

Graft Copolymerization of Methyl Methacrylate onto Reduced Wool with Potassium Peroxydiphosphate as Initiator

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SUMMARY

In order to ascertain the role of mercaptan groups during grafting, the graft copolymerization of methyl methacrylate (MMA) onto reduced Indian Chokla Wool fibers in an aqueous medium was investigated using potassium peroxydiphosphate (PP) as initiator. The percentage of grafting was determined as a function of concentration of initiator PP, monomer MMA and sulfuric acid, time, temperature and the presence of solvents. The molecular weight of the grafted polymer decreased as the extent of grafting increased. A kinetic scheme was developed based upon the dependence of the rate of grafting upon the reactant concentrations.

INTRODUCTION

In recent years numerous attempts have been made to modify natural fibers by graft copolymerization (MISHRA 1980; NAYAK 1976). During the past few decades, peroxydisulfate salts have been used extensively as water soluble initiators in emulsion polymerization. The peroxydiphosphate ion, $P_2O_8^{4-}$, which is iso-electronic and isostructural with the peroxysulfate ion received little attention until Edwards and his associates (ANDERSON et al. 1969; LUSSIER et al. 1970; CHAFFEE et al. 1971; EDWARDS 1972) recognized this ion as a free radical initiator. We have recently reported the graft copolymerization of methyl methacrylate (MMA) onto natural polypeptides using potassium peroxydiphosphate (PP) alone and in conjunction with organic reductants (NAYAK et al. 1980a, 1980b, 1980c, 1981a, 1981b; LENKA et al. 1980).

Wool is a natural polypeptide that contains numerous functional groups including -OH, -NH₂, -NH, -COOH and -SH as well as -SS-linkages. These functional groups are all capable of forming complexes with the initiator. A free radical is generated by

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the abstraction of hydrogen from these groups upon decomposition of the complex and the grafting of vinyl monomers can occur from these sites. However, it has not been possible to identify the functional groups which are responsible for the grafting of MMA onto wool fibers in the presence of a peroxydiphosphate as initiator.

It appears that -OH, -NH₂ and -SH groups may play a major role in providing active sites for grafting. KANTOUCH et al. (1971) have indicated that both -OH and -NH₂ groups are involved in the ceric ion-induced grafting of MMA onto wool. The role of sulfur compounds in initiating graft copolymerization has been reported (NAYAK et al. 1980b, 1980c, 1981a). LIPSON (1949) reported that graft copolymerization onto wool occurs from -SH groups formed by the reduction of the cystine in the wool. NEGESHI et al. (1967) investigated grafting onto wool in the presence of a LiBr-S₂O₈²⁻ initiating system and concluded that the -SH groups in the wool provides active sites for grafting. However, MISRA et al. (1980) reported that, in the grafting of ethyl acrylate onto reduced wool with ceric sulfate as initiator, -SH groups do not play a significant role and do not promote grafting.

In a previous communication, the grafting of MMA onto wool using potassium peroxydiphosphate (PP) as initiator was reported (NAYAK et al. 1980a). The present communication presents the results obtained in the graft copolymerization of MMA onto reduced wool using PP as initiator.

EXPERIMENTAL

Indian Chokla wool and methyl methacrylate were purified as described previously (NAYAK et al. 1980a). Potassium peroxydiphosphate (FMC Corp.) and thioglycolic acid (BDH) were used as received.

Reduction and Graft Copolymerization onto Wool

Reduced wool was prepared by immersing purified wool in 0.1N thioglycolic acid for 24 hrs at room temperature, with a wool/water weight ratio of 1/40. The reduced wool was washed with water and methanol several times and then dried. The graft copolymerization with MMA was carried out as described earlier (NAYAK et al. 1980a). The percentage of grafting was calculated as the percentage increase in weight over the original weight of the wool. The isolation of the grafted PMMA was carried out in accordance with a previously reported procedure (ARAI et al. 1970).

TABLE I
Effect of Reaction Conditions on Grafting of MMA Onto Reduced Wool^a

No.	[PP] x 10 ⁴ mole/l	[MMA] x 10 ² mole/l	[H ₂ SO ₄] x 10 ² mole/l	Temp OC	Hrs	Graft, %			
						1	2	3	4
1	50	46.94	0.148	50	62.1	129.0	236.1	240.0	248.5
2	60	46.94	0.148	50	83.9	180.5	253.0	260.0	287.2
3	80	46.94	0.148	50	182.9	245.6	269.7	285.0	328.8
4	100	46.94	0.148	50	70.5	210.5	230.5	250.0	265.1
5	120	46.94	0.148	50	50.9	145.0	200.6	225.0	239.5
6	80	27.98	0.148	50	105.0	119.5	184.2	195.0	200.0
7	80	65.72	0.148	50	202.3	287.9	300.8	391.7	450.6
8	80	84.50	0.148	50	253.6	345.8	384.6	433.9	496.4
9	80	103.27	0.148	50	267.9	361.3	390.3	568.1	598.4
10	80	46.94	0.048	50	98.6	150.4	155.2	187.9	191.1
11	80	46.94	0.098	50	160.1	181.3	199.7	203.5	370.9
12	80	46.94	0.248	50	165.2	198.3	201.5	210.3	298.1
13	80	46.94	0.498	50	100.1	123.3	167.3	200.1	205.6
14	80	46.94	0.148	45	174.1	230.5	252.1	263.3	289.1
15	80	46.94	0.148	55	200.0	260.0	280.7	290.8	362.6

