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Grafting Vinyl Monomers onto Wool Fibers: Graft Copolymerization of Methyl Methacrylate onto Wool Using Ferric Acetylacetonate Complex

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ABSTRACT

The graft copolymerization of methyl methacrylate (MMA) onto native and reduced Indian Chokla wool fibers was studied in aqueous solution using an acetylacetonate complex of Fe(III). Perchloric acid was found to catalyze the reaction. The rate of grafting was investigated by varying the concentration of the monomer and the complex, the acidity of the medium, and the solvent composition of the reaction medium. The graft yield increases with increasing concentration of the initiator and with increasing temperature. An increase of monomer concentration up to 0.5634 mol/L and of the $HClO_4$ concentration up to 0.01 mol/L increases the graft yield. Reduced and oxidized wools were found to be better substrates than untreated, esterified,

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cross-linked, and trinitrophenylated wools. Among the various monomers studied, MMA was found to be the most active. A suitable kinetic scheme is proposed. From the activation energy data, average molecular weight, and spectral studies, the reactivity of –SH groups, and the extent of chain transfer is ascertained.

INTRODUCTION

The use of chelate complexes for initiating vinyl polymerization has attracted attention in recent years [1-7]. Arnett and Mendelsohn [3] observed that metal chelates produce free radicals upon heating, the initiating radical being generated by homolysis of the M–O bond. Kasting et al. [4, 8] reported that among the simple acetylacetonates, those of Mn(III) and Co(III) are most active. Bamford and Lind [1] and Otsu et al. [6, 7] reported the polymerization of vinyl monomers using a number of acetylacetonates. Graft copolymerization of vinyl monomers onto natural [9-11] and synthetic fibers [12] by employing metal acetylacetonates has been reported. We recently reported the graft copolymerization of MMA onto wool using $Mn(acac)_3$ and $VO(acac)_2$ as initiators [13, 14]. In an attempt to determine the role of active groups on a wool backbone and the –SH groups generated by the reduction of wool, several workers graft copolymerized MMA onto chemically modified wool [15-18].

This communication presents the kinetics and mechanism of graft copolymerization of MMA onto wool and chemically treated wool fibers using the $Fe(acac)_3$ complex. The PMR spectra, x-ray diffractograms, SEM studies, and thermogravimetric analysis of grafted samples will be reported in later communications.

EXPERIMENTAL

The purification of wool, monomers, solvents, method of rate measurement, and calculation of percentage of graft yield have been reported in a previous communication [19]. Wool was chemically modified by following a standard procedure [20].

DISCUSSIONS

Nature of the Substrate

The various chemically modified wool fibers follow an order of reactivity: reduced > oxidized > native > esterified > cross-linked > trinitrophenylated (Fig. 1).

