

Grafting Vinyl Monomers Onto Wool Fibers. V. Graft Copolymerization of Methyl Methacrylate Onto Wool Using Peroxydiphosphate as Initiator*

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Synopsis

Graft copolymerization of methyl methacrylate onto wool was investigated in aqueous solution using potassium peroxydiphosphate as initiator. The rate of grafting was determined by varying monomer, peroxydiphosphate ion, temperature, solvent, and nature of wool. The graft yield increases with increase in monomer concentration. The graft yield increases significantly by increasing peroxydiphosphate ion up to 80×10^{-4} mole/l.; with further increase of peroxydiphosphate ion the graft yield decreases. The rate of grafting increases with increase in temperature. The effect of acid- and water-soluble solvents on the rate of grafting was investigated and a suitable rate expression has been derived.

INTRODUCTION

Polymer chemists have been successful in applying polymerization techniques to develop copolymers of natural and synthetic macromolecules. The literature abounds with examples of successful formation of copolymers from natural and synthetic macromolecules. Copolymerization is attractive to the chemist as a means of modification of macromolecules since, in general, degradation can be minimized. Despite the heterogeneity and complexity of copolymers, much has been achieved in their characterization. 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 wool by graft copolymerization has received considerable interest¹⁻⁵ since the preformed polymers are incapable of diffusing into the internal structure of the polymer. With the wide variety of vinyl and other monomers available today, grafting promises to be a powerful method for producing substantial modification of fiber properties.⁶ A variety of property changes could be imparted to wool through grafting. Some of the most dramatic changes in property which have been brought out by grafting wool⁶ are viscoelasticity, stereoregularity, hygroscopicity, water repellency, improved adhesion to a variety of substances, improved dyeability and settability, soil resistance, bacteriocidal properties, antistatic properties, and thermal stability.

In recent years much interest has been focused on vinyl graft copolymerization

* Dedicated to Professor R. D. Patel on his 60th birthday.

through chemical initiation.¹ Methods of chemical initiation yield free radicals which are not necessarily part of the substrate, and the covalent bond is only formed between the natural material and the added polymer through chain transfer.

The Egyptian workers Hebeish, Bendak, and co-workers have used a large number of initiators for grafting a multitude of vinyl monomers onto wool fibers. This includes Ce(IV),⁷ Mn(IV),⁸ periodate ion,⁹ Cu(II)-acetyl acetone-trichloroacetic acid complex,¹⁰⁻¹³ azobisisobutyronitrile,¹⁴ dimethylaniline-benzyl chloride,¹⁵ hydrogen peroxide-thiourea,¹⁶ and Fe(III)-thiourea¹⁷ redox systems. Arai and co-workers¹⁸⁻²⁰ have used persulfate alone or as part of a redox system as initiator for grafting vinyl monomers onto wool fibers. They have reported very interesting results using persulfate as initiator.

Among the inorganic compounds containing peroxide bonds, peroxydisulfate, $S_2O_8^{2-}$, has been used in extensive oxidation studies.^{21,22} Studies involving peroxydiphosphate are very rare in the literature. The minimum oxidation potential of peroxydiphosphate is 2.07 V, while that of peroxydisulfate is 2.01 V. This indicates that the former should be a slightly stronger oxidizing agent than the latter.

Studies involving peroxydiphosphate are very few in the literature. Edwards and co-workers²⁵⁻²⁷ investigated the photochemical oxidation of water, ethanol, propan-2-ol, and some metal complexes by peroxydiphosphate. Santappa and co-workers²⁸⁻³⁰ have studied the kinetics of self-decomposition of peroxydiphosphate in aqueous sulfuric acid medium. In a recent paper²⁹ they have reported the kinetics of oxidation of water and pinacol by peroxydiphosphate. Gupta and co-workers³¹ have investigated the kinetics of oxidation of a large number of inorganic substrates. Nayak and co-workers have reported the graft copolymerization of MMA onto wool using Cr^{6+} ,³² V^{5+} ,^{33,34} Mn^{4+} ,³⁵ and peroxydisulfate³⁶ as initiators.

In the present investigation the graft copolymerization of MMA onto wool was investigated by using peroxydiphosphate as initiator.

EXPERIMENTAL

Indian Chokla wool fibers were purified by Soxhlet extraction with acetone for about 24 hr followed by cold distilled water washing and air drying.

