

Graft Copolymerization of Poly (butyl Methacrylate) onto Wool in the Presence of Air and Nitrogen Atmosphere. I

J. S. SHUKLA, S. C. TIWARI and SUBODH K. DIXIT, *Department of Chemistry, Lucknow University, Lucknow, India*

Synopsis

Poly (butyl methacrylate) (PBMA) was grafted onto wool in the presence of air and nitrogen atmosphere using potassium persulphate (KPS) and thioacetic acid (TAA) as redox pair under different reaction conditions. The percentage grafting and efficiency were compared. The graft copolymer was characterized by scanning electron micrograph, thermogravimetry, and molecular weight.

INTRODUCTION

The oxygen-free atmosphere required for graft copolymerization is not economical in textile industry; furthermore, the expensive monomer and other reagents are wasted due to formation of a large amount of homopolymer during graft copolymerization. To face this problem, many scientists are engaged in investigating suitable initiating systems for graft copolymerization and for imparting better properties onto wool by grafting some novel polymers.¹⁻⁵

In our project we have already grafted poly (methyl methacrylate) onto wool in the presence of air, with very interesting results, so that the necessity of inert atmosphere may be excluded. Different initiating systems were used, e.g., potassium persulfate–thiomalic acid,¹ potassium bromate–thiomalic acid,² potassium permanganate–thiolactic acid,³ ceric ammonium nitrate–thioglycolic acid,⁴ and potassium persulfate–thiourea.⁵

It was needful to carry out a comparative study of graft copolymerization under air and nitrogen atmosphere. So the present study was carried out by grafting a novel monomer, butyl methacrylate, onto wool in the presence of air and nitrogen atmosphere, separately using KPS–TAA as redox pair.

EXPERIMENTAL

Materials

The wool obtained from U.P., India, was purified and characterized by the method described in our previous publication.² The monomer butyl methacrylate was washed by 10% NaOH solution and distilled water to remove inhibitor and alkali, respectively. Then it is distilled under reduced pressure and the middle fraction was collected. Other chemicals used were of A.R. grade.

Graft Copolymerization in Air

A known amount of wool was taken in a reaction flask, followed by calculated quantity of water, activator (TAA) and initiator (KPS), under continuous stirring at $45 \pm 0.2^\circ\text{C}$. A known amount of the monomer was added dropwise to the reaction mixture. At the end of the reaction excess of methanol was added to quench the reaction and a sufficient quantity of neutral magnesium sulfate was used to break the colloidal phase. Isolation, separation, and estimation of graft copolymer was carried out by the reported methods.¹ Percentage grafting and percentage efficiency were calculated by the following formula

$$\% \text{ Grafting} = [(W_2 - W_1)/W_1] \times 100$$

$$\% \text{ Efficiency} = [(W_2 - W_1)/W_3] \times 100$$

where W_1 , W_2 , and W_3 are the weights of wool, the grafted wool, and the monomer used, respectively.

Graft Copolymerization in Nitrogen Atmosphere

A known amount of purified wool was taken in a three-necked flask, followed by calculated quantity of water. Then the contents of the flask were deaerated by flushing purified nitrogen gas for 30 min before adding the activator and initiator. A known amount of monomer was added dropwise to the reaction mixture. A continuous flow of nitrogen gas was maintained throughout the reaction. Further procedure was similar to that followed under air atmosphere.

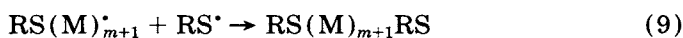
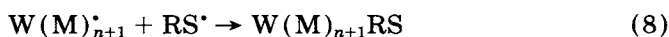
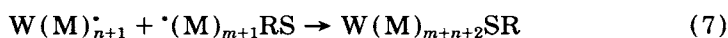
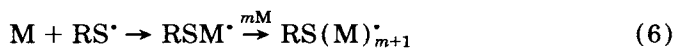
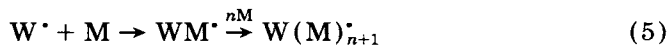
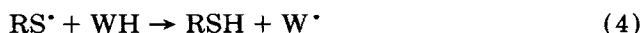
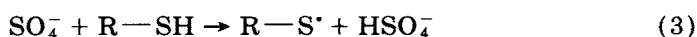
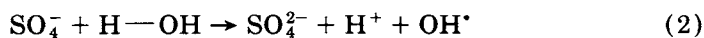
Evidence of Grafting

1. The graft copolymer was identified by IR spectroscopy and the ninhydrin test.¹⁻⁵
2. Further a comparative study of a scanning electron micrograph of purified wool and a grafted sample with different degree of polymer deposited indicated that grafting had taken place.¹⁻⁵

