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FREE RADICAL POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF PHASE TRANSFER CATALYST—A KINETIC STUDY

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The kinetics of free radical polymerization of methyl methacrylate (MMA) using potassium peroxydisulfate as initiator in the presence of propiophenonebenzyltrimethylammonium chloride as phase transfer catalyst were studied. The reactions were carried out under inert and unstirred conditions at constant temperature of 60°C in cyclohexanone/water biphasic media. The dependence of the rate of polymerization on various experimental conditions, such as different concentrations of monomer, initiator and phase transfer catalyst (PTC) and different ionic strength, temperature and volume fraction of aqueous phase was studied. The order with respect to monomer, initiator and phase transfer catalyst was found to be 1, 0.5 and 0.5 respectively. The rate of polymerization (R_p) is independent of ionic strength and pH. However, an increase in the polarity of solvent and volume fraction of aqueous phase has slightly increased the R_p value. Based on the results obtained, a mechanism has been proposed for the polymerization reaction.

Keywords: Kinetics, methyl methacrylate, initiator, phase transfer catalyst, rate of polymerization

INTRODUCTION

Free radical polymerization of water insoluble olefinic monomers using phase transfer catalyst (PTC) has gained importance in recent years owing to its high reaction rates at low temperature. Phase transfer catalysis is a technique in which a substrate soluble in an organic solvent reacts with an ionic reagent with the help of a phase transfer

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catalyst (PTC). Phase transfer catalysis involves two important processes: transfer of one reagent from its original phase to the other phase and reaction of the transferred reagent or ion pair with the non-transferred reagent within the organic layer [1]. Rasmussen and Smith opened a new avenue of research in phase transfer catalyzed free radical polymerization of olefinic monomers by reporting the polymerization of butyl acrylate using crown ethers and quaternary ammonium salts as phase transfer catalysts and potassium peroxydisulfate as the water soluble initiator [2]. Kunieda and coworkers [3, 4] used cyclodextrin as a phase transfer catalyst to study the transfer of organic soluble initiator into aqueous media for the polymerization of water-soluble monomers. Jayakrishnan and Shah reported the polymerization of acrylonitrile and methyl methacrylate with ammonium peroxydisulfate and hexadecylpyridinium chloride in ethyl acetate/water biphasic media [5]. Recently, we have reported the free radical polymerization of glycidyl methacrylate in the presence of phase transfer catalyst using potassium peroxydisulfate as initiator [6]. In the present work, the kinetics of the free radical polymerization of methyl methacrylate (MMA) was studied using potassium peroxydisulfate and propiophenonebenzyltrimethylammonium chloride (PPBDMAC) as phase transfer catalysts in cyclohexanone/water biphasic media.

EXPERIMENTAL

MMA, potassium peroxydisulfate, methanol, cyclohexanone and benzene were purified by standard procedure. PPBDMAC [7] was synthesized and used for this study. The polymerization reactions were carried out under inert and unstirred conditions at 60°C in cyclohexanone/water biphasic media by taking equal volumes of aqueous and organic phase (10 ml each). Aqueous phase contains PTC, K_2SO_4 and H_2SO_4 (for maintaining the uniform acid and ionic strength, respectively). The organic phase contains the monomer and solvent. Polymerization started when the initiator was added to the reaction mixture and precipitation of the polymer was observed. The reaction was arrested by pouring the mixture into ice-cold methanol containing traces of hydroquinone. The polymer was filtered quantitatively through a G-4 sintered glass crucible, washed several times with distilled water followed by methanol, and dried in vacuum at 60°C to constant weight. The rate of polymerization (R_p) was determined gravimetrically [8].

Viscosity measurements of the polymer solutions in benzene were carried out at 30°C in an Ubbelohde viscometer. Intrinsic viscosity was evaluated from the linear plot of η_{sp}/c versus C . Average degree of

polymerization (\bar{P}_n) was calculated from the intrinsic viscosity data by making use of the Mark-Houwink [9] equation.

RESULTS AND DISCUSSION

The steady state rate of polymerization was first arrived at by determining the rate of polymerization (R_p) at different time intervals and it was found to be reached at 30 minutes (Table 1). The reaction time was fixed at 30 minutes to carry out the experiments with variation in other parameters.

Dependence of R_p on the Concentration of Monomer

The dependence of R_p on the concentration of monomer was examined by varying its concentration in the range of 0.7 to 1.9 mol.dm⁻³ at constant levels of other reaction parameters such as initiator, PTC, ionic and acid strength. R_p increases with increasing monomer concentration. The order of the reaction was obtained from a plot of log R_p versus log [MMA] and was found to be unity. A plot of R_p versus [MMA]¹ is linear passing through the origin, and confirming the above observation (Table 2). A similar order of unity with respect to concentration of monomer has been reported for the polymerization of MMA with other PTC using potassium peroxydisulfate as initiator [5, 10].