MMA was washed with 5% sodium hydroxide solution; it was then dried with anhydrous sodium sulfate and distilled under reduced pressure in nitrogen before use. Peroxydiphosphate was of BDH (Analar) grade. All other reagents were of Analar grade.

The reactions were carried out according to our previous procedures³² by using peroxydiphosphate from 50×10^{-4} to 120×10^{-4} mole/l. at temperatures from 40 to 55°C. The graft yield was calculated as the percentage increase in weight over the original weight of the sample.

Effect of Peroxydiphosphate on Graft Yield

The effect of the concentration of peroxydiphosphate ion on grafting of methyl methacrylate onto wool is shown in Figure 1. The rate of grafting has been investigated by changing the peroxydiphosphate concentration within the range

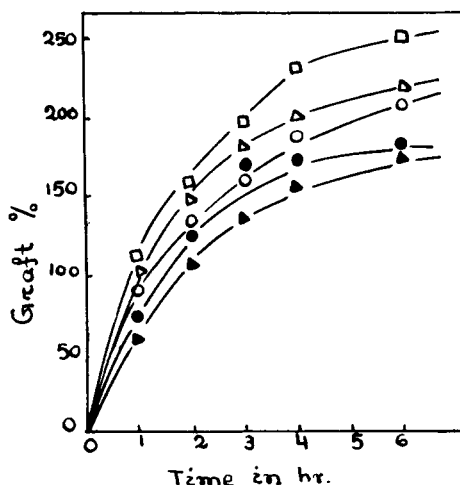
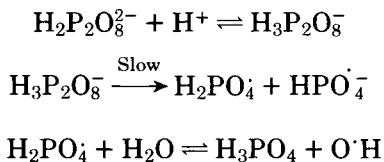


Fig. 1. Effect of peroxydiphosphate (PP) concentration on graft yield: $[\text{H}_2\text{SO}_4] = 0.15$ mole/l.; $[\text{MMA}] = 0.4694$ mole/l.; temperature = 50°C ; M:L (material:liquor) = 1:100; (○) $[\text{PP}] = 50 \times 10^{-4}$ mole/l.; (△) $[\text{PP}] = 60 \times 10^{-4}$ mole/l.; (□) $[\text{PP}] = 80 \times 10^{-4}$ mole/l.; (●) $[\text{PP}] = 100 \times 10^{-4}$ mole/l.; (▲) $[\text{PP}] = 120 \times 10^{-4}$ mole/l.

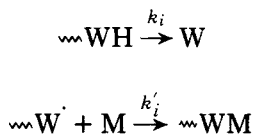
of 50×10^{-4} to 120×10^{-4} mole/l. The data indicate that increasing peroxydiphosphate concentration up to 80×10^{-4} mole/l. is accompanied by a significant increase in graft yield; and with further increase of peroxydiphosphate concentration there is a marked fall in the graft yield. A possible explanation for these observations might be as follows:

In a system consisting of peroxydiphosphate ion, H_2SO_4 , MMA, and wool, the following reaction might be taking place:



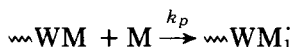
Hence radicals such as H_2PO_4 , $\text{OH}\cdot$, and HPO_4^- which are produced during the reaction interact with the groups present in wool backbone producing wool macroradicals. The wool macroradicals react with monomer resulting in grafting as represented below:

Initiation



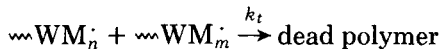
where $\sim\text{WH}$ represents the reactive group in the wool backbone, M is the monomer, and $\sim\text{W}\cdot$ and $\sim\text{WM}\cdot$ are the corresponding growing radicals.

Propagation





Termination



Now

$$d[\text{W}]/dt = k_i[\text{WH}] - k'_i[\text{W}][\text{M}] = 0$$

$$k_i[\text{WH}] = k'_i[\text{W}][\text{M}]$$

$$[\text{W}] = \left(\frac{k_i}{k'_i}\right) \frac{[\text{WH}]}{[\text{M}]}$$

Again,

$$\frac{d[\text{WM}]}{dt} = k'_i[\text{W}][\text{M}] - k_t[\text{WM}_n]^2 = 0$$

$$[\text{WM}_n]^2 = \frac{k'_i}{k_t} \cdot \frac{k_i}{k'_i} \frac{[\text{WH}][\text{M}]}{[\text{M}]} = \frac{k_i}{k_t} [\text{WH}]$$

$$[\text{WM}_n] = \frac{k_i^{1/2}}{k_t^{1/2}} [\text{WH}]^{1/2}$$

The rate of polymerization is

$$R_p = k_p[\text{WM}_n][\text{M}] = k_p \left(\frac{k_i^{1/2}}{k_t^{1/2}}\right) [\text{WH}]^{1/2}[\text{M}]$$

Thus, the plot of $\log R_p$ vs. $\log [\text{M}]$ should be linear passing through the origin, which has been observed in Figure 2.

