European Polymer Journal Vol. 17, pp. 1225 to 1226, 1981
Printed in Great Britain. All rights reserved

0014-3057/81/121225-02$02.00/0

GRAFTING VINYL MONOMERS ONTO NATURAL FIBRES

GRAFT COPOLYMERIZATION OF METHYL METHACRYLATE ONTO WOOL AND SILK USING PEROXYDIPHOSPHATE–TARTARIC ACID REDOX SYSTEM

M. K. Mishra[1] and A. K. Tripathy[2]

[1]78A, Kalapana Area, Bhubaneswar-751014 Orissa and [2]Department of Chemistry, Ravenshaw College, Cuttack-753 003, India

(*Received* 18 *April* 1980; *in revised form* 14 *July* 1980)

Abstract—Methyl methacrylate has been grafted onto wool and silk using the redox system peroxydiphosphate/tartaric acid. The alkali solubility falls with increased grafting.

INTRODUCTION

Grafting of side-chains to proteinaceous materials offers an attractive technique for improving the properties of the materials [1, 2]. Vinyl graft copolymerization onto wool and silk has been studied extensively using a variety of methods. Chemical methods have attracted considerable interest [2–4].

Peroxydisulphate has been extensively used as a water soluble initiator in emulsion polymerization [5] but peroxydiphosphate (PP), $P_2O_8^{4-}$, which is isoelectronic and isostructural [6] with peroxydiphosphate, has received relatively little attention until Edwards *et al.* [7] recognized this ion as a free radical initiator. Hariharan and Meenakshi [8] reported the polymerization of vinyl monomers using PP as the initiator. This communication presents the results of a study of the graft copolymerization of methylmethacrylate (MMA) onto wool and silk using the redox system consisting of PP with tartaric acid (TA).

$$\mathrm{TA} + \mathrm{P_2O_8^{4-}} \overset{K}{\rightleftharpoons} \mathrm{complex} \xrightarrow[\text{slow}]{k_1} \mathrm{TA}^{\bullet} + \mathrm{PO_4^{\bullet 2-}} + \mathrm{HPO_4^{2-}}$$

$$2\mathrm{TA} + \mathrm{P_2O_8^{4-}} \rightarrow 2\mathrm{TA}^{\bullet} + 2\mathrm{HPO_4^{2-}}.$$

EXPERIMENTAL

The reaction was carried out according to our previous communications [3, 4].

The alkali solubility of wool was tested in an aqueous solution of 0.1 N NaOH for 1 hr at 65° using a wool liquor ratio of 1:100. The intrinsic viscosity of poly(methyl methacrylate) was calculated using a single point method as described by Valles *et al.* [9]. Use was made of the equation

$$[\eta] = 9.6 \times 10^{-5}\, M^{0.69}.$$

The percentage of graft uptake was calculated as follows:

$$\%\,\text{Grafting} = \frac{\text{increase in weight of sample}}{\text{dry weight of original sample}} \times 100.$$

RESULTS AND DISCUSSION

The natural fibres, wool and silk, contain thiol, amino and hydroxy groups. Free radicals are generated by abstraction of hydrogen from these groups.

In the presence of TA, PP decomposes to yield HPO_4^{2-}, $PO_4^{\bullet 2-}$ and TA radicals as shown below. These free radicals might participate in direct abstraction of hydrogen from the fibre back-bone to create macroradicals capable of initiating grafting.

An alternative possibility might be that $H_2PO_4^{\bullet}$, $O^{\bullet}H$ and $HPO_4^{\bullet -}$ radicals, produced during the reaction as shown below, interact with the groups present in the fibre back-bone producing macroradicals which initiate grafting.

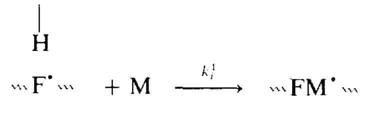
$$\mathrm{H_2P_2O_8^{2-}} + \mathrm{H^+} \overset{K}{\rightleftharpoons} \mathrm{H_3P_2O_8^-};$$

$$\mathrm{H_3P_2O_8^-} \xrightarrow{\text{slow}} \mathrm{H_2PO_4^{\bullet}} + \mathrm{HPO_4^{\bullet -}}$$

$$\mathrm{H_2PO_4^{\bullet}} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3PO_4} + {}^{\bullet}\mathrm{OH};$$

$$\mathrm{HPO_4^{\bullet -}} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_2PO_4} + {}^{\bullet}\mathrm{OH}.$$

Initiation



$$\underset{\substack{|\\ \mathrm{H}}}{\sim\mathrm{F}\sim} \xrightarrow{k_i} \sim\mathrm{F}^{\bullet}\sim$$

$$\sim\mathrm{F}^{\bullet}\sim + \mathrm{M} \xrightarrow{k_i^1} \sim\mathrm{FM}^{\bullet}\sim$$

Where $\underset{\substack{|\\ \mathrm{H}}}{\sim\mathrm{F}\sim}$ represents the reactive group in the fibre back-bone (i.e. wool or silk), M the monomer, $\sim\mathrm{F}^{\bullet}\sim$ and $\sim\mathrm{FM}^{\bullet}\sim$ the corresponding radicals.