^a Reduced wool, 0.2 g; dioxane, 0.5 ml; reaction volume including water, 20 ml

Determination of PMMA Molecular Weight

The intrinsic viscosities of the polymers were determined in acetone solution at $25 \pm 0.05^\circ\text{C}$ using a Ubbelohde viscometer. The molecular weight of the PMMA was calculated from the intrinsic viscosity using the equation (CHINAI et al. 1955)

$$[\eta] = 9.6 \times 10^{-5} \times M_w^{0.69}$$

RESULTS AND DISCUSSION

The effect of the reaction conditions on the grafting of MMA onto reduced wool in the presence of PP is shown in Table I. More grafting occurred onto reduced wool than onto unreduced wool (Table II).

TABLE II
Extent of Grafting Onto Reduced and Unreduced Wool

No. ^a	% Graft after 6 hrs ^b	
	Reduced Wool	Unreduced Wool
1	248.5	206.4
2	287.2	218.5
3	328.8	250.5
4	265.1	183.2
5	239.5	174.0
6	200.0	157.7
7	450.6	264.5
8	496.4	274.5
9	598.4	304.7

^a Numbers correspond to numbers and conditions shown in Table I

^b Data from NAYAK et al. (1980a)

The increase in the percentage of grafting onto reduced wool may be explained on the basis that the reduction of cystine disulfide bonds with thioglycolic acid results in an increase in the number of thiol groups which act as the active centers for grafting.

The effect of the initiator concentration was studied within the range of 50×10^{-4} to 120×10^{-4} mole/l. The results indicate that the rate of grafting increased up to an initiator concentration of 80×10^{-4} mole/l and thereafter decreased. The effect of monomer concentration was studied within the range of 27.98×10^{-2} to 103.27×10^{-2} mole/l. The percentage of grafting increased with increasing monomer concentration.

An increase in the percentage of grafting was noted when the H_2SO_4 concentration was increased from 0.048 to 0.148 mole/l, but the yield of graft copolymer decreased with further increase in the acid concentration. The graft yield decreased with increasing temperature within the $45\text{--}55^\circ\text{C}$ range. The reasons for the changes in the percentage of grafting have been discussed in our previous communication (NAYAK et al. 1980a).

From the Arrhenius plot of $\log R_p$ vs $1/T$, where R_p was determined after 6 hrs, the overall activation energy E_a was calculated as 5.0 Kcal/mole (Fig. 1).

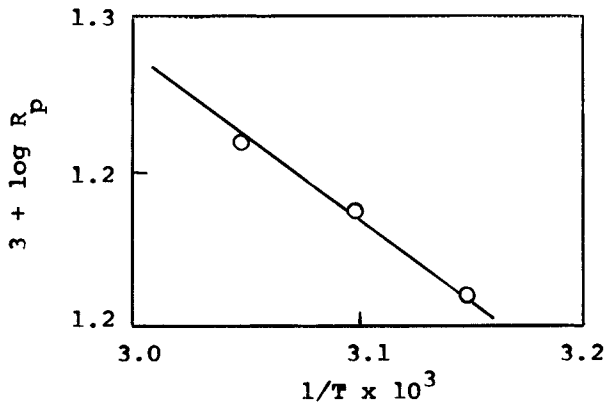
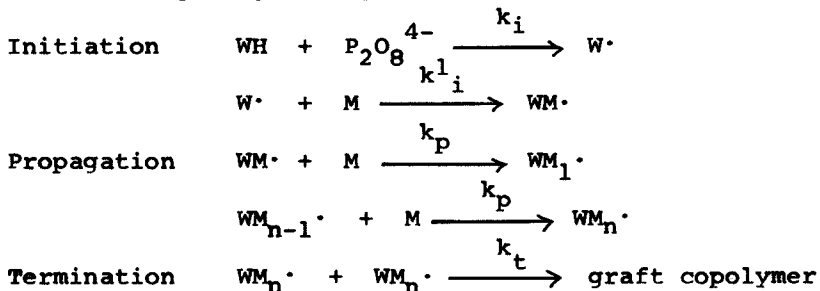


Fig. 1. Arrhenius plot of $\log R_p$ vs $1/T$ for grafting of MMA onto reduced wool