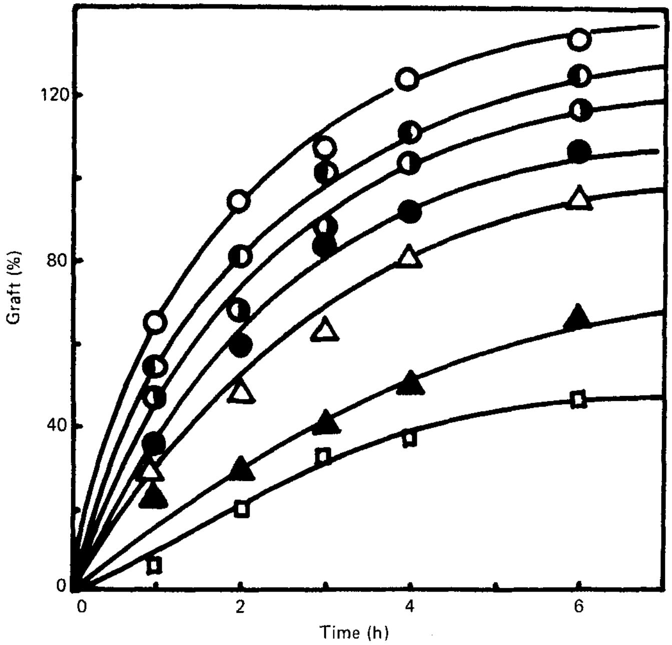


FIG. 1. Effect of modified wool on graft yield: $[Fe(acac)_3] = 2.8 \times 10^{-3}$ mol/L, [MMA] = 0.4694 mol/L, $[HClO_4]$ = 0.008 mol/L, [EtOH] = 1.72 mol/L, M:L = 1:100, 50°C, (○) reduced (0.5 M TGA), (◑) reduced (0.3 M TGA), (●) reduced (0.1 M TGA), (◐) oxidized, (△) native, (▲) esterified, (□) cross-linked.

Reduced wool undergoes graft copolymerization relatively easily under moderate reaction conditions, the reaction proceeding without a considerable induction period. The –SH groups formed by homolytic cleavage of the cystine disulfide linkage are known as active grafting sites [21], and the abstraction of hydrogen from the thiol groups by initiating radicals seems to proceed much more easily than from other groups. Besides, treatment of wool with TGA might increase its accessibility or swelling and hence enhance grafting [15]. When reduced wool was methylated and esterified, the graft yield is suppressed below that of native wool because of methylation and acetylation of the –SH groups generated. Further, graft yield was found to increase with increasing concentration of the reducing agent. This suggests that the extent of grafting is mostly dependent upon the concentration of the –SH groups.

Oxidation of wool with H_2O_2 also enhances grafting, but the graft percentage is lower than that with reduced wool. Oxidation most probably converts cystine to cysteic acid, and creation of a free radical is more difficult on cysteic acid than on the –SH group.

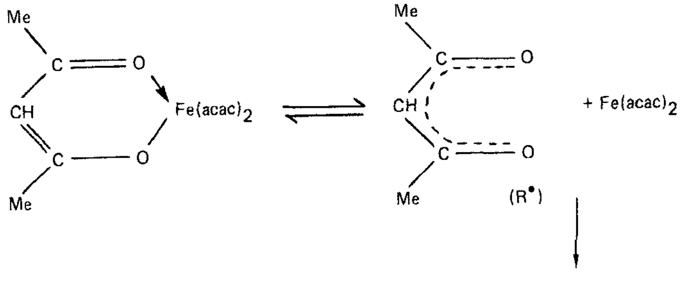
Decreased graft yield in the case of esterified, cross-linked, and TNP wool is due to 1) blocking of the active grafting sites; 2) lowering of the swellability of the fiber, leading to suppressed adsorption of $Fe(acac)_3$ and MMA; and 3) repulsion of MMA molecules by the negatively charged substituted nitro groups.

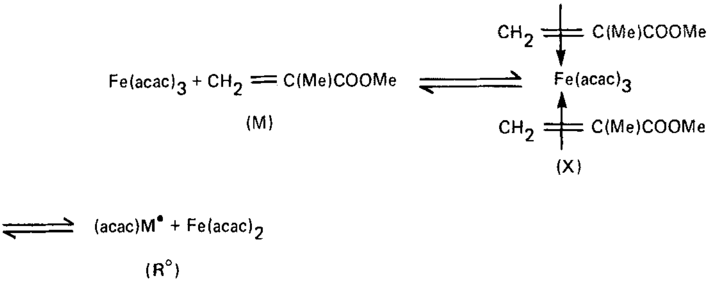
It was observed that wool reduced by a high concentration of the reducing agent (TGA) tends to decrease the fiber character, which might be due to the degradation of the base polymer during chemical treatment. Similar observations are reported by Sudhir and co-workers [22]. From x-ray diffraction data, SEM, and thermogravimetric analysis, these authors concluded that treatment of Chokla wool with TGA, H_2O_2, and peracetic acid resulted in considerable chemical damage to the base polymer, leading to decreased fiber strength.

