Graft Copolymerization of Methyl Methacrylate (MMA) onto Silk Using Potassium Peroxydiphosphate–Cysteine (PP–Cys) Redox System*

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Synopsis

Poly(methyl methacrylate) has been grafted onto mulberry silk in an aqueous medium by using potassium peroxydiphosphate–cysteine (PP–Cys) redox initiator. Various effects upon grafting such as concentration of cysteine, concentration of peroxydiphosphate, concentration of monomer, concentration of sulfuric acid, and temperature were studied. At a low range of cysteine concentration (6.25×10^{-4} mol/L), the rate of polymerization R_p (%/s) is proportional to cysteine concentration and the exponent is calculated to be 0.8. The monomer exponent is calculated to be unity up to the concentration of 65.72×10^{-2} mol/L. From the Arrhenius plot of log R_p vs. $1/T$ (T = absolute temperature) the overall activation energy is computed to be 15.19 kcal/mol. A suitable kinetic path has been pictured and a rate expression has been derived.

INTRODUCTION

Polymer chemists have been successful in applying copolymerization techniques to develop graft copolymers of natural and synthetic macromolecules. Copolymerization is attractive to the chemist as a means of modification of macromolecules since, in general, degradation can be minimized. The desirable properties of the original polymer are retained, and additional properties are provided by the addition. The added polymer may be formed *in situ* by polymerization of a monomer or monomers, by condensation of reactants, or by the deposition of a preformed polymer.

In recent years chemical modification of silk[1] has received considerable interest since the preformed polymers are incapable of diffusing into the internal structure of the polymer. In our earlier communications we have used[2-7] peroxydiphosphate alone or coupled with organic substrates to bring about homopolymerization and graft copolymerization onto fibrous protein. This communication is concerned with some noteworthy effects encountered during grafting of methyl methacrylate onto silk, with special attention to the feasibility of the system to initiate grafting, the factors affecting the magnitude of polymerization, and elucidation of reaction mechanism.

EXPERIMENTAL

All chemicals used were of BDH (AR) grade. Silk fibers and monomer were purified by the method mentioned in our previous communications.[3,4] The grafting reaction and separation of homopolymer were carried out according to our previous procedure described elsewhere.[3-7] The graft yield was calculated as percentage increase in weight over the original weight of the sample after complete removal of the homopolymer from the grafted branch.

RESULTS AND DISCUSSION

The results of graft copolymerization are presented in Table I.

Cysteine Exponent

The graft copolymerization of MMA onto silk is carried out at varying concentrations of cysteine (3.75×10^{-4}–10.00×10^{-4} mol/L). At low cysteine concentration [Cys] = (3.75×10^{-4}–6.25×10^{-4} mol/L), R_p is found to increase with [Cys]. This is quite evident from Table I, and Figure 1 shows a plot of log R_p against log [Cys] (R_p is calculated at 6 h). The cysteine exponent is 0.8 to about 6.25×10^{-4} mol/L. The graft yield increases up to 6.25×10^{-4} mol/L and then decreases. The decrease in graft yield might be due to the abundance of cysteine free radical at a higher concentration which terminates the growing polymer chain and facilitates the formation of the homopolymer. It is also possible that at a higher concentration of cysteine the latter might act as radical scavenger, thereby decreasing grafting. Similar observations we have noticed in our earlier communication.[6]

Monomer Exponent

The effect of monomer is studied by varying the monomer concentration within the range of 27.98×10^{-2}–103.27×10^{-2} mol/L. The monomer exponent, i.e., the slope of the plot of log R_p vs. log [M] (R_p is calculated at 6 h), where [M] is the methyl methacrylate concentration, is found to be unity up to 65.72×10^{-2} mol/L (Fig. 1). The graft percentage increases up to 65.72×10^{-2} mol/L. Beyond this concentration, the graft percentage is decreased sharply. An increase in concentration of monomer should enhance grafting as the monomer participates in the grafting process. It is observed from Table I that with an increase in concentration of MMA, percent grafting increases and reaches the maximum value of 371.9% for a monomer concentration of 65.72×10^{-2} mol/L. At higher monomer concentration, homopolymerization occurs preferentially. We have also noted similar observations while grafting onto wool.[6] Misra et al. also noticed similar observations in their recent communications.[8,9]