Dependence of R_p on Solvent Polarity

The effect of solvent on R_p was examined by carrying out the polymerization reaction for MMA in the three solvents cyclohexane, ethyl

TABLE 1 Steady State Rate of Polymerization

Time, Min	$R_p \times 10^4$, mol.dm ⁻³ S ⁻¹
5	2.06
10	1.94
15	1.72
20	1.59
25	1.44
30	1.29
35	1.26
40	1.27
45	1.27

[MMA]: 2.0 mol.dm⁻³; [K₂S₂O₈]: 2.0 × 10⁻² mol.dm⁻³; [PPBDMAC]: 2.0 × 10⁻² mol.dm⁻³; [H⁺]: 0.2 mol.dm⁻³; μ : 0.5 mol.dm⁻³; Temp: 60°C.

TABLE 2 Dependence of R_p on [MMA]

[MMA], mol.dm ⁻³	$R_p \times 10^5$ mol.dm ⁻³ S ⁻¹	$3 + \log$ [MMA]	$6 + \log R_p$
0.7	4.52	2.8450	1.6551
0.9	5.57	2.9542	1.7458
1.1	6.94	3.0413	1.8413
1.3	8.38	3.1139	1.9232
1.5	9.44	3.1760	1.9749
1.7	10.86	3.2304	2.0358
1.9	12.26	3.2787	2.0884

[K₂S₂O₈]: 2.0×10^{-2} mol.dm⁻³; [PPBDMAC]: 2.0×10^{-2} mol.dm⁻³; [H⁺]: 0.2 mol.dm⁻³; μ : 0.5 mol.dm⁻³; Temp: 60°C.

acetate and cyclohexanone having the dielectric constants 2.02, 6.02 and 18.3, respectively. It was found that the R_p decreased in the following order:

Cyclohexanone > ethyl acetate > cyclohexane

The decrease in the rate of polymerization may be due to the increase in the polarity of the organic medium, which facilitates greater transfer of peroxydisulfate to the organic phase.

Dependence of R_p on the Concentration of Initiator

At constant levels of other reaction parameters, the dependence of R_p on the concentration of initiator was examined by varying the concentration of the potassium peroxydisulfate initiator in the range 0.011 to 0.021 mol.dm⁻³ (Table 3). A similar square root relationship between R_p and [K₂S₂O₈] has been already reported by many authors [5, 10, 11].

Dependence of R_p on the Concentration of PTC

The effect of concentration of PPBDMAC on R_p was studied by varying its concentration in the range 0.006 to 0.016 mol.dm⁻³ at constant levels of other reaction parameters. R_p was found to increase with increased concentration of PPBDMAC and the order with respect to [PPBDMAC] was found to be around 0.5 from a plot of $\log R_p$ versus \log [PTC]. A plot of R_p versus [PPBDMAC]^{0.5} was found to be linear passing through the origin confirming the above results (Table 4).

TABLE 3 Dependence of R_p on $[K_2S_2O_8]$

$[K_2S_2O_8] \times 10^2$ mol.dm ⁻³	$[K_2S_2O_8]^{1/2} \times 10^2$ (mol.dm ⁻³) ^{1/2}	$R_p \times 10^5$ mol.dm ⁻³ S ⁻¹	$3 + \log [K_2S_2O_8]$	$6 + \log R_p$
1.1	0.1048	9.12	1.0413	1.9599
1.3	0.1140	10.17	1.1139	2.0073
1.5	0.1224	10.80	1.1760	2.0334
1.7	0.1303	11.63	1.2304	2.0655
1.9	0.1378	12.26	1.2787	2.0884
2.1	0.1449	13.39	1.3222	2.1267

[MMA]: 2.0×10^{-2} mol.dm⁻³; [PPBDMAC]: 2.0×10^{-2} mol.dm⁻³; [H⁺]: 0.2 mol.dm⁻³; μ : 0.5 mol.dm⁻³; Temp: 60°C.

TABLE 4 Dependence of R_p on [PPBDMAC]

[PPBDMAC] $\times 10^2$ mol.dm ⁻³	[PPBDMAC] ^{1/2} $\times 10^5$ (mol.dm ⁻³) ^{1/2}	$R_p \times 10^5$ mol.dm ⁻³ S ⁻¹	$3 + \log [PPBDMAC]$	$6 + \log R_p$
0.6	0.0774	7.01	0.7781	1.8457
0.8	0.0894	7.80	0.9030	1.8920
1.0	0.1000	8.73	1.0000	1.9410
1.2	0.1095	9.56	1.0791	1.9804
1.4	0.1183	10.41	1.1461	2.0174
1.6	0.1264	11.20	1.2041	2.0492

[MMA]: 2.0×10^{-2} mol.dm⁻³; [K₂S₂O₈]: 2.0×10^{-2} mol.dm⁻³; [H⁺]: 0.2 mol.dm⁻³; μ : 0.5 mol.dm⁻³; Temp: 60°C.