Effect of Initiator Concentration

Within the range of 2.0 to 10.0×10^{-3} mol/L, the graft yield increases with increasing concentration of the complex (Fig. 2). In the initial stages a charge transfer complex is probably formed between the groups on the wool backbone, the chelate, and the monomer. Hence the concentrations of the chelate and the monomer are increased in the vicinity of the wool matrix. This assists the breakage of the acetylacetonate linkage of the chelate, and a free radical is formed on the methylene carbon atom. The formation of this free radical is assisted by the solvent [1], the acidity of the medium [1], and the monomer [20]. The solvent presumably weakens the M–O bond by hydrogen bonding with oxygen.

The free radical thus formed interacts with the grafting sites on the wool backbone to form a wool macroradical which interacts with the vinyl monomers, resulting in the formation of a graft copolymer. The chelate decomposes to yield acetylacetonate free radical or radical in combination with the monomer:





$$\underset{}{Fe(acac)_3} + \underset{(M)}{CH_2{=}C(Me)COOMe} \rightleftharpoons \underset{(X)}{\begin{array}{c} CH_2{=}C(Me)COOMe \\ \downarrow \\ Fe(acac)_3 \\ \uparrow \\ CH_2{=}C(Me)COOMe \end{array}}$$

$$\rightleftharpoons \underset{(R^\circ)}{(acac)M^\bullet} + Fe(acac)_2$$

Production of a free radical on the wool backbone is

$$WH + R^\bullet \xrightarrow{k} W^\bullet + RH$$

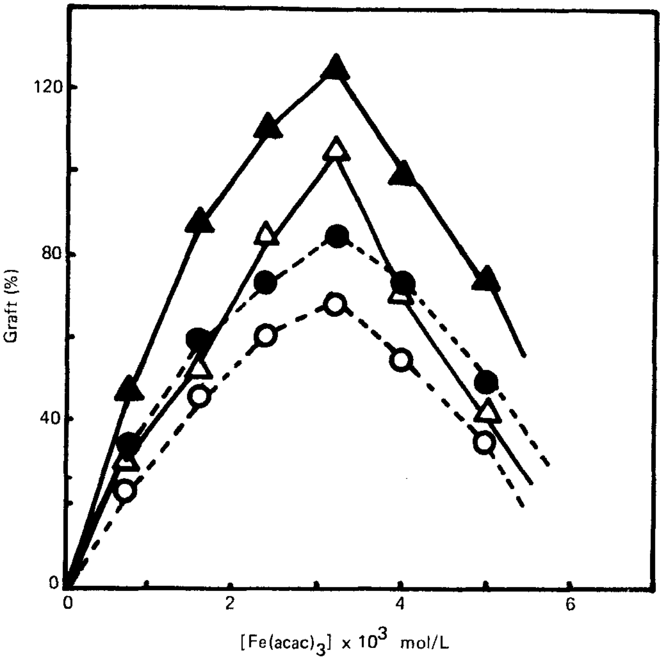


FIG. 2. Effect of [Fe(acac)$_3$] on graft yield: [MMA] = 0.3756 mol/L, [HClO$_4$] = 0.006 mol/L, [EtOH] = 2.15 mol/L, M:L = 1:100, 50°C. Native wool: (○) 3 h, (●) 6 h. Reduced wool: (△) 3 h, (▲) 6 h.

