

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

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Synopsis

Poly(butyl methacrylate) (PBMA) was grafted onto wool in the presence of air and nitrogen atmosphere using potassium bromate and thioacetic acid (TAA) as redox initiating system, under different reaction conditions. The percentage grafting and percentage efficiency have been determined as a function of various reaction variables and the results have been compared. The graftcopolymer was characterized by scanning electron micrograph, thermogravimetry, and molecular weight.

INTRODUCTION

In the previous communications we have reported the graft copolymerization of poly(methyl methacrylate) in the presence of air using different redox initiating systems.¹⁻⁵ Thereafter PBMA was grafted onto wool in the presence of air and nitrogen atmospheres separately, using potassium persulfate and thioacetic acid, and the data obtained were compared.

The present study has been carried out with a view to get the maximum yield of graft copolymer. Hence KBrO_3 and TAA have been used as a redox pair.

EXPERIMENTAL

The monomer, wool and other chemicals were purified as reported earlier.¹⁻⁵ The procedure followed for graft copolymerization and estimation of polymer have also been reported. All experiments were carried out for 150 min at $45 \pm 0.2^\circ\text{C}$, if otherwise not mentioned.

Evidence of grafting was confirmed by IR spectroscopy, the ninhydrin test, and scanning electron micrographs.¹⁻⁵

RESULTS AND DISCUSSION

Mechanism

The mechanism has been proposed according to the mechanism given by Shukla et al. for graft copolymerization of methyl methacrylate by $\text{K}_2\text{S}_2\text{O}_8$ -thiomallic acid² and ceric ammonium nitrate-thioglycolic acid.³ In the present case the oxidant KBrO_3 and thioacetic acid (TAA) produce thio free radicals (TAA-S^\cdot), which abstract hydrogen from the reactive functional groups of wool (WH) to generate wool free radicals (W^\cdot). Grafting is initiated when the wool free radical attacks the monomer molecule (M).

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

Sample no.	KBrO ₃ (mmol/L)	Grafting in air atm (%)	Grafting in N ₂ atm (%)	Efficiency in air atm (%)	Efficiency in N ₂ atm (%)
1	10	15.72	30.4	4.39	8.49
2	20	28.70	47.12	8.02	13.16
3	30	33.84	51.00	9.44	14.24
4	40	39.92	58.26	11.15	16.28
5	50	29.96	47.20	8.37	13.18
6	60	18.90	34.70	5.28	9.69

^a Reaction conditions: TAA = 20 mmol/L; BMA = 12.604×10^{-2} mol/L; time = 150 min; temp = 45°C; wool, 0.5 g; H₂O, 100 mL.

Effect of Variation of Initiator, Activator, and Monomer Concentration

The initiator concentration varied from 10 to 60 mmol/L of KBrO₃ and the data obtained were recorded in Table I. Percentage grafting and efficiency increased up to 40.0 mmol/L concentration of KBrO₃ and thereafter both parameters registered a decrease.

In the case of the activator, maximum graft yield was obtained at 25.0 mmol/L concentration of TAA (Table II).

With the increase in the concentration of KBrO₃ (from 10 to 40 mmol/L) and TAA (from 5 to 25 mmol/L) the formation of TAA-S' free radicals increased; hence an increase in graft yield was observed. At higher concentration of KBrO₃ (> 40.0 mmol/L) and TAA (> 25.0 mmol/L) the graft chain terminated due to the formation of large amount of homopolymer, abundance of free radicals and inhibitory action of oxygen.^{1,2}

On increasing the monomer concentration from 6.302 to 25.208×10^{-2} mol/L the percentage grafting increased continuously while efficiency decreased (Table III). Similar results have been reported by Sudhakar et al.,⁶ Verma and Ray,⁷ Hiroshi,⁸ Mukerjee and Sanyal⁹ and Basu et al.¹⁰

TABLE II
Effect of Activator Concentration on Percentage Grafting and Efficiency^a

Sample no.	TAA (mmol/L)	Grafting in air atm (%)	Grafting in N ₂ atm (%)	Efficiency in air atm (%)	Efficiency in N ₂ atm (%)
1	5	14.60	32.20	4.08	8.99
2	10	26.04	40.92	7.27	11.43
3	15	31.70	51.00	8.86	14.24
4	25	33.00	53.00	9.21	14.80
5	35	22.64	48.00	6.32	13.41
6	45	19.62	43.70	5.48	12.21

^a Reaction conditions: KBrO₃ = 40.0 mmol/L; BMA = 12.604×10^{-2} mol/L; time = 150 min; temp = 45°C; wool, 0.5 g; H₂O, 100 mL.

TABLE III
Effect of Monomer Concentration on Percentage Grafting and Efficiency^a

Sample no.	BMA ($\times 10^{-2}$ mol/L)	Grafting in air atm (%)	Grafting in N ₂ atm (%)	Efficiency in air atm (%)	Efficiency in N ₂ atm (%)
1	6.302	23.02	52.42	12.86	29.29
2	12.604	40.67	58.72	11.36	16.40
3	18.906	48.72	62.04	9.07	11.55
4	25.208	53.07	67.07	7.41	9.37

^a Reaction conditions: KBrO₃ = 40.0 mmol/L; TAA = 20.0 mmol/L; time = 150 min; temp = 45°C; wool, 0.5 g; H₂O, 100 mL.

