Graft Copolymerization of Methyl Methacrylate onto Wool in Presence of Vanadyl Sulfate–Potassium Bromate in Aqueous Medium

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Synopsis

Graft copolymerization of methyl methacrylate onto wool was studied in the presence of vanadyl sulfate and potassium bromate. The experimental results suggested that the wool radicals produced in the reaction initiated the graft copolymerization and that the graft polymer radicals terminated by mutual combination. An appropriate kinetic scheme was proposed and the rate and energy parameters were evaluated. Alkaline solubility, dye uptake, and tensile strength of the wool samples were determined before and after grafting.

INTRODUCTION

In the graft copolymerization of vinyl monomers onto wool backbone,[1-6] not much kinetic work has been done. The redox couple, namely, vanadyl sulfate–potassium bromate, was used for the first time by us to study the detailed kinetics of graft copolymerization of methyl methacrylate onto wool backbone. The kinetic study was carried out in aqueous medium in the temperature range 30–55°C, and the results are presented in this report.

EXPERIMENTAL

Most of the reagents used were AnalaR grade. Wool obtained from Binny Ltd. Bangalore, was used as such. A 0.05-mL solution of vanadyl sulfate was prepared with distilled water once in three days.[7,8] Kinetic experiments were carried out in conical flasks (250 ml) fitted with inlet and outlet tubes. The graft copolymerization was heterogeneous since the wool used in the reaction was not solubilized. Wool (0.5 g) and required amounts of potassium bromate solution, monomer, and water were taken in the reaction vessel and the reaction mixture was thermostated at 50 ± 0.1°C for 20 min. The system was flushed with oxygen-free nitrogen for 20 min. At the end of deaeration, the required amount of vanadyl sulfate solution was added to the reaction mixture. The reaction vessel was sealed with rubber gaskets to ensure inert atmosphere.

At the end of the reaction time, the reaction was arrested by immediately cooling the reaction vessel in ice-cold water. The grafted wool was filtered from the reaction mixture using a glass filter (1G 3 Jena) washed several times with distilled water, dried at 60°C, conditioned at 65% RH, and weighed to constant weight. The grafted wool was Soxhlet extracted with acetone for 24 h and then washed with water, dried, and conditioned to constant weight as above. The

difference between the weight of wool after grafting and the weight of original wool taken gave the weight of the graft.

Rate of grafting (R_g) and % grafting were calculated using the above data. The side chains were isolated and purified from the grafted wool by a two-step hydrochloric acid digestion method.[9] Chain lengths were calculated from the intrinsic viscosities (η) of poly(methyl methacrylate) graft side chains in benzene determined at 25°C. Infrared spectra for the graft polymer samples obtained by acid hydrolysis were taken using a Perkin–Elmer model 337 grating infrared spectrophotometer using potassium bromide pellets (500 mg) containing 2–6 mg powdered polymer. NMR spectra of poly(methyl methacrylate) side chains were taken using a 15% solution of the polymer in chloroform using a Varian 60 MH_2 spectrophotometer. Alkaline solubility was determined by the method of Harris.[10] Dye uptake[11] for both grafted and control wool samples was studied using the dye alizarin blue. The tensile strength of the fibers was also determined using an Instron tensile tester at a crosshead speed of 0.5 cm/min and chart speed of 10 cm/min. The diameter was calculated using a piler micrometer.

The cross-sectional area was found using the relationship

$$\text{cross-sectional area} = \frac{\pi d^2}{4}$$

where d is the diameter of the fiber.

The breaking load of the fiber was also determined. The tensile strength was found from the data using the expression

$$\text{tensile strength (in kg/mm}^2) = \frac{\text{breaking load (in kg)}}{\text{cross-sectional area (in mm}^2)}$$

RESULTS AND DISCUSSION

All experiments were carried out under nitrogen since the reaction rate R_g was much reduced in the presence of air.

Rate of Graft Copolymerization R_g

Effect of Monomer on R_g. The rate of grafting increased with increasing amount of monomer when monomer was varied from 0.0169 to 0.1183 m/L at constant $[KBrO_3] = 4 \times 10^{-3}$ and 8×10^{-3} m/L, $[VO^{2+}] = 0.05 \times 10^{-3}$ m/L, wool = 0.5 g. Plots of R_g vs. [MMA] were straight lines passing through the origin. Thus, the rate was directly dependent on $[MMA]^{1.0}$ [Figs. 1(a) and 1(b)].