With increasing peroxydiphosphate concentration, large numbers of H_2PO_4 , OH , and HPO_4^- radicals are produced which interact with the wool backbone giving rise to free radicals at several sites which initiate grafting, thereby increasing the graft yield. With further increase in peroxydiphosphate ion beyond 80×10^{-4} mole/l., there is a marked fall in graft yield which might be due to the

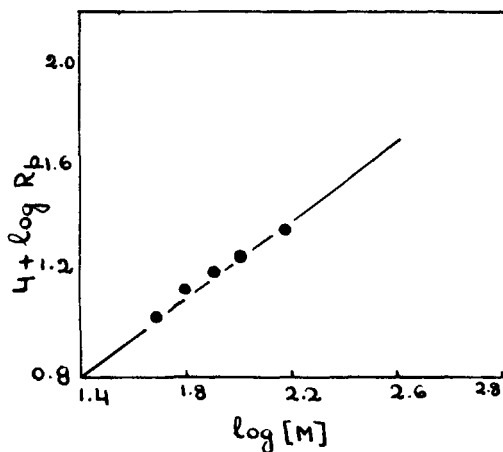
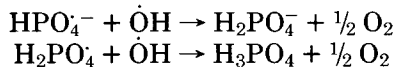


Fig. 2. Plot of $\log [\text{M}]$ vs. $\log R_p$.

following reasons: (i) With the increase of the oxidant concentration there will be an abundance of free radicals which might terminate the grafted chain. (ii) The second reason might be that the oxidant could react with the growing free radicals giving rise to oxidation products. (iii) At the higher concentration of oxidant there is a possibility of formation of homopolymer. (iv) With increasing oxidant, the increase in the formation of K^+ ions might effect grafting. All these factors in a cumulating way decrease the percentage of grafting at the higher concentration of oxidant.

At higher concentration of peroxydiphosphate, the following reaction might be taking place:



The formation of oxygen might affect the growth of the chain and hence the percentage of grafting decreases.

Effect of Monomer Concentration on Graft Yield

The effect of monomer concentration on grafting was investigated by varying the monomer concentration from 27.98×10^{-2} mole/l. to 103.27×10^{-2} mole/l. (Fig. 3). There is a marked increase in graft yield with increasing monomer concentration. Since the copolymerization reaction was carried out at the same temperature and at the same reaction conditions, it is possible that the concentration, nature, and efficiency of the free radicals and other species generated during the process of grafting would be the same.

The higher rate of grafting observed upon increasing the monomer concentration in this system could be attributed to a variety of reasons. (1) Complexation of the wool with the monomer, which is required for enhancing monomer reactivity, would be favored at higher monomer concentrations. (2) The monomer molecule might form some type of charge transfer complex with the

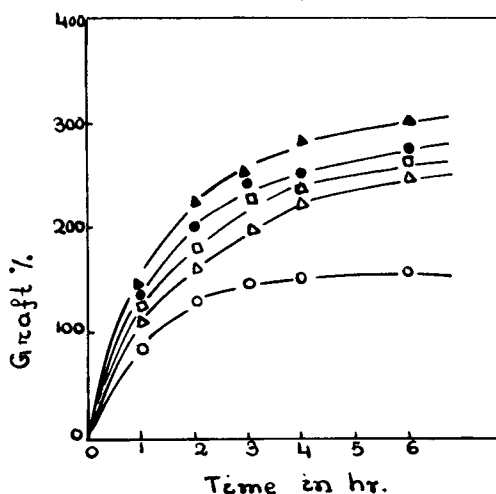


Fig. 3. Effect of MMA concentration on graft yield: [peroxydiphosphate] = 80×10^{-4} mole/l.; $[\text{H}_2\text{SO}_4] = 0.15$ mole/l.; temperature = 50°C ; M:L = 1:100; (○) [MMA] = 27.98×10^{-2} mole/l.; (△) [MMA] = 46.94×10^{-2} mole/l.; (□) [MMA] = 65.72×10^{-2} mole/l.; (●) [MMA] = 84.50×10^{-2} mole/l.; (▲) [MMA] = 103.27×10^{-2} mole/l.