Initiation:

$$\mathrm{W^{\bullet}} + \mathrm{M} \xrightarrow{k_i} \mathrm{WM^{\bullet}}$$

$$\mathrm{R^{\bullet}} + \mathrm{M} \xrightarrow{k_i'} \mathrm{RM^{\bullet}}$$

Propagation:

$$\mathrm{WM^{\bullet}_{n-1}} + \mathrm{M} \xrightarrow{k_p} \mathrm{WM_n^{\bullet}}$$

$$\mathrm{RM^{\bullet}_{n-1}} + \mathrm{M} \xrightarrow{k_p'} \mathrm{RM_n^{\bullet}}$$

Termination:

$$\mathrm{WM_n^{\bullet}} + \mathrm{WM_n^{\bullet}} \xrightarrow{k_t} \text{grafted polymer}$$

$$\mathrm{RM_n^{\bullet}} + \mathrm{R^{\bullet}} \xrightarrow{k_t'} \text{homopolymer}$$

Oxidation:

$$\mathrm{W^{\bullet}} + \mathrm{Fe(acac)_3} \longrightarrow \text{oxidation products of wool} + \mathrm{Fe(acac)_2}$$

where WH is wool, M is monomer, and $\mathrm{W^{\bullet}}$ and $\mathrm{M^{\bullet}}$ are the corresponding radicals. Assuming mutual termination and applying the steady-state principle, the rate of graft copolymerization was found to be [13]

$$R_p = k_p \left[\frac{k}{k_t}\right]^{1/2} [\mathrm{WH}]^{1/2} [\mathrm{complex}]^{1/2} [\mathrm{M}]$$

Plots of R_p versus [M] (Fig. 3) and R_p versus $[\mathrm{complex}]^{1/2}$ (Fig. 4) for both native and reduced wools are linear, confirming the validity of the above reaction scheme.

Effect of Monomer Concentration

Native and reduced wools were graft copolymerized within the range of 0.1878 to 0.9388 mol/L of MMA concentration. It is observed that for native wool, the graft yield increases up to 0.5634 mol/L, decreas-

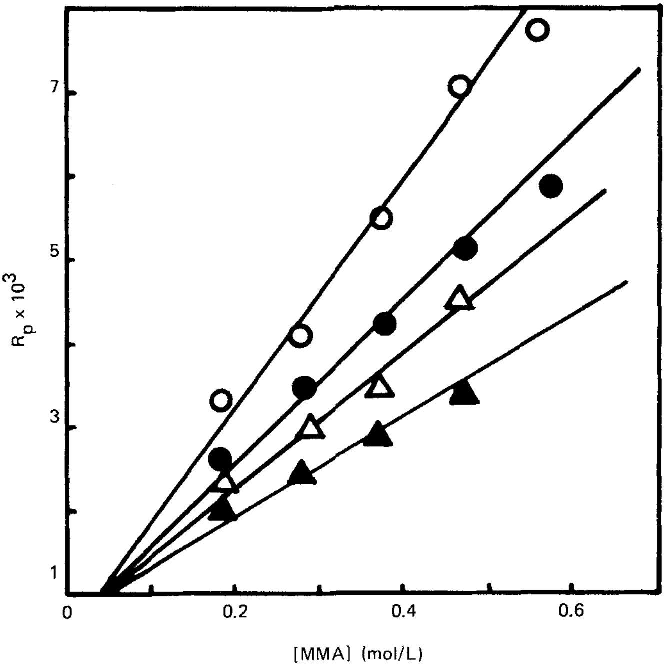


FIG. 3. Plot of R_p versus [M]. Native wool: (△) 4 h, (▲) 6 h. Reduced wool: (○) 4 h, (●) 6 h.

ing thereafter, whereas for reduced wool the graft yield increases with an increase in monomer concentration within the range of study (Fig. 5). This increasing trend in the case of reduced wool and the initial increasing trend in the case of native wool can be ascribed to 1) complexation of wool with monomer, 2) ease of formation of charge transfer complex such as $\overline{X}$, and 3) gel effect [23]. At higher concentrations of the monomer, the rate of combination and disproportionation of PMMA macroradicals is increased faster than their combination with wool [24]. Besides, the rate of monomer diffusion is bound to be progressively affected by the polymer deposit formed, and this is more pronounced at higher concentrations of the monomer [25].