Effect of Other Variables upon Grafting

The effect of peroxydiphosphate concentration is studied by varying it from 50×10^{-4} to 100×10^{-4} mol/L. A perusal of the result indicates that the rate of grafting increases up to 60×10^{-4} mol/L and thereafter it decreases. When the concentration of peroxydiphosphate is increased, a large number of $H_2PO_4^-$,

TABLE I

Effect of Different Variables on Graft Copolymerization of MMA onto Silk Initiated by Peroxydiphosphate–Cysteine Redox System[a]

Sample no.	[Cys] × 10⁴ (mol/L)	[PP] × 10⁴ (mol/L)	[MMA] × 10² (mol/L)	[H₂SO₄] × 10² (mol/L)	Temp (°C)	Graft (%/h)					$R_p \times 10^4$ (%/s)
						1	2	3	4	6	
1	3.75	60	46.94	14.8	50	8.0	18.7	31.0	42.9	111.5	51.6
2	5.00	60	46.94	14.8	50	12.2	29.5	60.2	88.2	131.1	60.6
3	6.25	60	46.94	14.8	50	14.3	47.7	95.5	108.7	158.9	73.5
4	7.50	60	46.94	14.8	50	7.3	40.6	62.5	81.6	87.5	40.5
5	10.00	60	46.94	14.8	50	5.4	33.5	50.5	60.9	75.5	34.9
6	6.25	50	46.94	14.8	50	3.4	12.9	54.3	91.6	102.1	—
7	6.25	80	46.94	14.8	50	4.3	16.4	37.9	85.0	145.6	—
8	6.25	100	46.94	14.8	50	2.0	10.8	28.2	55.1	127.5	—
9	6.25	60	27.98	9.8	50	21.4	33.0	64.6	73.8	150.0	69.4
10	6.25	60	46.94	9.8	50	20.0	60.5	70.8	98.4	246.3	114.0
11	6.25	60	65.72	9.8	50	25.0	66.6	76.1	114.6	371.9	172.1
12	6.25	60	84.50	9.8	50	15.0	23.1	34.8	48.9	178.5	82.6
13	6.25	60	103.27	9.8	50	5.0	15.9	27.9	37.9	110.5	51.1
14	6.25	60	46.94	4.8	50	10.0	35.7	65.0	88.5	180.3	—
15	6.25	60	46.94	24.8	50	10.2	19.4	32.3	98.6	104.3	—
16	6.25	60	46.94	32.5	50	1.4	4.9	29.1	65.6	83.5	—
17	6.25	60	46.94	9.8	45	12.9	40.0	50.1	61.2	98.1	—
18	6.25	60	46.94	9.8	55	46.4	86.1	150.5	200.4	262.1	—

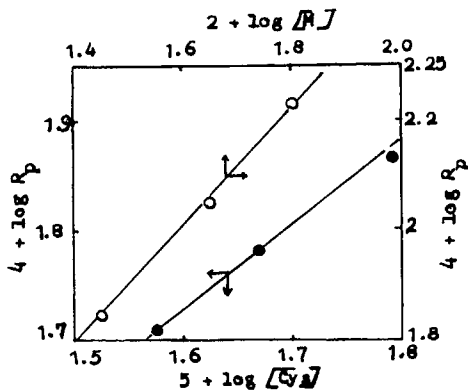[a] Reaction condition = total volume = 20 cc; silk = 0.2 (g); dioxane = 0.5 cc.

Fig. 1. Plot of log R_p vs. log [Cys] and log [M].

ȮH and $HPO_4^{\cdot-}$ radicals are formed.[5] These radicals interact with the silk backbone, giving rise to silk radicals at several sites, which initiate grafting, thereby increasing graft yield. The decrease in graft yield beyond 60×10^{-4} mol/L might be due to an abundane of free radicals which terminate the growing chain, facilitate the formation of homopolymer, oxidize the silk fiber to give more oxidation products, and hence the percentage graft on decreases.