Effect of Potassium Bromate on R_g. When $[KBrO_3]$ was varied from 0.25 to 10×10^{-3} m/L at constant [MMA] = 0.094 m/L, $[VO^{2+}] = 0.05 \times 10^{-3}$ m/L and wool = 0.5 g, an increase in the grafting rate with increasing $[KBrO_3]$ (< 4 $\times 10^{-3}$ m/L) was observed. At higher $[KBrO_3]$ (> 4×10^{-3} m/L), R_g was decreased. Plot of log R_g vs. log $[KBrO_3]$ in the increasing range gave a straight line of slope 0.5 [Fig. 1(c)].

Effect of Vanadyl Sulfate on R_g. When $[VOSO_4]$ was varied from 0.025 $\times 10^{-3}$ to 0.5×10^{-3} m/L, at constant $[KBrO_3] = 4 \times 10^{-3}$ m/L, [MMA] = 0.094 m/L, and wool = 0.5 g, an initial increase in R_g was noted. Above $[VOSO_4] = 0.24 \times 10^{-3}$ m/L, R_g decreased. Plot of log R_g vs. log $[VOSO_4]$ at lower concentration of $VOSO_4$ gave a slope of 0.5 [Fig. 1(d)].
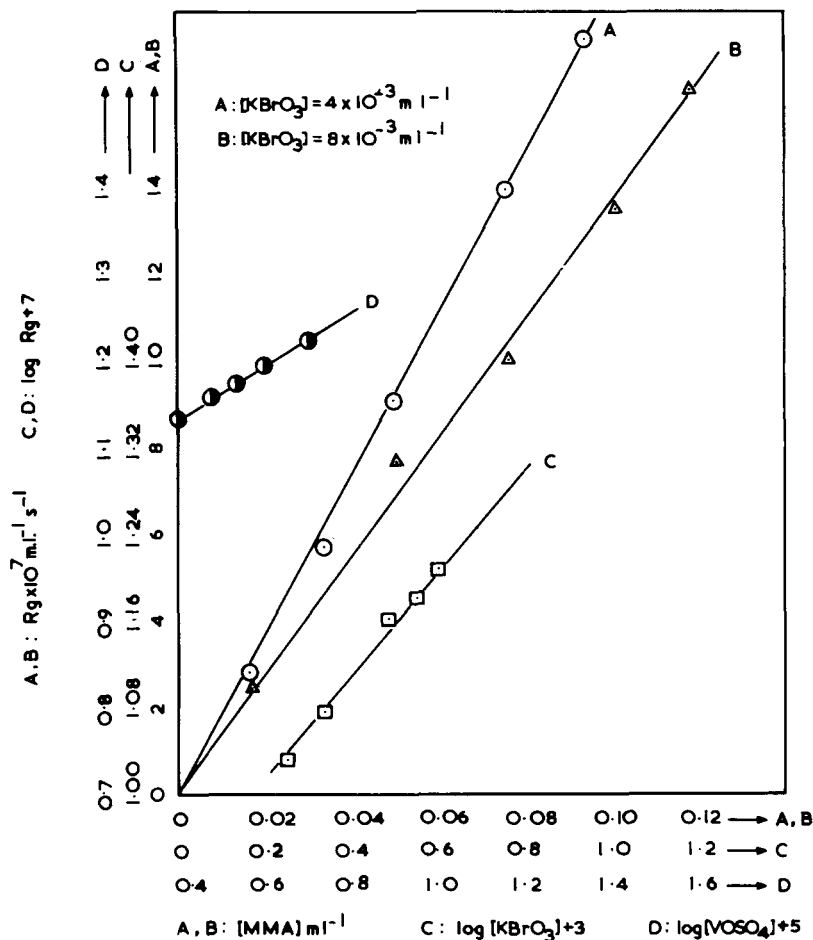
Fig. 1. $KBrO_3$–$VOSO_4$–MMA–wool system. (A)(B) [monomer] variation; (C) [$KBrO_3$] variation; (D) [$VOSO_4$] variation.

Effect of Wool on R_g. At constant [$KBrO_3$] = 4 × 10^{-3} m/L, [$VOSO_4$] = 0.05 × 10^{-3} m/L and [MMA] = 0.094 m/L, and the weight of wool was varied, R_g increased upto 0.5 g wool. Further increase in the weight of wool decreased the rate. The plot of log R_g vs. log wool was a straight line of unit slope in the increasing range [Fig. 2(a)].