The plots of the % grafting vs PP concentration are shown in Fig. 1. The concentration range studied was from 50×10^{-4} to 120×10^{-4} mol/l for wool and silk respectively and thereafter decreased.

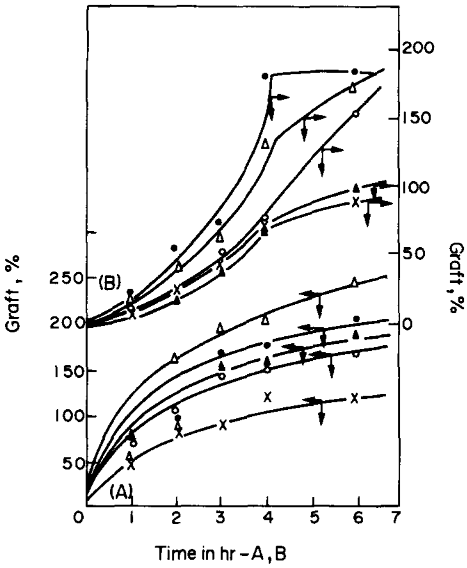


Fig. 1. (A) Wool; (B) silk. [TA] = 0.04 mol/l; [MMA] = 0.4694 mol/l; Temp. = 50°. Material:Liquor = 1:100. × [PP] = 50 × 10^{-4} mol/l; ○ [PP] = 60 × 10^{-4} mol/l; △ [PP] = 80 × 10^{-4} mol/l; ● [PP] = 100 × 10^{-4} mol/l; ▲ [PP] = 120 × 10^{-4} mol/l.

With increase of PP concentration up to the mentioned value, a large number of $H_2PO_4^{\bullet}$, $O^{\bullet}H$ and $HPO_4^{\bullet -}$ radicals are produced and interact with the fibre backbone giving rise to free radicals at several sites, so facilitating grafting. At higher concentration of PP, there is a fall in graft yield because some of the free radicals formed can terminate the grafted chain.

The rate of grafting was investigated by varying the TA concentration from 0.01 to 0.04 mol/l. The graft yield increased with increase in TA concentration. This may be attributed to the fact that, with increase in [TA] more free radicals are produced and may produce more grafting sites thereby increasing graft yield.

The rate of grafting was also studied for [MMA] from 27.98 × 10^{-2} to 103.27 × 10^{-2} mol/l. The % grafting increased with increasing monomer concentration. The % grafting increased with temperature. The grafting was also conducted using modified forms of wool. The order of the graft yield was, reduced wool > oxidized wool > unmodified wool > cross linked wool.

Table 1. Effect of grafting on alkali solubility

Graft (%)	Alkali solubility (%)
Nil	76
84	21
120	20
153	18
187	15
207	14

Table 2. Effecting of grafting on molecular weight

Graft (%)	$\overline{M}_w \times 10^{-5}$	$\overline{DP} \times 10^{-3}$
185	4.46	4.45
216	5.47	5.46
389	5.67	5.66
569	6.38	6.37

Alkali solubility and the molecular weight of the isolated poly(methyl methacrylate) of grafted wool

It is observed that the alkali solubility decreases as the percentage of grafting increases (see Table 1) and the average molecular weight increases with increased grafting (see Table 2).

REFERENCES

1. K. Arai, *Block and Graft copolymer* **1,** 193 (1970).
2. P. L. Nayak, *J. Macromolec. Sci. Rev. Macromolec. Chem.* **C14(2),** 193 (1976).
3. P. L. Nayak, S. Lenka and M. K. Mishra, *J. appl. Polym. Sci.* **25,** 63 (1980).
4. S. Lenka, P. L. Nayak and M. K. Mishra, *Angew Makromolek. Chem.* **84,** 183 (1980).
5. J. W. Vanderhoff, in *Vinyl Polymerization* Part II (Edited by G. E. Ham), Chapter 1, Marcel Dekker, New York (1969).
6. W. K. Wilmarth and A. Haim. *Peroxide Reaction Mechanisms* (Edited by J. O. Edwards) p. 175. Interscience, New York (1962).
7. M. Anderson, J. O. Edwards, Sir A. A. Green and Sir M. D. Wiswell, *Inorg. Chem. Acta* **3,** 655 (1969).
8. S. S. Hariharan and A. Meenakshi, *Polym. Lett. ed.* **51,** 1 (1977).
9. R. J. Valles, M. C. Otzinger and D. W. Lewis, *J. appl. Polym. Sci.* **4,** 92 (1960).
10. S. Chinai, A. Resnik and T. Matlack, *J. Polym. Sci.* **17,** 391 (1955).