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Potassium Bromate-Thiourea Redox Initiated Grafting of Methyl Methacrylate onto Polyethylene Terephthalate

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ABSTRACT

Some kinetic features of the grafting of methyl methacrylate onto polyethylene terephthalate initiated by the potassium bromate-thiourea redox system have been investigated in aqueous solution. The effects of potassium bromate, thiourea, monomer, acid, and temperature upon percentage grafting have been determined. The activation energy of the reaction has been computed from an Arrhenius plot. Grafting experiments have been carried out in the presence of such conventional chain-transfer agents as CCl_4 and $CHCl_3$. The effect of $CuSO_4$ upon grafting is also studied. The reaction mechanism involved during grafting is pictured.

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INTRODUCTION

Although potassium bromate is a powerful oxidizing agent with an oxidation potential of 1.4 V in acidic medium, it has been used as a source of Br_2 in the presence of Br^- ions. The kinetics of the oxidation of organic compounds [1-3] by potassium bromate has recently received considerable interest. In an earlier publication Palit et al. [4] showed the feasibility of the bromate-Fe^{2+} redox system for the polymerization of methyl methacrylate (MMA). The use of thiourea as a redox component to initiate graft copolymerization [5-8] has been reported. Nayak et al. have recently reported the polymerization of acrylonitrile [9] and methyl methacrylate [10] with the use of the $KBrO_3$-thiourea redox system.

In recent years the chemical modification of polyethylene terephthalate (PET) [11, 12] has received considerable interest since the preformed polymers are incapable of diffusing into the internal structure of the polymer. In our earlier communications we have used higher valent metal ions [13, 14] to initiate grafting onto PET.

The present work deals with the graft polymerization of MMA onto PET by the potassium bromate-thiourea (PB-TU) redox system for the purpose of finding 1) the feasibility of this system to initiate grafting, 2) the factors affecting the magnitude of polymerization, and 3) elucidation of the reaction mechanism.

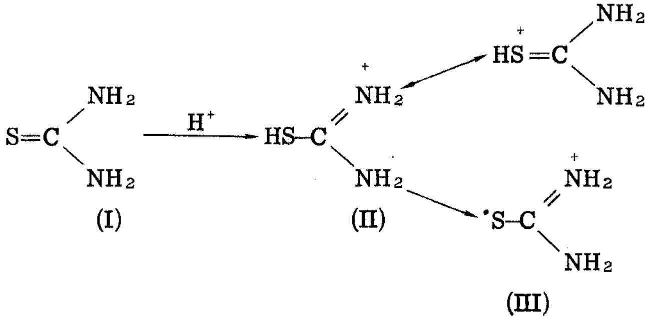
EXPERIMENTAL

PET fibers of J. K. Synthetics (Raj), India, were used. The PET fibers were treated in a Soxhlet with methanol and acetone and dried under vacuum to constant weight before use. All chemicals used were of best quality A.R. grade and purified wherever necessary. The grafting reaction and separation of homopolymer from the grafted fiber were carried out according to our previous procedure [13-15]. The graft percentage was calculated as the percent increase in weight over the original weight of the fiber. The rate of polymerization R_p was calculated as percentage graft per second.

RESULTS AND DISCUSSION

Reaction Mechanism

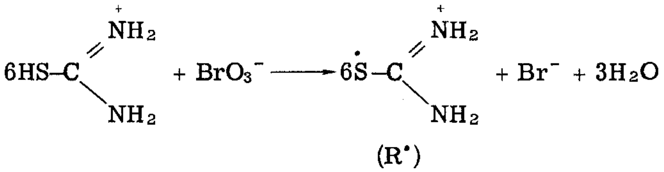
Sugimura et al. [16] suggested that in all the initiating systems containing thiourea (I), the redox component is isothiourea (II). A thiol (existing in a tautomeria equilibrium with thiourea in an aqueous solution) is the reductant. The primary radical formed by abstraction of the reactive hydrogen atom attached to the sulfur atom in isothiourea, generating the isothiocarbamide radical (III):



(1)

Mukharjee et al. [17] studied a number of initiating systems with thiourea as the reductant for vinyl polymerization. The initiating efficiency of the acidified bromate-thiourea redox system was very high. Nitrogen-bearing groups in thiourea do not take part in radical generation [16].

The mechanism for initiating radical generation might be as follows:



$$6HS\text{–}C(=\overset{+}{N}H_2)NH_2 + BrO_3^- \longrightarrow 6\dot{S}\text{–}C(=\overset{+}{N}H_2)NH_2 + Br^- + 3H_2O \qquad (2)$$

(R•)

These radicals (R•) abstract hydrogen from the PET backbone to yield a fiber macroradical. This subsequently combines with monomer to propagate the chain. The termination may be of the mutual or linear type. The steps are represented below, where M is the monomer and k_i, k_i', k_p, and k_t are the corresponding rate constants.