The effect of various monomers on graft yield has been investigated. MMA was found to be the most active vinyl monomer, the order of reactivity being methyl methacrylate > methyl acrylate > ethyl acrylate > n-butyl acrylate > acrylic acid. This trend suggests that the formation of the initiating radical is monomer-assisted, leading to the formation $\overline{X}$. The ease of formation of such a complex will be maximum with MMA because of increased π-electron density

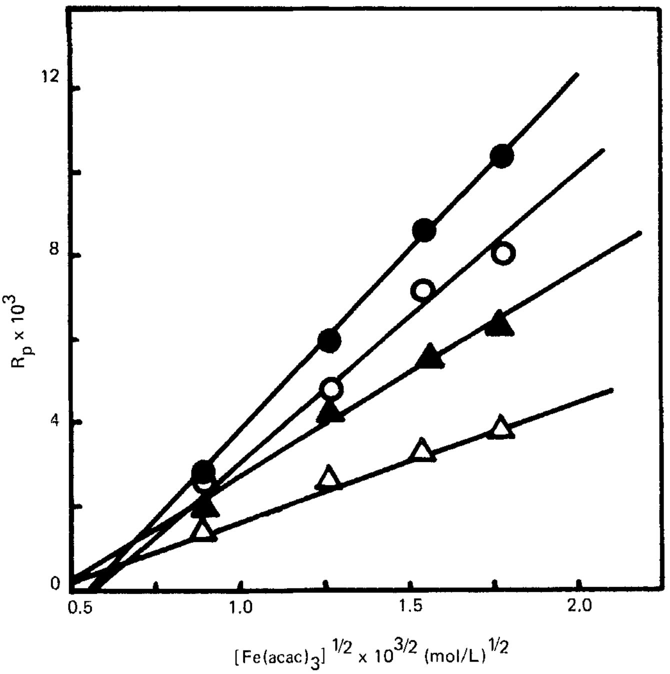


FIG. 4. Plot of R_p versus $[\text{complex}]^{1/2}$. Native wool: (▲) 3 h, (△) 6 h. Reduced wool: (●) 2 h, (○) 4 h.

due to the +I effect of the substituted methyl group. In AA, the –COOH group significantly decreases the π-electron density, making it least reactive. The decreasing order of graft yield from MA to BA is largely due to steric hindrance. The approach of the monomer to form the charge transfer complex with the active groups on wool matrix and with the initiator is not facilitated.

Effect of Temperature

Within the range from 40 to 55°C, graft yield increases with increasing temperature. This can be ascribed to 1) greater ease of acetylacetonate free radical formation and 2) increased solubility and enhanced diffusion rate of the monomer. The Arrhenius plot of log R_p versus 1/T (Fig. 6) is a straight line. The overall energy of activation was found to be 46.2 and 34.2 kJ/mol for native and reduced wool, respectively. The overall activation energy (E_a) accounts for