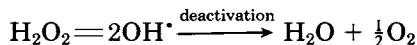
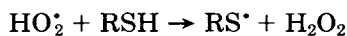
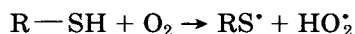
RESULTS AND DISCUSSION

Mechanism

The initiator KPS produces $\text{S}_2\text{O}_8^{2-}$ radicals in the system which react with activator TAA (R-SH) to create free radicals (RS^\bullet), which abstract H from the reactive functional groups of wool (WH), and the monomer butyl methacrylate (M) gets attached to the wool as shown below.¹



In steps (7) and (8) graft copolymer is formed and in step (9) homopolymer is formed. In the presence of air, in addition to the above process, free radicals are also produced as below:



Effect of Variations of Initiator Concentration

Grafting fairly takes place in air but the percentage grafting and efficiency were found slightly higher in nitrogen atmosphere. The observations are recorded in Table I.

Effect of Activator Concentration

The percentage grafting and efficiency increased in the range of 5.0–20.0 mmol/L of TAA and thereafter it decreased (Table II), as reported earlier.⁶⁻⁸

TABLE I
Effect of Initiator Concentration on % Grafting and Efficiency^a

Sample no.	[K ₂ S ₂ O ₈] (mmol/L)	% Grafting in air	% Grafting in N ₂ atm	% Efficiency in air	% Efficiency in N ₂ atm
1	10.0	11.00	14.62	3.07	4.08
2	20.0	15.82	20.00	4.42	5.59
3	25.0	16.60	22.20	4.64	6.20
4	35.0	19.06	26.04	5.32	7.27
5	40.0	20.00	27.72	5.59	7.74
6	50.0	18.24	25.06	5.09	7.00

^a Reaction conditions: [TAA] = 20.0 mmol/L, [BMA] = 12.604 × 10⁻² mol/L; time = 150 min; temperature = 45°C; wool = 0.5 g, H₂O = 100 mL.

TABLE II
Effect of Activator Concentration on % Grafting and Efficiency*

Sample no.	[TAA] (mmol/L)	% Grafting in air	% Grafting in N ₂ atm	% Efficiency in air	% Efficiency in N ₂ atm
1	5.0	10.00	14.62	2.79	4.08
2	10.0	15.64	22.10	4.37	6.17
3	15.0	18.72	25.40	5.23	7.09
4	20.0	20.74	28.06	5.79	7.84
5	25.0	19.80	27.42	5.53	7.66
6	30.0	18.04	24.66	5.04	6.89

* Reaction conditions: [K₂S₂O₈] = 40.0 mmol/L, [BMA] = 12.604 × 10⁻² mol/L; time = 150 min; temperature = 45°C; wool = 0.5 g, H₂O = 100 mL.

Percentage grafting and efficiency were found to be slightly higher in nitrogen atmosphere.

Effect of Monomer Concentration

It was found that percentage grafting increased with increasing monomer concentration in both air and nitrogen atmospheres, whereas the percentage efficiency decreased continuously^{9,10} (Table III). Percentage grafting and efficiency were slightly better in nitrogen atmosphere.

Effect of Wool

Wool variation shows the same effect in air and nitrogen atmospheres on percentage grafting and efficiency (Table IV).

Effect of Temperature

Percentage grafting and efficiency were better at lower temperatures but there was a slight increase in percentage grafting from 25 to 45°C (Table V). The maximum graft yield at 45°C may be due to favorable influence of temperature. At higher temperature (beyond 45°C) a decrement in graft yield may be attributed to termination of grafted chain free radicals and large amount of homopolymer formation.¹¹⁻¹⁴

TABLE III
Effect of Monomer Concentration on % Grafting and Efficiency*

Sample no.	[BMA] (× 10 ⁻² mol/L)	% Grafting in air	% Grafting in N ₂ atm	% Efficiency in air	% Efficiency in N ₂ atm
1	6.302	17.62	20.06	9.84	11.20
2	12.604	20.70	28.80	5.78	8.04
3	18.906	23.22	37.42	4.32	6.97
4	25.208	28.64	43.16	4.00	6.02

* Reaction conditions: [K₂S₂O₈] = 40.0 mmol/L, [TAA] = 20.0 mmol/L; time = 150 min; temperature = 45°C; wool = 0.5 g, H₂O = 100 mL.