Effect of Time, Temperature, and Wool

The percentage grafting and efficiency increased up to 150 min and thereafter both decreased (Table IV). Similar observations have been reported by Bendak and Hebeish.¹¹

Mukerjee and Sanyal⁹ and Namasivam et al.¹² have also observed that with long polymerization time the branches may shorten by the reaction with the initiator and the fragmented PBMA radicals can become attached to new polymer sites in the polymer chain.

The maximum graft yield was observed at 45°C (Table V). Beyond this temperature a decrease in graft yield might be due to the termination of

TABLE IV
Effect of Time on Percentage Grafting and Efficiency^a

Sample no.	Time (in min)	Grafting in air atm (%)	Grafting in N ₂ atm (%)	Efficiency in air atm (%)	Efficiency in N ₂ atm (%)
1	30	12.04	21.42	3.36	5.98
2	60	17.30	27.64	4.83	7.72
3	90	22.94	34.07	6.41	9.51
4	120	28.92	49.71	8.08	13.89
5	150	39.78	58.06	11.11	16.21
6	180	32.04	54.04	8.95	15.10

^a Reaction conditions: KBrO₃ = 40.0 mmol/L; TAA = 20.0 mmol/L; BMA = 12.604×10^{-2} mol/L; temp = 45°C; wool, 0.5 g; H₂O, 100 mL.

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

Sample no.	Temperature (°C)	Grafting in air atm (%)	Grafting in N ₂ atm (%)	Efficiency in air atm (%)	Efficiency in N ₂ atm (%)
1	25	15.76	42.06	4.40	11.74
2	35	28.68	50.00	8.01	13.96
3	45	39.46	58.62	11.03	16.37
4	55	18.06	43.06	5.04	12.02

^a Reaction conditions: KBrO₃ = 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 Amount of Wool on Percentage Grafting and Efficiency^a

Sample no.	Wool (g)	Grafting in air atm (%)	Grafting in N ₂ atm (%)	Efficiency in air atm (%)	Efficiency in N ₂ atm (%)
1	0.25	43.8	63.40	6.12	8.86
2	0.5	39.0	57.60	10.89	16.09
3	1.0	20.0	32.00	11.17	17.87
4	1.5	16.4	24.00	13.74	20.11

^aReaction conditions: KBrO₃ = 40.0 mmol/L; TAA = 20.0 mmol/L; BMA = 12.604 × 10⁻² mol/L; temp = 45°C; time = 150 min; H₂O, 100 mL.

grafted chain free radicals and predominance of homopolymer formation over graft copolymerization.¹³

On increasing the amount of wool the chances of creation of more active sites were increased, leading to increased efficiency, and the percentage grafting decreased (Table VI) due to primary free radicals, which remain almost constant.²

Thermal Behavior of Grafted and Ungrafted Wool

Thermogravimetric analysis of grafted and ungrafted samples were carried out in air at the rate of 6°C/min, in the temperature range of 50–600°C. The thermal stability of the grafted wool improved up to 325°C.

After grafting, the elimination of molecules like H₂O, NH₃, H₂S, CO₂, CH₃SH, etc., might have decreased¹⁴ due to the formation of crosslinkages, which help in increasing the decomposition temperature of wool. Above 325°C the decrease in thermal stability of grafted wool may be due to the early decomposition of the grafted PBMA as compared to the polypeptide chain of wool fiber.

The initial weight loss due to moisture for pure and grafted wool occurred up to 165 and 135°C, respectively. These results were in agreement with the results of Shukla et al.¹ and Verma and Sarkar.¹⁵

Viscosity Average Molecular Weight

The viscosity average molecular weight of grafted PBMA separated by acid hydrolysis, and of homopolymer formed during graft copolymerization, were determined by the Mark–Houwink equation (Table VII).

TABLE VII
Viscosity Average Molecular Weight

Sample no.	Add-on (%)	Molecular weight of	
		Grafted PBMA	Homopolymer
1	32	208,400	258,800
2	45	198,600	236,600
3	58	177,400	187,100

It was observed that, as the graft yield increased, there was a decrease in the molecular weight. The molecular weight of homopolymer was found to be higher than that of the grafted PBMA. It might be due to the degradation of grafted PBMA during its separation, from the wool.¹

Comparative Study of the Graft Copolymerization in Air and Nitrogen Atmosphere

It was observed from the data recorded in the tables (Tables I–VI) that grafting took place fairly in air but percentage grafting and efficiency were higher in nitrogen atmosphere.

In air, the oxygen terminates the growing polymer chains due to its chain terminating reactions¹⁶ and formation of stable peroxide radicals.¹⁷ However, the oxygen reacts with the activator (TAA) directly and creates free radicals, showing its catalytic action.

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