Initiation:

$$PET + R^\bullet \xrightarrow{k_i} PET^\bullet + RH; \qquad PET^\bullet + M \xrightarrow{k_i'} PETM^\bullet$$

Propagation:

$$PETM^\bullet + M \xrightarrow{k_p} PETM; \qquad PETM^\bullet_{n-1} + M \xrightarrow{k_p} PETM_n^\bullet$$

Termination:

$$\mathrm{PETM}_n^{\bullet} + \mathrm{PETM}_n^{\bullet} \xrightarrow{k_i} \text{graft polymer}$$

$$\mathrm{PETM}_n^{\bullet} + \mathrm{R}^{\bullet} \xrightarrow{k_t} \text{graft polymer}$$

Effect of Different Variables on Grafting

The results of grafting are presented in Table 1. The effect of thiourea concentration on graft yield has been investigated by varying the thiourea over a wide range (2.5×10^{-3} to 12.5×10^{-3} mol/L) of concentration. It is observed that the graft yield reaches a maximum value at a thiourea concentration of 7.5×10^{-3} mol/L. Beyond this concentration, graft yield decreases. Several reasons might be responsible for the decrease of graft yield with increasing thiourea concentration.

1. Bromate interacts with thiourea to produce the isothiocarbamide radical. There will be abundance of this free radical species in the polymerization medium with increasing thiourea concentration, and this might terminate the growing polymer chain by reducing the percentage of grafting.
2. It is also possible that at a higher concentration of thiourea the latter might act as a radical scavenger, thereby decreasing grafting.
3. The isothiocarbamide radical produced in the system might react with the monomer, giving rise to homopolymer. There will be competition between homopolymerization and grafting. The homopolymerization reaction exceeds grafting at higher concentrations of thiourea.

The effect of bromate concentration was studied by varying it from 5×10^{-3} to 25×10^{-3} mol/L. A perusal of the results indicates that the rate of grafting increases up to 20×10^{-3} mol/L and thereafter it decreases. The decrease of grafting at a higher concentration of bromate is due to the fact that at a higher concentration of bromate the isothiocarbamide radical generation is larger. This favors the formation of homopolymer and termination of grafted chain, thereby affecting the percentage of grafting.

In accordance with the above postulated mechanism, the percentage of grafting should increase with an increase in monomer concentration. It is apparent from Table 1 that as the monomer concentration increases, the percentage of grafting increases. This indicates monomer participates in the grafting process. Similar observations were noted in our earlier publications [5, 18], and reasons have been given.

TABLE 1. Effect of Different Variables on Graft Copolymerization of Methyl Methacrylate onto PET[a]

Sample no.	[TU] × 10^3 mol/L	[$KBrO_3$] × 10^3 mol/L	[MMA] × 10^2 mol/L	[HCl] × 10^2 mol/L	Temperature (°C)	Time (h)	Graft (%)
1	2.5	20	46.94	90	70	6	12.9
2	5.0	20	46.94	90	70	6	16.9
3	7.5	20	46.94	90	70	6	24.6
4	10.0	20	46.94	90	70	6	21.8
5	12.5	20	46.94	90	70	6	18.7
6	7.5	5	46.94	90	70	6	10.7
7	7.5	10	46.94	90	70	6	12.9
8	7.5	15	46.94	90	70	6	17.6
9	7.5	25	46.94	90	70	6	20.7
10	7.5	20	28.16	90	70	6	18.8
11	7.5	20	65.71	90	70	6	28.3
12	7.5	20	84.49	90	70	6	34.4
13	7.5	20	103.21	90	70	6	37.8
14	10	20	46.94	9	70	6	16.3
15	10	20	46.94	27	70	6	19.1
16	10	20	49.94	45	70	6	21.6
17	10	20	46.94	63	70	6	25.5
18	10	20	46.94	90	70	6	21.3
19	7.5	20	46.94	90	60	3	6.8
20	7.5	20	46.94	90	60	4	10.1
21	7.5	20	46.94	90	60	5	14.4
22	7.5	20	46.94	90	60	6	18.3
23	7.5	20	46.94	90	70	3	12.4
24	7.5	20	46.94	90	70	4	15.3
25	7.5	20	46.94	90	70	5	19.4
26	7.5	20	46.94	90	75	3	15.2

(continued)

TABLE 1 (continued)

Sample no.	[TU] × 10^3 mol/L	[$KBrO_3$] × 10^3 mol/L	[MMA] × 10^2 mol/L	[HCl] × 10^2 mol/L	Temperature (°C)	Time (h)	Graft (%)
27	7.5	20	46.94	90	75	4	19.4
28	7.5	20	46.94	90	75	5	25.3
29	7.5	20	46.94	90	75	6	32.1

[a] Reaction volume including water = 20 cm^3, PET = 0.2 g, and 2-ethoxy ethanol = 0.5 cm^3.

