Kinetics of Vinyl Polymerization of Methyl Methacrylate Initiated by Ce(IV)-Vanillin Redox System

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Abstract: The kinetics of polymerization of methyl methacrylate initiated by Ce(IV)-Vanillin redox system was studied in aqueous solution of sulfuric acid at 40 °C. The rate of polymerization (R_p) and the reaction orders with respect to monomer, initiator and ligand have been determined and found to be 1.5, 0.5 and 0.5 respectively. The effect of concentration of sulfuric acid on the polymerization was also studied. The rate of polymerization was found to increase with increasing temperature 30-60 °C and decreases at higher temperature (>60 °C). The overall activation energy (E_a) was found to be 36.7 kJ/mol. A suitable kinetic scheme has been proposed.

Keywords: Kinetics study, Methyl methacrylate, Redox system, Vanillin

Introduction

Kinetic studies on aqueous polymerization of MMA have been reported^{1,2}. Several reports have appeared on the mechanism and kinetics of vinyl polymerization initiated by a variety of initiators³⁻⁶. Ceric ion has been used in vinyl polymerization in the presence of various organic reducing agents such as alcohols⁷, acids⁸, amides⁹, amines¹⁰, etc. Rout *et al.*¹¹ have proposed a linear termination step involving interaction of polymer radicals with ceric ion¹². The redox system involving complex between both an organic substrate and an inorganic salt was already reported¹³⁻¹⁵. A direct oxidation mechanism, without complex formation has been suggested for oxidation in sulfuric acid^{16,17}. This reaction involves the formation of an intermediate complex between the metal ion and the protonated species of the reductant¹⁸. The literature survey reveals that no systematic investigation of the kinetics of polymerization of MMA with Ce(IV) and vanillin has been carried out.

Experimental

Methyl methacrylate was washed with 5% NaOH solution and then with water and dried over calcium chloride. After the drying agent was removed by filtration the monomer was distilled in a nitrogen atmosphere under reduced pressure and stored in a refrigerator¹⁵. All the reagents used were of Analar grade. Vanillin analytical grade sample was distilled under reduced pressure. Distillated and deionized water were employed in the preparation of the reagents and solutions. The polymerization procedure was as follows: The appropriate quantities of the methyl methacrylate and vanillin were introduced under nitrogen atmosphere. The iodine flasks placed in a thermostated water bath at 40 °C and then cerium salt was added. The polymerization reactions started almost instantaneously, indicated by the appearance of turbidity that increased with the progress of polymerization, ultimately the polymers precipitated out. After desired intervals the polymerization were halted by adding 2 mL of ferrous ammonium sulfate. The precipitated polymethyl methacrylate were filtered, washed several times with water and the conversion of MMA was determined by directly weighing the PMMA dried in vacuum at 60 °C. The percentage conversion was obtained from the ratio between the amount of polymer formed and the initial amount of monomer in the mentioned reaction time.

Results and Discussion

Rate dependence on concentration of monomer

The effect of monomer concentration on the rate of polymerization was studied by varying concentration of methyl methacrylate (MMA) in the range 1.0 to 5.0 M, at fixed concentration of Ce(IV), Vanillin (Vn) and H₂SO₄. The rate of polymerization was found to increase linearly with increasing monomer concentration. The Plot of log[MMA] vs. logRp were linear (slope = 1.504; r² = 0.984), (Table 1, Figure 1), thus indicating that the order of reaction is 1.5 with respect to monomer concentration.