oxidant at higher monomer concentration thereby increasing grafting. (3) The third reason might be gel effect,³⁷ i.e., increase in viscosity of medium due to solubility of poly(methyl methacrylate) in its own monomer would be more pronounced at a higher monomer concentration. This causes hindrance in termination, particularly by coupling of growing polymer chains. Besides, the gel effect also causes swelling of wool, thus facilitating diffusion of monomer to the growing chains and active sites on the wool backbone, thereby enhancing grafting. (4) The fourth reason might be that some species, which are either present or generated during the copolymerization reaction, are acting as efficient radical scavengers. Competition between this and the monomer in capturing the free wool radical could play a key role in the amount of graft formation. It is likely that the capturing of wool radicals by monomer predominates at higher monomer concentration.

Effect of Acid Concentration on Graft Yield

The grafting reaction was carried out by varying the acid concentration from 0.028 mole/l. to 0.5 mole/l (Fig. 4). A perusal of the result indicates that the percentage graft-on increases with increasing acid concentration up to 0.15 mole/l., and with further increase of the acid concentration the graft yield decreases.

It has been known for a long time that the rates of oxianion reactions are markedly dependent on acid concentration.³⁸⁻⁴⁰ It is presumed that the role of protons is to labilize oxygen by converting it from oxide ion to hydroxide ion and into water. The addition of protons to oxide ion in an oxyanion should make it easier to break the bond. In oxidations involving oxyanions, since covalent bonds to oxygen are generally broken simultaneously by electron transfer, they are found to be acid catalyzed. The reactions of peroxides are also subject to acid catalysis.⁴¹ Hence, it will not be surprising if the reactions of peroxydi-

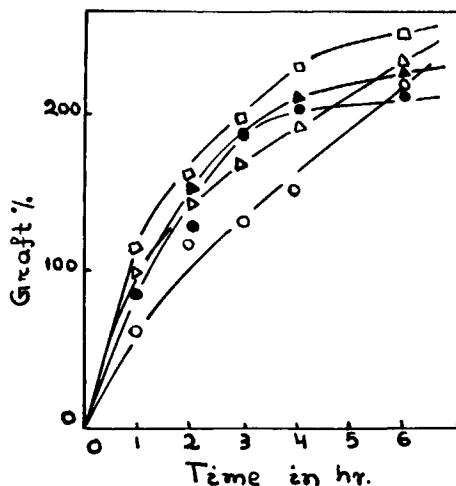


Fig. 4. Effect of H₂SO₄ concentration on graft yield: [peroxydiphosphate] = 80×10^{-4} mole/l.; [MMA] = 0.4694 mole/l.; temperature = 50°C; M:L = 1:100; (○) [H₂SO₄] = 0.028 mole/l.; (△) [H₂SO₄] = 0.048 mole/l.; (□) [H₂SO₄] = 0.148 mole/l.; (▲) [H₂SO₄] = 0.248 mole/l.; (●) [H₂SO₄] = 0.498 mole/l.

phosphate, which is both a peroxide and an oxyanion, i.e., oxyanion derivative of $\text{H}-\text{O}-\text{O}-\text{H}$, are strongly subject to acid catalysis. Peroxydiphosphate, $\text{P}_2\text{O}_8^{4-}$, is extensively protonated in acid medium due to the accumulation of high negative charges. The various species present are $\text{P}_2\text{O}_8^{4-}$, $\text{HP}_2\text{O}_8^{3-}$, $\text{H}_2\text{P}_2\text{O}_8^{2-}$, $\text{H}_3\text{P}_2\text{O}_8^-$, and $\text{H}_4\text{P}_2\text{O}_8$, and the concentration of these species varies drastically with change in pH (species involving the protonation of peroxidic oxygen, $\text{H}_5\text{P}_2\text{O}_8^+$, may also be present along with the other protonated species). The population of the different species as a function of pH is given by Crutchfield.⁴² It has been stated by Santappa and co-workers^{29,30} that the reaction rate as well as the concentration of $\text{H}_3\text{P}_2\text{O}_8^-$ and $\text{H}_4\text{P}_2\text{O}_8$ are increasing with increase in $[\text{H}^+]$. Hence, it is probable that one or both of the species are active in the lower concentration range of the acid, that is, from 0.02 mole/l. to 0.15 mole/l. The most active specie, $\text{H}_3\text{P}_2\text{O}_8^-$, 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 0.15 mole/l.; the formation of less active species might be favored, thereby decreasing the percentage of grafting as has been noted in our case.