Amino acids such as glutamic acid, aspartic acid, leucine, isoleucine, valine, tryptophane, tyrosine, methionine, histidine, arginine, threonine, and cysteine were used in the place of wool for homopolymerization of MMA. It was found that cysteine (6 to 14%) alone was able to initiate homopolymerization, showing that the cysteine radical may be the initiating species in grafting also [Fig. 2(b)].

Effect of Sulfuric Acid on R_g. At constant [$KBrO_3$] = 4 × 10^{-3} m/L, [$VOSO_4$] = 0.05 × 10^{-3} m/L, and [MMA] = 0.094 m/L and wool = 0.5 g, [H_2SO_4] was varied from 0.1 to 1.2 m/L with and without keeping the ionic strength constant. In the former case, sodium sulfate was used to maintain ionic strength (μ = 1.7 m/L). When [H_2SO_4] was varied, R_g increased gradually with increasing
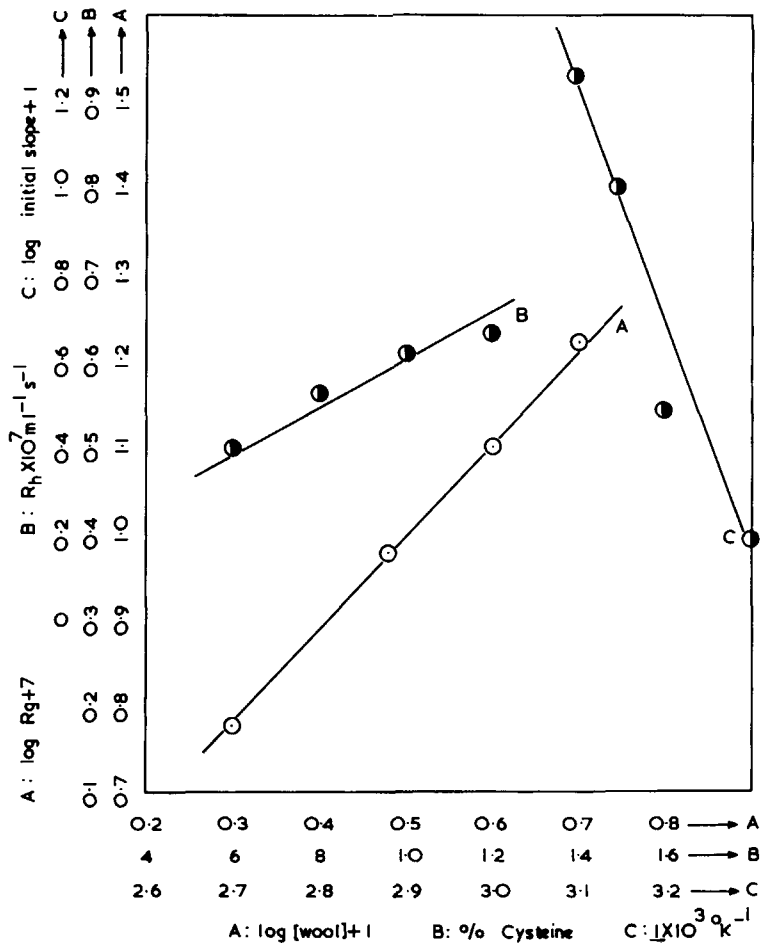
Fig. 2. $KBrO_3$–$VOSO_4$–MMA–wool system. (A) wool variation; (B) Cysteine variation; (C) temperature variation.

addition of sulfuric acid in the beginning and decreased afterward. When μ was maintained constant, the increase and decrease were found to be sharp; a maximum R_g was obtained at $[H_2SO_4]$ = 0.4 m/L (Table I).

Effect of Ionic Strength (μ) on R_g. When ionic strength was varied from 0.04 to 3.04 m/L using sodium sulfate, at constant $[KBrO_3]$ = 4 × 10^{-3} and 8 × 10^{-3} m/L, $[VOSO_4]$ = 0.05 × 10^{-3} m/L, [MMA] = 0.094 m/L, and wool = 0.5 g, R_g decreased continuously; and beyond μ = 1.74 m/L, no grafting was observed (Table II).

Effect of Other Salts on R_g. The effect of tetraalkylammonium bromide (0.2–4.8 × 10^{-3} m/L) on the grafting of MMA onto wool was studied at constant $[KBrO_3]$ = 4 × 10^{-3} m/L, $[VOSO_4]$ = 0.05 × 10^{-3} m/L, and [MMA] = 0.094 m/L and wool = 0.5 g. The rate of grafting increased with increasing amounts of tetramethylammonium bromide (Table III). But the rate values were far less than that when no tetramethylammonium bromide was used. The swellability of wool[12] in the presence of such a salt would probably be reduced due to the bulkiness of the anion, and hence the rate of grafting decreased (Table IIIa).