Table 1. Dependence of rate on monomer concentration
[Ce(IV)] = 0.0025M; [Vn] = 0.002M; [H⁺] = 0.1M; Temp. 40 °C; Time: 60 min

[MMA], mol/L	2+log[MMA]	Rp×10 ⁶	6+logRp	% conversion
0.10	1.000	4.855	0.686	2.8
0.15	1.176	6.866	0.837	3.9
0.20	1.301	10.265	1.011	5.9
0.25	1.397	14.565	1.163	8.4
0.30	1.477	19.768	1.296	11.4
0.35	1.544	26.079	1.416	15.0
0.40	1.602	32.877	1.516	18.9
0.45	1.653	41.755	1.621	24.0
0.50	1.699	50.634	1.704	29.2

Rate dependence on concentration of initiator

The effect of initiator concentration on the rate of polymerization was studied by varying the concentration of the Ce(IV), in the range of 1.0×10⁻³ to 5.0×10⁻³ M, at fixed concentration of monomer, ligand and H₂SO₄. The rate of polymerization increases with increasing concentration of initiator from 1.0×10⁻³ M to 3.0×10⁻³ M. While the concentration of initiator changes from 3.0×10⁻³ M to 5.0 ×10⁻³ M the rate was found to increase then decrease at higher concentration. The decrease of rate of polymerization at higher [Ce(IV)] can be accounted

for the oxidation and termination process increases. Similar behavior was also studied by Fernandez and Guzman *et al.*¹⁶ in the polymerization of MMA initiated by the redox system.

Figure 1. Plot $\log [\text{MMA}]$ vs. $\log R_p$

Rate dependence on concentration of ligand

The effect of ligand concentration on the rate of polymerization was studied by varying the concentration of the vanillin (Vn), in the range of 1.0×10^{-3} M to 1.0×10^{-4} M, at fixed concentration of monomer, initiator and acid. The rate of polymerization increases with an increase in the [Vn]. The plot of $\log[\text{Vn}]$ vs. $\log R_p$ is linear with order of 0.5 (slope = 0.532; $r^2 = 0.984$) (Table 2; Figure 2).

Table 2. Dependence of rate on Ligand concentration

[MMA] = 0.25 M; [Ce(IV)] = 0.0025 M; $[\text{H}^+] = 0.1$ M; Temp. = 40 °C; Time: 60 min

$[\text{Vn}] \times 10^3$, mol/L	$3 + \log[\text{Vn}]$	$R_p \times 10^6$	$6 + \log R_p$	% conversion
1.0	1.000	10.682	1.029	6.1
1.5	1.176	12.832	1.108	7.4
2.0	1.301	13.525	1.152	7.8
2.5	1.397	14.565	1.193	8.4
3.0	1.477	18.380	1.264	10.6
3.5	1.544	20.531	1.312	11.8
4.0	1.602	21.433	1.331	12.4
4.5	1.653	23.583	1.373	13.6
5.0	1.699	24.346	1.386	14.0

Rate dependence on concentration of acid

The effect on polymer on the addition of acid at different concentration to the polymerization system was studied. It is clear that the addition of sulfuric acid causes a substantial increase in polymerization and at higher concentration of sulfuric acid decreases the rate of polymerization. It is evident that at low acid concentration, the reducing agent may be deprotonated and the coordination becomes easier for the ceric salt whereas at high acid concentration the R_p is decreases may be due to the high complexation.

Figure 2. Plot log [Vn] vs. log Rp

Rate dependence on temperature

The polymerization was carried out at 30-80 °C keeping the concentration of all reagents fixed. The rate of polymerization increases with increasing the temperature and the overall activation energy (E_a) for MMA was calculated from the Arrhenius plot. The activation energy is 36.7 kJ/mol. At above 60 °C reduction becomes very fast, resulting in a local over concentration of free radicals. Hence the polymer yield decreases.

On the basis of above results and discussion, the following reaction scheme and mechanism is suggested.

The reaction of primary radical (R°) with Ce(IV): $\text{R}^\circ + \text{Ce(IV)} \rightarrow \text{Product}$. Considering the steady-state condition for the polymerization, the following rate expression has been derived.

$$R_p = k_p[M]^{1.5} [\text{Ce(IV)}]^{1/2} / k_t^{1/2} (k_k[R]/[M] + k_0/k_t [\text{Ce(IV)}])^{1/2}$$

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