Effect of Temperature on Graft Yield

Graft copolymerization was carried out at four different temperatures ranging from 40 to 55°C, keeping the concentrations of all other reagents constant (Fig. 5). The results indicate that with increasing temperature, the percentage graft-on increases. In a complex system like this, several reactions might be taking place simultaneously, such as (i) solution of the monomer in the reaction medium and its diffusion from the solution phase to the fiber phase, (ii) adsorption of the monomer on the fiber and its complexation with the wool molecules to enhance availability and reactivity of the monomer, (iii) formation and propagation of graft on fiber, and (iv) enhancement of the activation of monomer. The net effect of all these factors is higher grafting with increase in temperature.

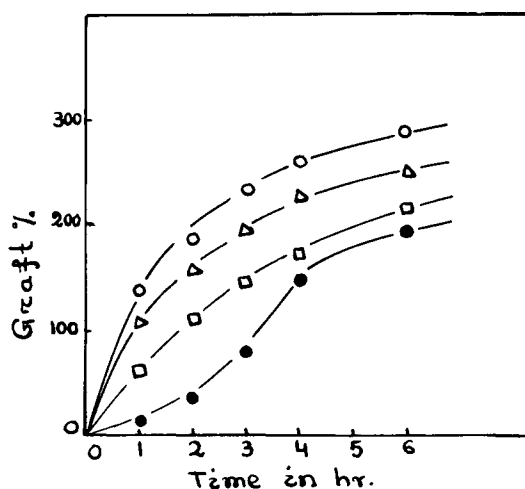


Fig. 5. Effect of temperature on graft yield: [peroxydiphosphate] = 80×10^{-4} mole/l.; $[\text{H}_2\text{SO}_4]$ = 0.15 mole/l.; [MMA] = 0.4694 mole/l.; M:L = 1:100; (O) temperature 55°C; (Δ) temperature 50°C; (\square) temperature 45°C; (\bullet) temperature 40°C.

From the Arrhenius plot of $\log R_p$ versus $1/T$, the overall activation energy was found to be 9.2 kcal/mole (Fig. 6). Using the value of $E_p - \frac{1}{2}E_t = 4-5$ kcal/mole given by Tobolsky,⁴³ 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. The value of E_d was calculated to be 9.4 kcal/mole.

Nature of the Substrate

The native wool was subjected to different physical and chemical modification by reduction, oxidation, trinitrophenylation, and crosslinking (Fig. 7). The order of the percentage of graft-on was as follows:

reduced wool > oxidized wool > untreated wool >
cross linked wool > trinitro phenylated wool

The increase in graft percentage of reduced wool (Fig. 8) over that of the other modified wool may be explained on the basis that the reduction of the cystine disulfide bond of wool with TGA increases the number of thiol groups ($-\text{SH}$) which act as active centers for grafting. It is known that the abstraction of hydrogen from thiol groups by initiating radicals seems to proceed much more easily than abstraction of hydrogen from amino and hydroxyl groups in the wool molecule. Further, treatment of wool with TGA might increase its accessibility or swelling and enhance grafting.

Upon oxidation of wool with H_2O_2 , the cystine content is slightly reduced and the cystine is most probably converted to cystic acid. It is easier to create free radicals on the sulfur by the extraction of hydrogen from cystine than create a free radical in case of cystic acid. However, the probability of creation of free radicals in case of cystic acid is greater than in the case of unmodified wool where there are $-\text{S}-\text{S}-$ linkages.

Trinitrophenylation of wool reduces significantly its ability toward grafting. When wool is subjected to trinitrophenylation, the amino hydroxyl and thiol

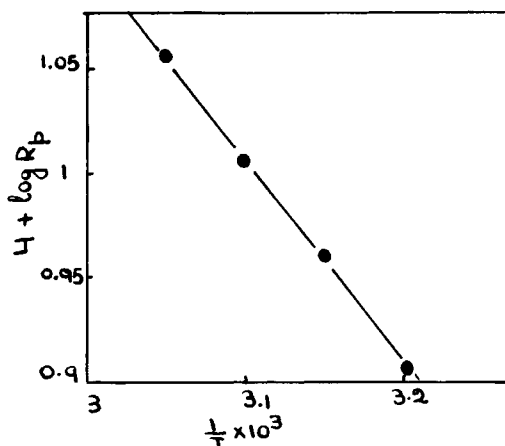


Fig. 6. Arrhenius plot of $1/T$ vs. $\log R_p$.