Sodium lauryl sulfate (NaLS) was varied from 0.2 to 4.8 × 10^{-3} m/L at constant

TABLE I

KBrO$_3$–VOSO$_4$–MMA–Wool System in Aqueous Medium. Sulphuric Acid Variation[a]

[H$_2$SO$_4$], m/L	$R_g \times 10^7$, m/L·s	
	μ not maintained constant	$\mu = 1.7$ m/L adjusted with sodium sulfate
0.00	17.36	—
0.01	22.18	—
0.02	23.57	—
0.04	24.82	—
0.08	26.03	—
0.10	25.45	9.03
0.20	25.05	—
0.30	25.12	27.09
0.40	—	35.70
0.60	17.44	20.02
0.80	—	4.27
1.20	—	2.52
1.60	—	0.63

[a] [KBrO$_3$] = 4 × 10^{-3} m/L; [VOSO$_4$] = 0.05 × 10^{-3} m/L; [MMA] = 0.094 m/L; temp. = 50°C; time = 240 min; wool = 0.5 g; solvent = water.

[KBrO$_3$] = 4 × 10^{-3} m/L, [VOSO$_4$] = 0.05 × 10^{-3} m/L, and [MMA] = 0.094 m/L and wool = 0.5 g. The presence of the surface-active substrate showed no favorable effect on the rate of grafting[13] (Table IIIb).

Monomer Reactivity. Different monomers such as acrylonitrile, ethyl acrylate, methacrylic acid, methyl methacrylate, and acrylic acid were used to graft wool at constant [KBrO$_3$] = 4 × 10^{-3} m/L and [VOSO$_4$] = 0.05 × 10^{-3} m/L and wool = 0.5 g. The order of reactivity was found to be acrylic acid > methyl methacrylate > methacrylic acid > ethyl acrylate > acrylonitrile [Figs. 3(a) to 3(e)].

Vinyl compounds react with wool itself forming compounds.[14a] Monomers such as acrylonitrile react with SH groups of proteins[14b] to form cyanoethyl cysteine:

$$\text{protein—S}^- + \text{CH}_2\!\!=\!\!\text{CH·CN} + \text{H}^+ \rightleftharpoons \text{protein—S—CH}_2\text{—CH}_2\text{CN}$$
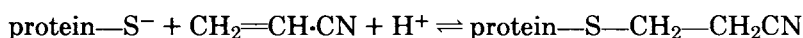
which reduces the active sites on the wool backbone, thus decreasing the rate of grafting. The difference in the rate of grafting with different monomers may be due to the difference in their reactivity toward wool backbone.

TABLE II

KBrO$_3$–VOSO$_4$–MMA–Wool System in Aqueous Medium. Ionic Strength Variation with Sodium Sulphate[a]

[KBrO$_3$] = 4 × 10^{-3} m/L		[KBrO$_3$] = 8 × 10^{-3} m/L	
μ, m/L	$R_g \times 10^7$, m/L·s	μ, m/L	$R_g \times 10^7$, m/L s^{-1}
0.04	17.36	0.04	11.05
0.14	5.24	0.08	11.79
0.24	2.66	0.18	7.73
0.44	—	0.28	6.65
0.84	—	0.48	5.09
1.04	—	0.88	3.51
1.34	—	1.08	2.29

[a] [VOSO$_4$] = 0.05 × 10^{-3} m/L; [MMA] = 0.094 m/L; temp. = 50°C; time = 240 min; wool = 0.5 g; solvent = water.

TABLE III
KBrO₃–VOSO₄–MMA–Wool System in Aqueous Medium[a]
A: Tetramethylammonium Bromide Variation

$(CH_3)_4 NBr \times 10^3$, m/L	$R_g \times 10^7$, m/L·s
0.0	17.36
0.2	1.02
0.4	1.22
0.8	2.04
1.2	2.74
2.4	4.40
4.8	8.33

B: Sodium Lauryl Sulfate Variation	
NaLS $\times 10^3$, m/L	$R_g \times 10^7$, m/L·s
0.0	17.36
0.2	0.48
0.4	1.33
0.8	3.61
1.2	2.16
2.4	0.33
4.8	—

[a] [KBrO₃] = 4 × 10⁻³ m/L; [VOSO₄] = 0.05 × 10⁻³ m/L; [MMA] = 0.094 m/L; temp. = 50°C; time = 240 min; wool = 0.5 g; solvent = water.