The grafting reaction is conducted by varying acid concentration from 4.8×10^{-2} to $32. \times 10^{-2}$ mol/L. It is observed that the graft percentage increases at initial stages and with further increase of acid concentration the same decreases. Peroxydiphosphate is protonated,[10] due to its high negative charge, giving rise to various species like $HP_2O_8^{3-}$, $H_2P_2O_8^{2-}$, $H_3P_2O_8^{-}$, $H_4P_2O_8$, $H_5P_2O_8^{+}$, and $H_6P_2O_8^{+2}$. In the lower range of the acid concentration,[11] the most active species $H_3P_2O_8^{-}$ might be formed, which interacts with various other species, giving rise to a multitude of free radicals, which enhance grafting. When the concentration of the acid increases beyond 9.8×10^{-2} m/L, the formation of less active species like $H_5P_2O_8^{+}$, $H_6P_2O_8^{+2}$ might be favored, thereby decreasing the percentage of grafting, as is noticed in the present investigation.

From the Arrhenius plot of log R_p vs. $1/T$ (R_p is calculated at 2 h), the overall activation energy is computed to be 15.19 kcal/mol (Fig. 2). Using the value of $E_p - \frac{1}{2}E_t = 4 \sim 5$ kcal/mol given by Tobolsky,[12] where E_p and E_t are energies of propagation and termination respectively, the activation energy of initiation, E_d, can be calculated from these values as follows: $E_d = 2E_a - (2E_p - E_t)$, where E_a is the overall activation energy; $E_d = 21.38$ kcal/mol for total conversion reaction of MMA to PMMA. The increase of grafting with increase of temper-
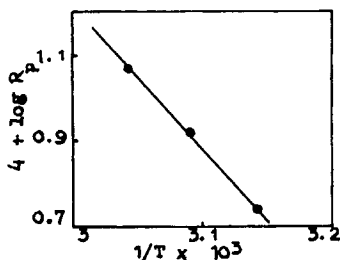

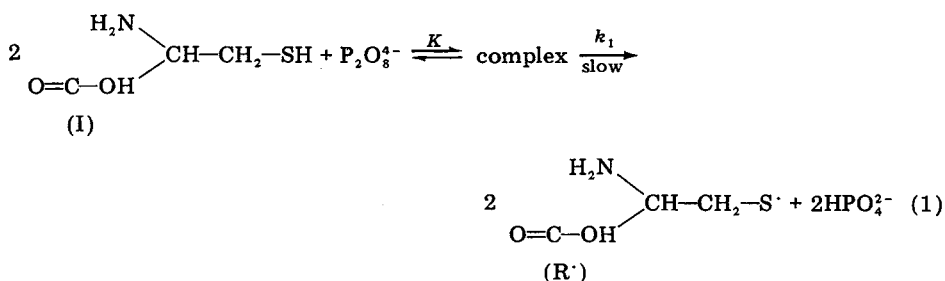Fig. 2. Arrhenius plot of log R_p vs. $1/T$ (T = abs. temp).

ature within the range studied (45–55°C) may be due to enhancement of the activation of monomer and its diffusion from the solution phase to the fiber phase and complexation with the silk macroradicals, which favors grafting. The grafting is also increased with time.

Effect of Reaction Medium on Graft Yield

The results of various solvents effecting the percentage of grafting are presented in Table II, and follows the order dioxane > acetone methanol > hexane > dimethyl sulfoxide. The variation of grafting upon using different solvents may be associated with difference in their (i) capability of swelling of silk fiber, (ii) miscibility of monomer, (iii) formation of the solvent radical from the primary radical species of the initiating system, and (iv) contribution of the solvent radical in the activation of silk and termination of the graft chain radical and silk macroradical via chain transfer. While the first three factors favored grafting, the last factor adversely affects grafting by lowering the molecular size of the graft.

Mechanism

In the light of the experimental observations, the following plausible mechanism has been suggested. In this initiating system the redox component is cysteine (I). The free radical is generated by abstraction of the reactive hydrogen from thiol groups. It is likely that $P_2O_8^{4-}$ first forms a complex with cysteine (I); the complex breaks down, slowly giving rise to cysteine radical which are the active species:

$$2 \quad \underset{O=C-OH}{\overset{H_2N}{\diagdown}} CH-CH_2-SH + P_2O_8^{4-} \underset{}{\overset{K}{\rightleftharpoons}} complex \xrightarrow[slow]{k_1}$$

(I)

$$2 \quad \underset{O=C-OH}{\overset{H_2N}{\diagdown}} CH-CH_2-S^{\cdot} + 2HPO_4^{2-} \quad (1)$$

(R·)

The R· abstracts hydrogen from the silk backbone to yield silk macroradicals.