Reaction mechanism

The grafting reaction presumably involves the interaction of the $\text{H}_2\text{PO}_4^\cdot$, HO^\cdot and $\text{HPO}_4^{\cdot-}$ radicals, which are produced by the decomposition of the peroxydiphosphate ion $\text{P}_2\text{O}_8^{4-}$, with the functional groups present in the backbone of the reduced wool, giving rise to wool macroradicals. The latter react with the monomer, resulting in grafting.



where W , M , $W\cdot$ and $WM\cdot$ represent wool backbone, monomer and the corresponding radicals, respectively, and k_i , k_i^1 , k_p and k_t are rate constants. Assuming steady states for both $[W\cdot]$ and $[WM\cdot]$, the rate of polymerization

$$R_p = k_p [WM\cdot] [M] = k_p \left(\frac{k_i^{\frac{1}{2}}}{k_t^{\frac{1}{2}}} \right) [P_2O_8^{4-}]^{\frac{1}{2}} [M]$$

The plots of $\log R_p$ vs $\log [PP]$ and $\log R_p$ vs $\log [M]$, where R_p is calculated after 4 hrs, are linear (Fig. 2) and, from the slopes, the initiator and monomer exponents are calculated to be 0.41 and 0.95, respectively. These exponents are reasonably close to 0.5 and 1.0, respectively, which are consistent with the rate expression.

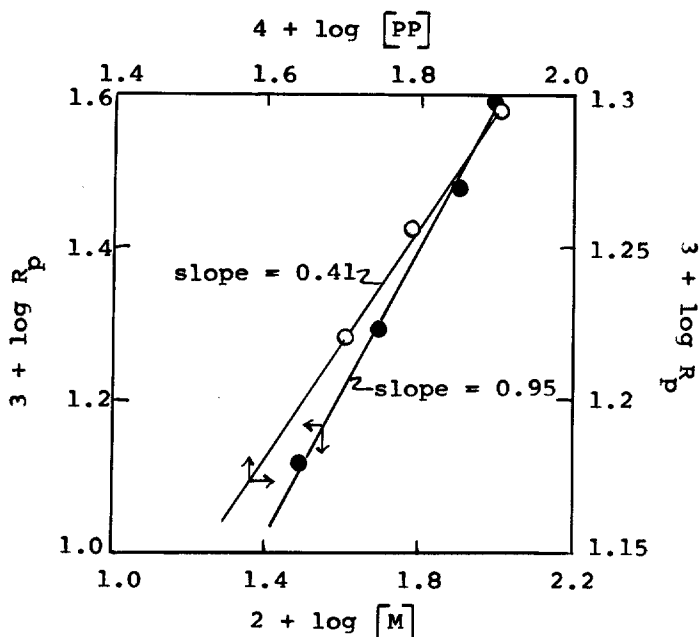


Fig. 2. Plot of $\log R_p$ vs $\log [M]$ and $\log [PP]$ for grafting P of MMA onto reduced wool

Effect of reaction medium on extent of grafting

The reaction medium plays an important role in the grafting of vinyl monomers onto wool. Water-soluble organic solvents influence the swelling of the wool. Any change in wool swellability would be reflected in the behavior of the wool towards the diffusion of the monomer and the initiator, the availability of functional groups which are the sites of grafting, the

propagation and termination of the grafting chain, etc., all of which affect the extent of grafting onto the wool. The percentage of grafting in various solvents (Table III) followed the order:

dioxane > acetone > methanol > dimethyl sulfoxide >
hexane > chloroform

TABLE III
Grafting Onto Reduced Wool in the Presence of Solvents^a

Solvent	Graft, %	Solvent	Graft, %
Dioxane	406.6	DMSO	233.9
Acetone	330.9	Hexane	82.7
Methanol	283.0	Chloroform	69.5

^a Reaction volume, 20 ml; $[PP]$ 80×10^{-4} mole/l; $[MMA]$ 46.94×10^{-2} mole/l; $[H_2SO_4]$ 0.148 mole/l; reduced wool, 0.2 g; solvent, 25%; temperature, 50°C; time, 6 hrs

In the present investigation, dioxane proved to be the best solvent for grafting. The variation in the extent of grafting when using different solvents, may be associated with their ability to swell the wool fiber, their miscibility with MMA, the formation of solvent radicals by attack of the primary radical species from the initiator and the contribution of the solvent radicals in the activation of the wool and the termination of the graft chain radical and the wool macroradical via chain transfer. While the first three factors enhance grafting, the last factor affects grafting by lowering the molecular weight of the grafted polymer.

The average molecular weight and the degree of polymerization of the grafted polymer are shown in Table IV. The results indicate that the molecular weight decreased as the percentage of grafting increased.

TABLE IV
Molecular Weights of Grafted PMMA

No. ^a	Time, hrs	Graft, %	$[\eta]$, dl/g	$\bar{M}_w \times 10^{-5}$	\bar{DP}
3	3	269.7	0.990	6.55	6550
7	4	391.7	0.831	5.07	5070
8	6	496.4	0.827	5.04	5040
9	6	598.4	0.462	2.16	2160

^a Numbers correspond to numbers and conditions shown in Table I

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