *J. Polym. Sci. A-1,* 15, 2603 (1977).

39. W. Gabara and S. Porejko, *J. Polym. Sci. A-1*, **5**, 1539 (1967).

40. W. Gabara and S. Porejko, *J. Polym. Sci. A-1*, **5**, 1547 (1967).

41. S. Haworth and J. R. Holkar, *J. Soc. Dyers Colour.*, **82**, 257 (1966).

42. P. L. Nayak, S. Lenka, and N. C. Pati, *J. Appl. Polym. Sci.*, **22**, 3301 (1978).

43. R. Steward and D. G. Lee, *Can J. Chem.*, **42**, 439 (1964).

44. A. Bendak and A. Hebeish, *J. Appl. Polym. Sci.*, **17**, 1953 (1973).

45. R. T. Hayes, *J. Polym. Sci.*, **11**, 531 (1953).

46. J. H. Fendler and E. J. Fendler, *Catalysis in Micellar and Macromolecular Chemistry*, Academic Press, New York, 1975.

47. P. L. Nayak and M. Santappa, *Ind. J. Sci. Ind. Res.*, **35**, 662 (1975).

48. T. Sugimura, N. Yasumoto, and Y. Minouro, *J. Polym. Sci.*, **A3**, 2935 (1965).

49. A. R. Mukherjee, R. P. Mittra, A. M. Biswas, and S. Maitai, *J. Polym. Sci.*, **5**, 135 (1967).

50. B. M. Mandal, U. S. Nandi, and S. R. Palit, *J. Polym. Sci. A1*, **7**, 1407 (1969).

51. A. Hebeish and A. Bendak, *J. Appl. Polym. Sci.*, **18**, 1305 (1974).

52. A. Hebeish, S. H. Abdel-Fattah, and A. Bendak, *Angew. Makromol. Chem.*, **37**, 11 (1974).