Effect of Temperature. Temperature was varied from 30 to 50°C at constant [KBrO₃] = 4 × 10⁻³ m/L and [VOSO₄] = 0.05 × 10⁻³ m/L and wool = 0.5 g. R_g values increased with increase in temperature from 30 to 50°C [Figure 2(c)], while at 55°C they decreased.

Effect of Metal Ions on R_g. The metal ions generally increased the rate of grafting at lower concentrations. At higher concentrations, with the exception of zinc and potassium, the rate was decreased. The increase in the rate at lower metal ion concentration might be due to the formation of an effective redox couple by the metal ion with the oxidant to initiate the grafting reaction. At higher concentrations, the same metal ion or the oxidized state of it may be involved in the termination reaction thus decreasing the rate of grafting (Figs. 4(a) to 4(c), Figs. 5(a) to 5(d)].

Chain Length Measurements

Chain length n was found to be directly proportional to $[MMA]^{1.0}$ and inversely proportional to $[KBrO_3]^{0.5}$, $[VOSO_4]^{0.5}$, and $[wool]^{1.0}$ [Figs. 6(a) to 6(d)].

Mechanism and Rate Law

From the foregoing kinetic results, a suitable reaction scheme was suggested as shown below:
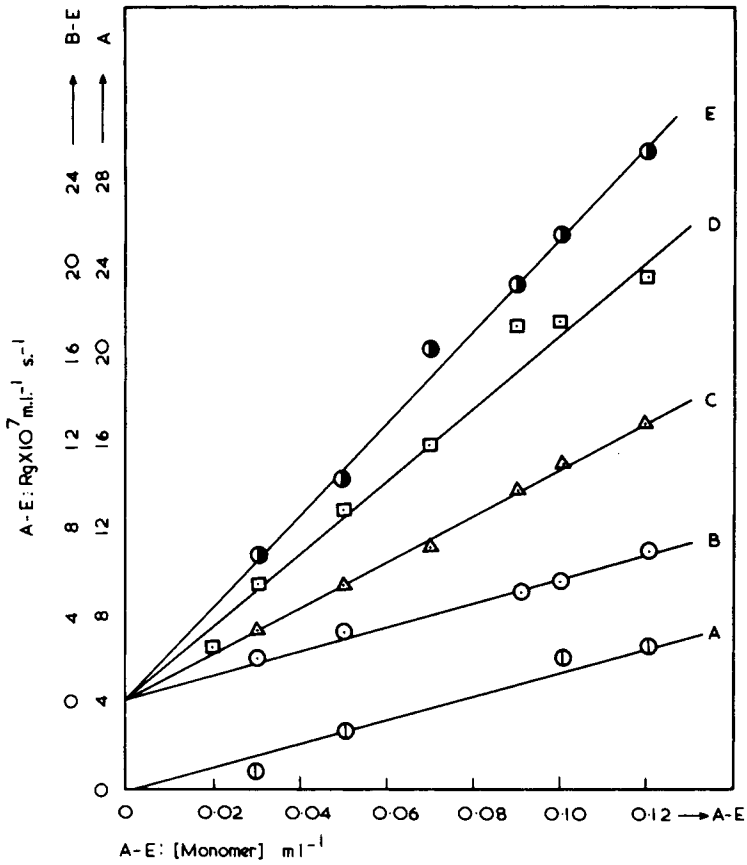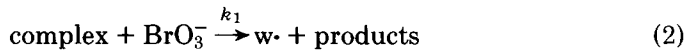Production of Wool radicals (w·) by Reaction of Complex (wool–VO²⁺–wool) with Bromate Ions:

$$w + VO^{2+} + w \overset{K}{\rightleftharpoons} complex \tag{1}$$
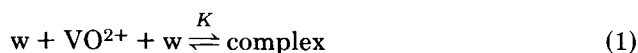
Fig. 3. KBrO$_3$–VOSO$_4$–MMA–wool system. Monomer reactivity. (A) acrylonitrile; (B) ethyl acrylate; (C) methacrylic acid; (D) methyl methacrylate; (E) acrylic acid.

$$\text{complex} + \text{BrO}_3^- \xrightarrow{k_1} \text{w} \cdot + \text{products} \qquad (2)$$