The second possibility may be due to the decomposition of peroxydiphosphate[5,10,13] in aqueous, sulfuric acid medium to the radicals like $H_2PO_4^{-}$, $\cdot OH$, and HPO_4^{-}, which may abstract hydrogen from silk backbone to bring about
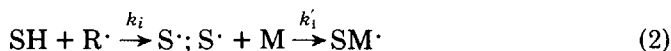
TABLE II
Effect of Solvents on Grafting of MMA onto Silk Initiated by PP–Cys Redox System[a]

Solvent (25% v/v)	Methanol	Acetene	Hexane	DMSO	Dioxane	No solvent
Graft %	94.5	132.5	27.3	3.2	292.5	199.8

[a] Reaction condition = [PP] = 60×10^{-4} mol/L; [MMA] = 46.94×10^{-2} mol/L; [Cys] = 6.25×10^{-4} mol/L; [H$^+$] = 9.8×10^{-2} mol/L; temp = 50°C; time = 6 h; total volume = 20 cc; silk = 0.2 (g).

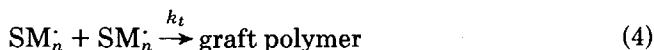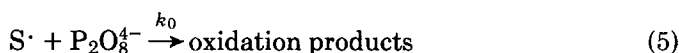grafting.   The steps during grafting are as follows:
   (i) Initiation:

$$SH + R\cdot \xrightarrow{k_i} S\cdot; S\cdot + M \xrightarrow{k_1'} SM\cdot \tag{2}$$

   (ii) Propagation:

$$SM\cdot + M \xrightarrow{k_p} SM_1\dot{} ; SM_{n-1}\dot{} + M \xrightarrow{k_p} SM_n\dot{} \tag{3}$$

   (iii) Termination:

$$SM_n\dot{} + SM_n\dot{} \xrightarrow{k_t} \text{graft polymer} \tag{4}$$

   (iv) Oxidation:

$$S\cdot + P_2O_8^{4-} \xrightarrow{k_0} \text{oxidation products} \tag{5}$$

where SH represents silk, M is monomer, and $S\cdot$ and $SM\cdot$ are the corresponding radicals. K, K_1, k_i, k_i', k_p, k_t, and k_0 are corresponding rate constants.

   Taking into account the above equations and applying steady state assumption to $[R\cdot]$, $[S\cdot]$, and $[SM\cdot]$, the following expression has been derived for rate of polymerization R_p:

$$R_p = k_p[SM\cdot][M] = k_p(KK_1/k_t)^{1/2}[Cys]P_2O_8^{4-}]^{1/2}[M].$$

The experimental results (a cysteine exponent of 0.8 which is nearly to unity up to 6.25×10^{-4} mol/L and a monomer exponent which is unity) up to 65.72×10^{-2} mol/L are in good agreement with the above proposed mechanism.   Taking into account eq. (5), the value of R_p will be

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

References

1. M. K. Mishra, *J. Macromol. Sci., Rev. Macromol. Chem.*, C19(2), 193 (1980).
2. P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Polym. Sci., Polym. Chem. Ed.*, 19, 839 (1981).
3. P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Polym. Sci., Polym. Chem. Ed.*, 18, 2247 (1980).
4. S. Lenka, P. L. Nayak, and M. K. Mishra, *Angew. Makromol. Chem.*, 84, 183 (1980).
5. P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Appl. Polym. Sci.*, 25, 63 (1980); 26, 733 (1981).
6. P. L. Nayak, S. Lenka, and M. K. Mishra, *Angew. Makromol. Chem.*, 90, 155 (1980).
7. P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Macromol. Sci. Chem.*, A16(4), 843 (1981).
8. B. N. Misra, I. K. Mehta, and R. Dogra, *J. Appl. Polym. Sci.*, 25, 235 (1980).
9. B. N. Misra, R. Dogra, I. K. Mehta, and A. S. Singha, *Angew. Makromol. Chem.*, 90, 83 (1980).
10. P. Maruthamuthu and M. Santappa, Ind. J. Chem. 14A, 35 (1976); *J. Inorg. Nucl. Chem.*, 37, 1305 (1975).
11. J. O. Edwards, *Coord. Chem. Rev.*, 8, 87 (1972).
12. A. V. Tobolsky, *J. Colloid Sci.*, 12, 325 (1957).
13. P. Maruthamuthu and K. V. Seshadri, *Ind. J. Chem.*, 10, 762 (1972).