TABLE IV
Effect of Amount of Wool on % Grafting and Efficiency^a

Sample no.	Wool (g)	% Grafting in air	% Grafting in N ₂ atm	% Efficiency in air	% Efficiency in N ₂ atm
1	0.25	25.73	34.07	3.59	4.76
2	0.50	22.42	29.00	6.26	8.10
3	1.00	18.06	22.62	10.08	12.6
4	1.50	14.00	16.42	11.73	13.75

^a Reaction conditions: [K₂S₂O₈] = 40.0 mmol/L, [TAA] = 20 mmol/L, [BMA] = 12.60 × 10⁻² mol/L; time = 150 min; temp = 45°C, H₂O = 100 mL.

TABLE V
Effect of Temperature on % Grafting and Efficiency^a

Sample no.	Temperature (°C)	% Grafting in air	% Grafting in N ₂ atm	% Efficiency in air	% Efficiency in N ₂ atm
1	25	13.04	18.28	3.64	5.11
2	35	18.02	23.00	5.03	6.42
3	45	22.80	28.06	6.37	7.84
4	55	17.04	22.84	4.76	6.38

^a Reaction conditions: [K₂S₂O₈] = 40.0 mmol/L, [TAA] = 20.0 mmol/L, [BMA] = 12.604 × 10⁻² mol/L; time = 150 min; wool = 0.5 g, H₂O = 100 mL.

TABLE VI
Effect of Time on % Grafting and Efficiency^a

Sample no.	Time	% Grafting in air	% Grafting in N ₂ atm	% Efficiency in air	% Efficiency in N ₂ atm
1	30	5.20	12.00	1.45	3.35
2	60	9.82	13.72	2.74	3.83
3	90	13.68	18.80	3.82	5.25
4	120	19.00	26.50	5.31	7.40
5	150	22.98	29.06	6.42	8.12
6	180	18.62	24.86	5.20	6.95

^a Reaction conditions: [K₂S₂O₈] = 40.0 mmol/L, [TAA] = 20.0 mmol/L, [BMA] = 12.604 × 10⁻² mol/L; temperature = 45°C; wool = 0.5 g, H₂O = 100 mL.

Effect of Time

Both percentage grafting and efficiency increased up to 150 min and thereafter decreased (Table VI). In the first 30 min the difference in percentage grafting and efficiency in the two atmospheres was found higher. It may be attributed to slight higher induction period in air.

Viscosity Average Molecular Weight

The Mark—Houwink equation¹⁵ was used for the determination of the viscosity average molecular weights.

TABLE VII
Viscosity Average Molecular Weight of Grafted PBMA and Homopolymer

Sample no.	Add-on (%)	Molecular weight of	
		Grafted PBMA	Homopolymer
1	20	404,600	415,900
2	28	380,200	385,500
3	32	354,000	365,600

$$[\eta] = KM_v^{\alpha}$$

The molecular weight of PBMA calculated were in the range of $3.5\text{--}4.0 \times 10^5$. It was observed (Table VII) that, as the graft yield increased, there was a decrease in the molecular weights of grafted PBMA onto wool.⁵ Further the molecular weight of grafted PBMA was found less than that of homopolymer. The reason may be that during hydrolysis the grafted PBMA onto wool undergoes degradation.

Thermal Behavior of Grafted and Ungrafted Wool

The pure wool and grafted wool were subjected to thermogravimetric analysis as described in our previous publication.⁵ It was observed that initial weight