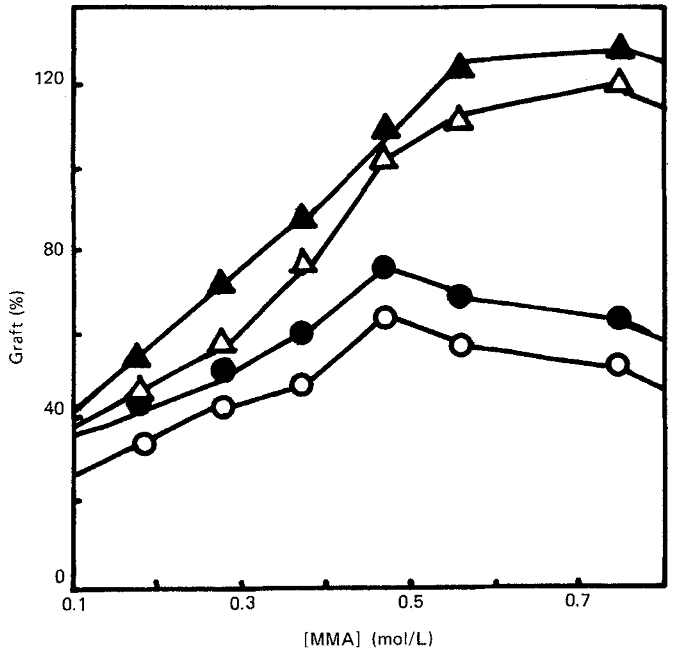


FIG. 5. Effect of [MMA] on graft yield: $[Fe(acac)_3] = 2.0 \times 10^{-3}$ mol/L, $[HClO_4] = 0.005$ mol/L, [EtOH] = 1.3 mol/L, M:L = 1:100, 50°C. Native wool: (○) 4 h, (●) 6 h. Reduced wool: (△) 4 h, (▲) 6 h.

1) the energy of activation for the decomposition of the catalyst (E_d), 2) the energy of activation for the growing radical to chain transfer with the backbone to form the wool macroradical (E_{tr}), 3) the activation energy of propagation (E_p), and 4) the activation energy for the termination process (E_t). These terms are related to E_a:

$$E_a = E_d/2 + E_{tr}/2 + [(E_p - E_t)/2]$$

Using the value of $(E_p - E_t)/2 = 18.8$ kJ/mol given by Tobolsky [26], the sum $\frac{1}{2}(E_d + E_{tr})$ for native wool is computed to be 27.4 kJ/mol and that for reduced wool to be 15.4 kJ/mol. For the initial stage of decomposition of the complex, E_d would be the same for both substrates. Hence the lower value for reduced wool is attributed to a lower energy

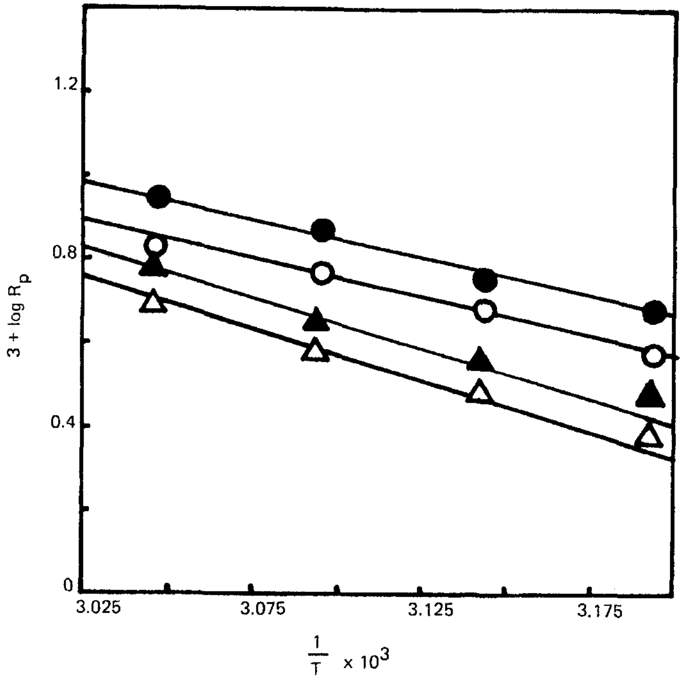


FIG. 6. Arrhenius plot of log R_p versus 1/T. Native wool: (●) 4 h, (○) 6 h. Reduced wool: (▲) 3 h, (△) 6 h.

of activation in the chain transfer process (lower E_{tr} value) in which free radicals are created on the –SH groups. Thus the thiol groups are preferred centers of grafting over other active groups.