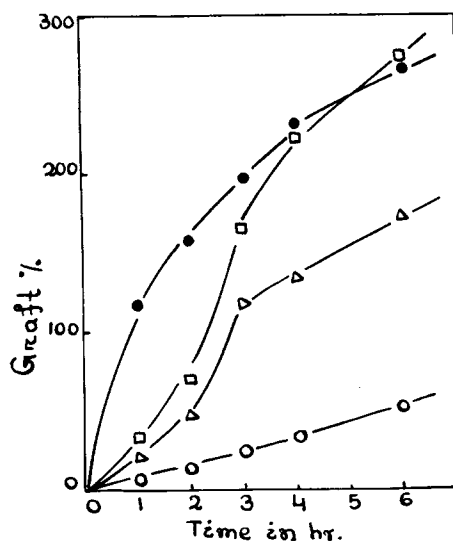


Fig. 7. Effect of nature of substrate on graft yield: [peroxydiphosphate] = 80×10^{-4} mole/l.; $[\text{H}_2\text{SO}_4]$ = 0.15 mole/l.; [MMA] = 0.4694 mole/l.; temperature = 50°C ; M:L = 1:100; (●) untreated wool; (○) phenylated wool; (△) crosslinked wool; (□) oxidized wool.

groups are blocked. Free radicals cannot be created at the wool backbone by the interaction of initiating radicals, as a result of which the graft yield decreases. Other reasons for low graft yield might be: (i) lowering of the swellability of wool fibers, and (ii) hindrance of adsorption of MMA molecule by the negatively charged substituted nitro group in the case of TNP wool. The net effect of all these factors is the decrease of grafting.

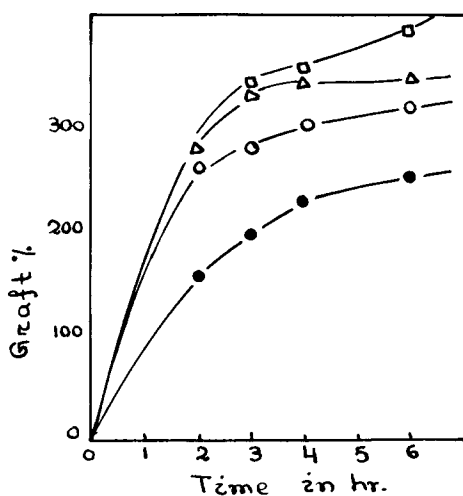


Fig. 8. Effect of reduced wool on grafting: [peroxydiphosphate] = 80×10^{-4} mole/l.; $[\text{H}_2\text{SO}_4]$ = 0.15 mole/l.; [MMA] = 0.4694 mole/l.; temperature = 50°C ; M:L = 1:100; (●) untreated wool; (○) [TGA] = 0.025N; (△) [TGA] = 0.05N; (□) [TGA] = 0.1N.

Effect of Solvent on Graft Yield

The effect of solvent on graft copolymerization was studied by using various protic, dipolar aprotic, and nonpolar solvents. It is important to select the most suitable solvents for the graft polymerization of MMA onto wool fibers. The results of various solvents affecting the percentage of grafting follow the order

dioxan > acetone > methanol > hexane > chloroform

It is seen from the data that grafting took place even in the absence of any added solvent. This may be due to the ability of the MMA molecule to penetrate into the internal regions of the wool.

In the present investigation, among the several solvents applied, dioxan proved to be best for grafting. The swelling of the internal structure of wool facilitated the diffusion, initiation, and propagation of methyl methacrylate monomer onto the wool. The variation of grafting with different solvents could be associated with differences in their (i) capability of swelling of wool, (ii) miscibility with monomer, (iii) formation of solvent radical from the primary radical species of the initiating system, (iv) contribution of the solvent radical in the activation of the wool, and (v) termination of the graft chain radical and wool 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.