Formation of the above complex was proposed in similarity with the VO^{2+} complex called amavadine,[15] where the vanadium(IV) is attached to two macromolecules in the mushroom Amanita muscaria. Chelation with vanadium(IV) is also found to be facilitated by the presence of cysteine.[16]
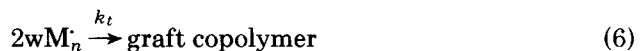
Initiation:

$$\text{w} \cdot + \text{M} \xrightarrow{k_2} \text{wM} \cdot \qquad (3)$$

Propagation:

$$\text{wM} \cdot + \text{M} \xrightarrow{k_p} \text{wM}_2^{\cdot} \qquad (4)$$

$$\text{wM}_{n-1}^{\cdot} + \text{M} \xrightarrow{k_p} \text{wM}_n^{\cdot} \qquad (5)$$

Mutual termination of growing polymer radicals:

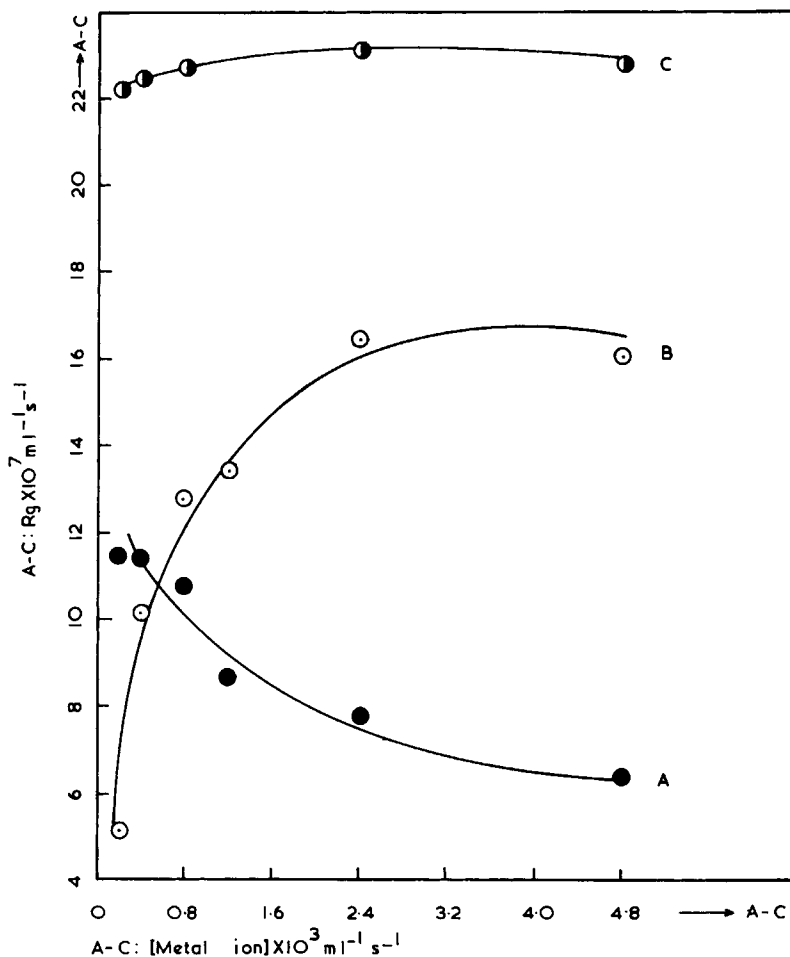$$2\text{wM}_n^{\cdot} \xrightarrow{k_t} \text{graft copolymer} \qquad (6)$$

Fig. 4. $KBrO_3$–$VOSO_4$–MMA–wool system.   Metal ion variation. (A) cobalt ion; (B) potassium ion; (C) zinc ion.

Assuming steady state conditions,

$$k_2[M][w] = k_t[wM_n]^2 \tag{7}$$

Substituting $[w]$ into eq. (7), we get

$$[wM_n] = \left\{\frac{k_1[BrO_3^-]K[w]^2[VO^{2+}]}{k_t}\right\}^{1/2} \tag{8}$$