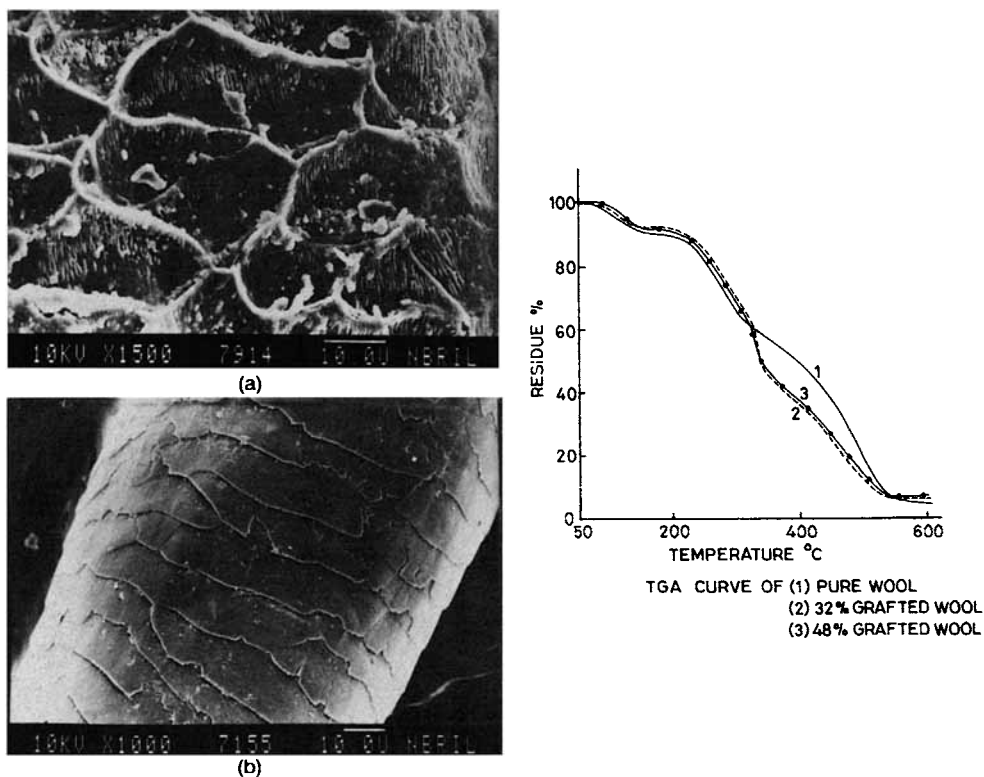


Fig. 1. Scanning electron micrograph of grafted wool (a) and pure wool (b).

loss due to moisture occurred up to 140 and 160°C for grafted and pure wool samples, respectively. Thermal stability improved with the graft up to 320°C due to new cross linkages formed after grafting. Beyond this temperature the decrease in thermal stability of grafted wool may be due to early decomposition of the PBMA as compared to the polypeptide chain of wool fibre. These results were in agreement with the results of Shukla et al.^{2,3,5} and Verma and Sarkar¹³ (Fig. 1).

Comparative Study of Graft Copolymerization in Air and Nitrogen Atmosphere

An attempt has also been made to compare the results of air and nitrogen atmospheres. It is evident from the results described in Tables I–VI that the percentage grafting and efficiency in nitrogen atmosphere were slightly higher. In air the oxygen terminates the growing polymer chains due to its chain ender reactions.^{14,16}

However, the thioacetic acid also reacts with the oxygen and creates free radicals directly,¹ showing catalytic action of oxygen.

Thanks are due to the Head of the Department of Chemistry, Lucknow University Lucknow, for providing departmental facilities.

References

1. J. S. Shukla, G. K. Sharma, R. K. Tiwari, and S. K. Shukla, *J. Macromol. Sci. Chem.*, **A21**, 225 (1984).
2. J. S. Shukla and G. K. Sharma, *Indian J. Chem.*, **24A**, 467 (1985).
3. J. S. Shukla and G. K. Sharma, *Indian J. Chem.*, **25A**, 463 (1986).
4. J. S. Shukla and G. K. Sharma, *J. Polym. Sci.*, **25**, 595 (1987).
5. J. S. Shukla, S. C. Tiwari, and G. K. Sharma, *J. Appl. Polym. Sci.*, **34**, 191 (1987).
6. S. S. Tripathy, S. Jena, and B. C. Singh, *J. Appl. Polym. Sci.*, **28**, 1811 (1983).
7. P. L. Nayak, S. Lenka, and M. K. Misra, *J. Appl. Polym. Sci.*, **26**, 733 (1981).
8. M. K. Misra, *J. Appl. Polym. Sci.*, **27**, 2403 (1982).
9. D. S. Verma and N. D. Ray, *Angew. Makromol. Chem.*, **32**, 81 (1973).
10. A. K. Mukerjee and S. Sanyal, *Cell. Chem. Technol.*, **3**, 13 (1979).
11. Padma L. Nayak, Subasini Lenka, and M. K. Misra, *J. Appl. Polym. Sci.*, **25**, 63 (1980).
12. K. S. Basu, K. P. Rao, K. T. Joseph, M. Santappa, and Y. M. Nayudamma, *Leather Sci.*, **28**, 355 (1981).
13. D. S. Verma and R. K. Sankar, *J. Appl. Polym. Sci.*, **15**, 2173 (1971).
14. J. H. Bexendale, *Trans. Faraday Soc.*, **42**, 155 (1946).
15. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Wiley-Interscience, New York, 1965.
16. M. M. Moglivic and V. D. Sukhov, *Izv. Vyssh. Ucheb. Zavod. Khim. Khim. Tekhnol.*, **17**(3), 432 (1974).

Received February 22, 1989

Accepted April 6, 1989