Effect of Acid Concentration and Polymerization Medium

Graft copolymerization was studied within the range from 3 to 15.0×10^{-3} mol/L of $HClO_4$ concentration. The graft yield increases with increasing concentration of the acid up to 7.5×10^{-3} mol/L and thereafter it decreases. Of the various solvents studied, a mixture of solvent/water at a ratio of 15:85 was most suitable for methanol; 10:90 for ethanol, n-PrOH, and i-PrOH; and 5:95 for n-butanol and amyl alcohol. Some chain transfer solvents and solvents acting as solubilizers of the monomer at a solvent/water ratio of 5:95 follow the order of reactivity $CHCl_3 > CCl_4 >$ EtSH ($< 1\%$) and $CH_3COOH >$

HCOOH > acetone > dioxane > DMF. Regardless of the solvent used, an increase in the amount of solvent in the reaction mixture tends to decrease the graft yield [10, 20].

Determination of Average Molecular Weight

Separation and purification of grafted polymer were carried out by 1) digesting in 5 M HCl, 2) extracting with a solution of diethyl ether in methanol (10:90), and 3) dissolving in ethyl acetate and reprecipitating by cold methanol repeatedly. The average molecular weight of grafted PMMA was determined viscometrically by employing the relationship [27]:

$$[\eta] = 9.6 \times 10^5 \, (\overline{M})^{0.69}$$

Several samples of reduced wool were graft copolymerized within the range of 0.1878 to 0.5634 mol/L of the monomer concentration. Within this range the average molecular weight of PMMA is found to be linearly related to monomer concentration (Fig. 7). By employing the relationship

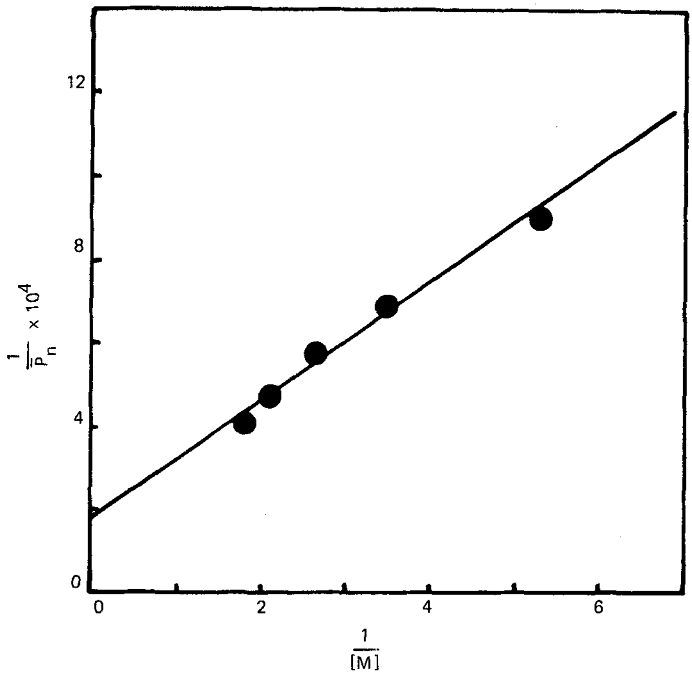


FIG. 7. Plot of $1/\overline{P}_n$ versus $1/[M]$. Substrate: Reduced wool.

$$\frac{1}{\bar{P}_n} = \left[\frac{1}{\bar{P}_n}\right]_o + C_m \frac{[S]}{[M]}$$

where [S] = concentration of the solvent, $\bar{P}_n$ = degree of polymerization, C_m, the chain transfer constant with respect to the monomer (MMA), is found to be 1.34×10^{-4} from the slope of the plot of $1/\bar{P}_n$ versus 1/[M] (Fig. 7).

Alkali Solubility

The solubility test was performed by following the procedure of Leaveau and co-workers [28]. It was observed that with an increase in graft percentage, the alkali solubility decreases. This suggests that PMMA chains act as diffusion barriers toward alkali penetration into wool fibers, thus protecting polypeptide chains, salt linkage, and disulfide bonds [29].

Spectral Study

The IR spectra of PMMA generated from grafted reduced wools were taken. Study of the spectra suggests that grafted PMMA chains have an atactic structure, the characteristic bands appearing at 750, 1730, and 3000 cm^{-1}. The band in the range from 600 to 750 cm^{-1} is due to the C–S–C system and is indicative of the grafting site, as expected.