Since

$$R_g = k_p[wM_n][M] \tag{9}$$

substituting the value of $[wM_n]$ into eq. (9), we get

$$R_g = k_p\left\{\frac{k_1K[BrO_3^-][VO^{2+}]}{k_t}\right\}^{1/2}[w][M] \tag{10}$$

and chain length

$$n = \frac{k_p[wM_n][M]}{k_t[wM_n]^2} \tag{11}$$
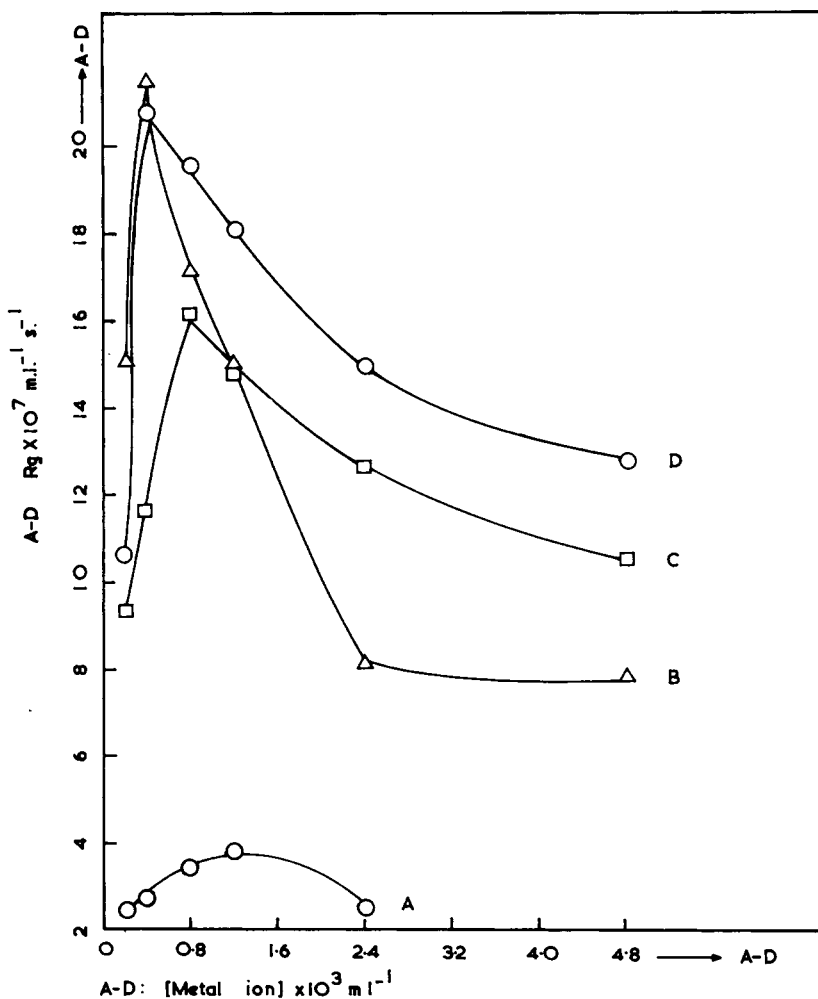
Fig. 5. $KBrO_3$–$VOSO_4$–MMA–wool system. Metal ion variation. (A) copper ion; (B) ferrous ion; (C) manganese ion; (D) nickel ion.

$$= \frac{k_p[\mathrm{M}]}{k_t^{1/2} \, k_1^{1/2} K^{1/2}[\mathrm{BrO_3^-}]^{1/2}[\mathrm{VO^{2+}}]^{1/2}[\mathrm{w}]} \tag{12}$$

Evaluation of Rate and Thermodynamic Parameters

The rate parameter values $k_p k_1^{1/2} K^{1/2}/k_t^{1/2}$ and $k_p/k_t^{1/2}$ were evaluated from the experimental results. The $k_p/k_t^{1/2}$ values agreed very well with the literature value.[17] E_a, $\Delta S^{\neq}$, $\Delta H^{\neq}$, and $\Delta G^{\neq}$ values were also evaluated (Table IV).