Effect of Different Acrylate Monomer on Grafting

Graft copolymerization was investigated with different acrylate monomers (methyl, ethyl, *n*-butyl, and methyl methacrylate) keeping the concentration of all other reagents constant. The order of reactivity so far as graft-on percentage is concerned is as follows:

MA > EA > MMA > *n*-butyl acrylate

Thus, as the size of the monomer is increased, the diffusion of the monomer to all available sites on the fiber is not possible. As a result, the percentage of graft-on decreases in case of bulkier monomers.

Redox System

During the past several years redox systems have been extensively used for the homopolymerization of vinyl monomers.⁴⁴⁻⁵⁰ The application of such systems for graft copolymerization onto natural macromolecules is rather limited. During the past few years, the use of thioureas and *N*-substituted thioureas for the initiation of aqueous vinyl polymerization has been examined. Hebeish and Bendak have reported the redox-initiated vinyl graft copolymerization onto wool fibers using H₂O₂-TU and Fe(III)-TU as cocatalyst.^{16,17}

The graft copolymerization of wool has been investigated by using the peroxydiphosphate-thiourea redox system changing the thiourea concentration over the range of 0.00025 to 0.0075 mole/l. (Fig. 9). The percentage of graft yield decreases with increase in thiourea concentration.

In all the initiating systems containing thiourea, the redox component is iso-

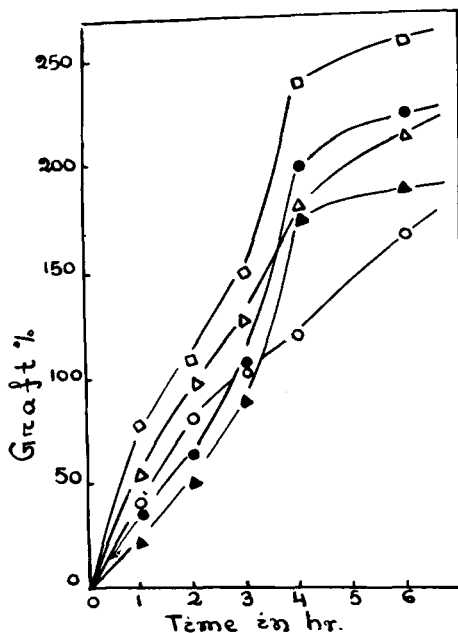
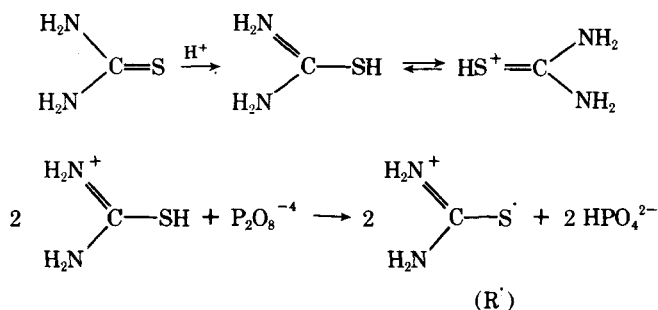
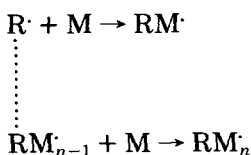


Fig. 9. Effect of thiourea concentration on graft yield: [peroxydiphosphate] = 80×10^{-4} mole/l.; $[\text{H}_2\text{SO}_4] = 0.15$ mole/l.; $[\text{MMA}] = 0.4694$ mole/l.; temperature = 50°C ; M:L = 1:100; (□): [thiourea] = 0.00025 mole/l.; (●): [thiourea] = 0.000375 mole/l.; (△): [thiourea] = 0.001 mole/l.; (▲): [thiourea] = 0.0035 mole/l.; (○): [thiourea] = 0.005 mole/l.; (■): [thiourea] = 0.0075 mole/l.

thiourea, a thiol existing in a tautomeric equilibrium with thiourea as the reductant:



The isothiocarbamido radicals (R^\cdot) abstract hydrogen from amino, thio, or carboxyl groups in the wool macroradical which initiates graft copolymerization. The isothiocarbamido radical might also react with the monomer to give rise to the monomer radical which initiates homopolymerization as shown below:



The decrease in the percentage of grafting with increasing thiourea concentration could be attributed to the following: (i) faster rate of termination probably owing to abundance of free-radical species in the polymerization system, (ii) the presence of free-radical inhibitor present in thiourea which might increase with increase in thiourea content, and (iii) an increase in the amount of thiourea, possibly facilitating the formation of disulfide and thus decreasing the concentration of isothiourea radical.

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