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REFERENCES

[1] C. H. Bamford and D. J. Lind, Chem. Ind. (London), p. 1627 (1965).
[2] C. H. Bamford and D. J. Lind, Chem. Commun., p. 792 (1966).
[3] E. M. Arnett and M. A. Mendelsohn, J. Am. Chem. Soc., 84, 3821 (1962).
[4] E. G. Kasting, H. Naarmann, H. Reis, and C. Berding, Angew. Chem., 77, 313 (1965).

[5] K. M. Riches, Macromol. Chem., 103, 175 (1967).
[6] T. Otsu, N. Minauii, and Y. Nishikawa, J. Macromol. Sci.–Chem., 2, 905 (1965).
[7] Y. Nishikawa and T. Otsu, J. Chem. Soc., Jpn., Ind. Chem. Sect., 72, 751 (1969).
[8] E. G. Kasting, M. A. Naarmann, H. Reis, and C. Berding, Angew. Chem. Int. Ed., 4, 3321 (1965).
[9] B. N. Mishra, I. Kaur, and D. S. Sood, J. Macromol. Sci.–Chem., A14(8), 1255 (1980).
[10] R. K. Samal, G. V. Suryanarayana, P. C. Das, G. Panda, and M. C. Nayak, J. Appl. Polym. Sci., 26(7), 2221 (1981).
[11] A. K. Tripathy, S. Lenka, and P. L. Nayak, Ibid., 26(4), 1413 (1981).
[12] S. Lenka and A. K. Tripathy, J. Polym. Sci., Polym. Chem. Ed., 20(4), 1139 (1982).
[13] P. L. Nayak, G. Sahu, and S. Samal, J. Macromol. Sci.–Chem., A16(7), 1309 (1981).
[14] S. Samal, G. Sahu, and P. L. Nayak, J. Appl. Polym. Sci., In Press.
[15] M. Negishi and K. Arai, J. Appl. Polym. Sci., 11, 115 (1967).
[16] M. Negishi, K. Arai, and S. Okada, Ibid., 12, 2585 (1968).
[17] J. Niezette, R. Geurts, and R. Erilli, J. Macromol. Sci.–Chem., A16(6), 1117 (1981).
[18] A. Hebeish, M. M. El-Rafie, M. A. Kashouti, and F. El-Sisi, J. Appl. Polym. Sci., 26(12), 3995 (1981).
[19] P. L. Nayak, S. Lenka, and M. K. Mishra, Angew. Macromol. Chem., 90, 155 (1980).
[20] S. Samal, G. Sahu, and P. L. Nayak, J. Macromol. Sci.–Chem., A20(2), 153 (1983).
[21] M. Negishi and K. Arai, J. Appl. Polym. Sci., 11, 1427 (1967).
[22] R. K. Sudhir, P. Bajaj, and V. P. Singh, Indian J. Text. Res., 5(2), 47 (1980).
[23] S. Dilli, J. L. Garnett, E. C. Martin, and D. H. Phvoc, J. Polym. Sci., Polym. Symp., C37, 57 (1972).
[24] W. Gabara and S. Porejko, J. Polym. Sci., Part A-1, 5, 1547 (1967).
[25] S. Haworth and J. R. Holker, J. Soc. Dyers Colour., 32, 257 (1966).
[26] A. V. Tobolsky, J. Colloid Sci., 12, 325 (1957).
[27] R. J. Valles, M. C. Otzingen, and D. W. Lewis, J. Appl. Polym. Sci., 4, 92 (1960).
[28] M. Leaveau, M. Calliet, and N. Demonart, Bull. Inst. Text. Fr., 90, 7 (1960).
[29] H. L. Needles, L. Sarsfield, and J. Dowhaniuk, Text. Res. J., 42, 558 (1972).

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