Infrared spectra of the poly(methyl methacrylate) side chains isolated from the wool grafts showed typical bands characteristic of amino acid residues and those corresponding to poly(methyl methacrylate). The characteristic amide I and II bands[18] at 1650 and 1550 cm^{-1} and absorption peaks due to the poly-(methyl methacrylate)[19] C=O stretching vibration in the ester at 1730 cm^{-1} and C—O stretching vibration at 1200 and 1080 cm^{-1} were also seen in the infrared spectra taken of the graft side chains. The NMR spectra of poly(methyl
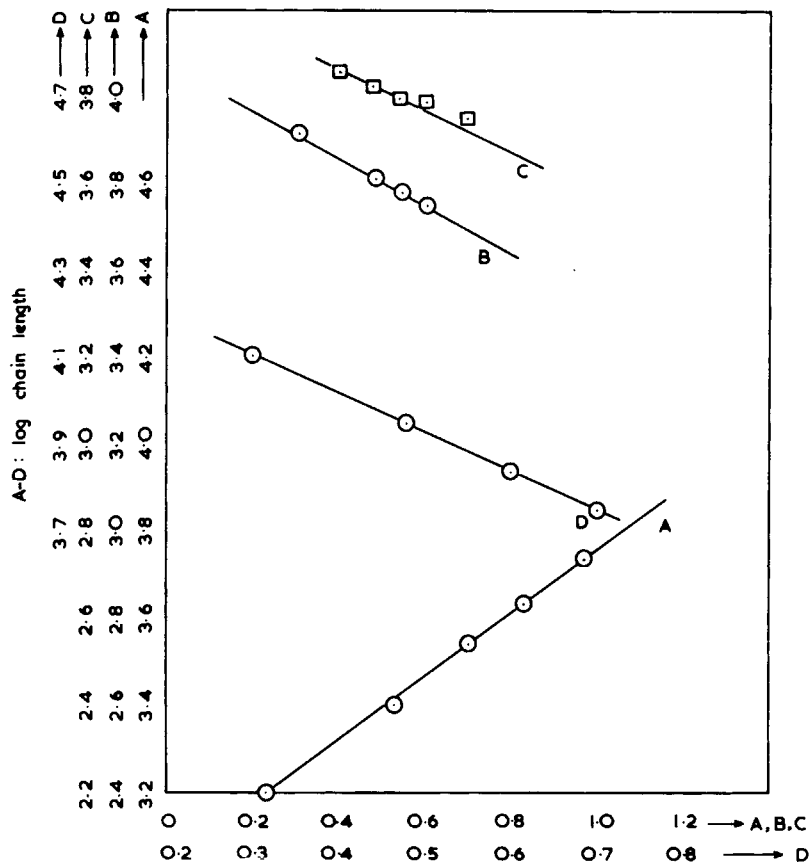
Fig. 6. KBrO₃–VOSO₄–MMA–wool system. Chain length dependence. (A) log [MMA] + 2; (B) log [KBrO₃] + 3; (C) log [VOSO₄] + 5; (D) log [wool] + 1.

methacrylate) side chain showed peaks at 8.7, 7.7, and 6.2 δ values.[20] Both provided evidence of graft copolymerization of methyl methacrylate onto wool.

Alkali breaks up the salt and cysteine linkages in the wool fiber and reacts with it producing soluble products. When wool samples, both original and grafted, were treated with alkali under identical conditions, the grafted wool samples were found to be more stable than the original sample. The solubility of the fiber decreased with increase in the percentage of grafting.[21] The decreased alkaline solubility of the grafted wool might be due to the formation of stable, new

TABLE IV
KBrO₃–VOSO₄–MMA–Wool System in Aqueous Medium. Rate and Thermodynamic Parameters[a]

Overall activation energy, kcal/mol	$k_p k_i^{1/2} K^{1/2}/k_t^{1/2}$				Temp. = 323°K		
	From R_g vs. [MMA] plot	From R_g vs. [VO²⁺]⁰·⁵ plot	From R_g vs. [BrO₃⁻]⁰·⁵ plot	From R_g vs. wool plot	$\Delta S \neq$ cal/deg. mol	$\Delta H \neq$ kcal/ mol	$\Delta G \neq$ kcal/ mol
24.40	0.042	0.0474	0.0383	0.044	+15.89	23.76	18.63

[a] $k_p/k_t^{1/2}$ (1/m.s)$^{1/2}$ = 1.014 (24).

TABLE V
Alkaline Solubility, Dye Uptake, and Tensile Property of Original and Grafted Wool Samples

% Grafting	Alkaline solubility	% Dye uptake	Tensile strength, kg/mm^2
0	16.86	14.45	17.79
7.98	9.16	18.07	18.85
16.11	8.70	20.48	120.00
18.65	—	25.28	—
22.13	—	—	154.00
27.71	8.10	30.72	—
28.91	—	—	196.00
34.64	7.51	31.32	—
49.37	6.46	32.53	—
57.19	6.45	33.13	—

crosslinkages in the wool backbone retarding the action of alkali (Table V). Dyeing with alizarin blue showed from the spectral studies that the % dye uptake was greater for the grafted sample than for the original wool sample. Due to the deposition of poly(MMA) in the interior regions of the fiber, the amorphous region in the wool fiber had been increased, thereby facilitating the diffusion of dye into the fiber[22,23] (Table V). The tensile strength of the fibers increased with increase in the percentage grafting. Grafting probably resulted in the formation of new linkages, thereby giving additional strength to the wool fiber (Table V).

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