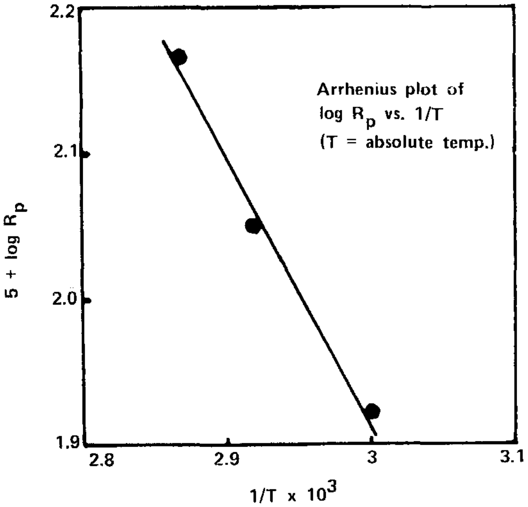


FIG. 1. Reaction volume including water = 20 cm^3, PET = 0.2 g, 2-ethoxy ethanol = 0.5 cm^3, [TU] = 7.5 × 10^{-3} mol/L, [$KBrO_3$] = 20 × 10^{-3} mol/L, [MMA] = 46.94 × 10^{-2} mol/L, [HCl] = 90 × 10^{-2} mol/L, time = 6 h.

The increase in HCl concentration from 9 × 10^{-2} to 63 × 10^{-2} mol/L increases the percentage of grafting. The graft percentage also increases with time. The effect of temperature on percent grafting has been studied, and it was observed that the graft percentage increases with temperature. This is in accordance with our previous communications [5, 18]. From the Arrhenius plot of log R_p vs 1/T (R_p computed at 6 h and T - absolute temperature), the overall activation energy is computed to be 8.7 kcal/mol (Fig. 1). Using the value of $E_p - \frac{1}{2}E_t = 4 \sim 5$ kcal/mol given by Tobolsky [19], where E_p

TABLE 2. Effect of Chain-Transfer Agents upon Percentage Grafting[a]

Solvent (% v/v)	CCl$_4$			CHCl$_3$		
	10	25	35	10	25	35
Graft %	8.4	6.3	5.9	11.2	10.3	7.4

[a] [KBrO$_3$] = 20 × 10^{-3} mol/L, [MMA] = 46.94 × 10^{-2} mol/L, [TU] = 7.5 × 10^{-3} mol/L, [HCl] = 90 × 10^{-2} mol/L, 2-ethoxy ethanol = 0.5 cm, temperature = 70° C, time = 6 h, total volume = 20 cm^3, PET = 0.2 g.

TABLE 3. Effect of CuSO$_4$ on Graft Copolymerization onto PET[a]

[CuSO$_4$] × 10^3 mol/L	2.5	3.0	5.0	7.5	10
Graft %	26.0	26.9	27.5	27.0	26.1

[a] [KBrO$_3$] = 20 × 10^{-3} mol/L, [MMA] = 46.94 × 10^{-2} mol/L, [TU] = 7.5 × 10^{-3} mol/L, [HCl] = 63 × 10^{-2} mol/L, 2-ethoxy ethanol = 0.5 cm^3, temperature = 70° C, time = 6 h, total volume = 20 cm^3, PET = 0.2 g.

and E_t are energies of propagation and termination, respectively, the activation energy of initiation, E_d, can be calculated from these values by

$$E_d = 2E_a - (2E_p - E_t)$$

where E_a is the overall activation energy and E_d = 8.4 kcal/mol for the total conversion reaction of MMA to PMMA.

Effect of Chain-Transfer Solvents on Grafting

Table 2 shows the effect of conventional chain-transfer agents like CCl$_4$ and CHCl$_3$ upon (PB-TU) redox-initiated grafting. It is observed that the chain-transfer agents CCl$_4$ and CHCl$_3$ reduce percent grafting. Mishra et al. [20] have made similar observations while grafting methyl acrylate onto cellulose by using benzoyl peroxide and azobisisobutyronitrile.

Effect of [$CuSO_4$] on Graft Yield

Of interest is the effect of $CuSO_4$ on the graft yield. The results are presented in Table 3. The graft yield increases up to 5.0×10^{-3} mol/L of $CuSO_4$ concentration. In the initial stages [21] there is formation of a lot of free radicals like $SO_4^{\cdot -}$ and $^{\cdot}OH$ by the interaction of PET macroradicals with SO_4^{2-}, which might enhance the graft percentage. Furthermore there is easy involvement of Cu^{2+} in the fiber-monomer complex, and this might facilitate the rate of grafting. The creation of free radical species under the influence of the Cu^{2+} ion would be near the fiber, thus assisting in the formation of fiber macroradicals. The sharp drop in the graft yield with a higher concentration of cupric sulfate can be attributed to a couple of reasons: 1) Cu^{2+} ions seem to act as radical traps and 2) a particular concentration of Cu^{2+} favors complexation of monomer with fiber but beyond this concentration the Cu^{2+} ion perturb such a complexation.

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