It has been noticed that in the absence of PTC no polymerization reaction was observed, even after several hours.

Dependence of R_p on Aqueous Phase Volume

Polymerization reactions were conducted with a constant volume of organic phase and different volumes of aqueous phase ($V_w/V_o = 0.5 - 1$) at fixed concentrations of monomer, K₂S₂O₈ and PTC. The rate of polymerization was found to increase with increasing volume of aqueous phase (Table 5).

Dependence of R_p on Temperature

The effect of temperature variation in the range of 50 to 65°C on R_p was studied by keeping other reaction parameters constant.

TABLE 5 Dependence of R_p on Aqueous Phase Volume

V_w/V_o	$1 + \log(V_w/V_o)$	$R_p \times 10^5 \text{ mol.dm}^{-3}\text{S}^{-1}$	$6 + \log R_p$
1.0	1.0000	12.85	2.1089
0.9	0.9542	12.52	2.0976
0.8	0.9030	12.10	2.0827
0.7	0.8450	11.75	2.0700
0.6	0.7781	11.38	2.0561
0.5	0.6989	10.83	2.0346

[MMA]: 2.0 mol.dm^{-3} ; $[\text{K}_2\text{S}_2\text{O}_8]$: $2.0 \times 10^{-2} \text{ mol.dm}^{-3}$; [PPBDMAC]: $2.0 \times 10^{-2} \text{ mol.dm}^{-3}$; $[\text{H}^+]$: 0.2 mol.dm^{-3} ; μ : 0.5 mol.dm^{-3} ; Temp: 60°C .

R_p increases with increased temperature. From the slope of the Arrhenius plot of $\log R_p$ versus $1/T$ the activation energy values for the polymerization reactions were evaluated (Table 6). The thermodynamic parameters, entropy of activation ΔS^\ddagger , enthalpy of activation ΔH^\ddagger and free energy of activation ΔG^\ddagger have been computed from the value of activation energy (Table 7).

Mechanism and Rate Law

Based on the above kinetic results, a suitable mechanism has been proposed for the polymerization reactions as shown in Scheme 1.

The subscripts (W) and (O) refer to aqueous phase and organic phase. Q refers to the catalyst. This mechanism involves the formation

TABLE 6 Dependence of R_p on Temperature

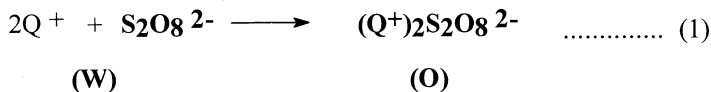
T, K	$R_p \times 10^5 \text{ mol.dm}^{-3}\text{S}^{-1}$	$1/T \times 10^3, \text{K}^{-1}$	$5 + \log R_p$
323	0.49	3.096	0.690
328	0.73	3.049	0.863
333	1.29	3.003	1.110
338	1.57	2.959	1.195

[MMA]: 2.0 mol.dm^{-3} ; $[\text{K}_2\text{S}_2\text{O}_8]$: $2.0 \times 10^{-2} \text{ mol.dm}^{-3}$; [PPBDMAC]: $2.0 \times 10^{-2} \text{ mol.dm}^{-3}$; $[\text{H}^+]$: mol.dm^{-3} ; μ : 0.5 mol.dm^{-3} .

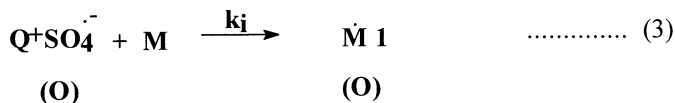
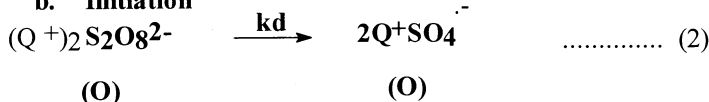
TABLE 7

$E_a \text{ k.cal.mol}^{-1}$	$\Delta S^\ddagger \text{ eu}$	$\Delta H^\ddagger \text{ k.cal.mol}^{-1}$	$\Delta G^\ddagger \text{ k.cal.mol}^{-1}$
17.67	- 28.35	17.00	26.35

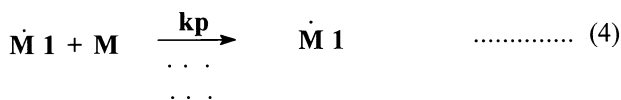
a. Phase Transfer



b. Initiation



c. Propagation



d. Termination



SCHEME 1

of quaternary ammonium peroxydisulfate complex $[(Q^+)_2S_2O_8^{2-}]$ in the aqueous phase, which is then transferred to the organic phase. The decomposition of this ion-pair takes place in the organic phase leading to the formation of $Q^+SO_4^{\cdot -}$, which initiates the polymerization.

Applying the general principles of free radical polymerization and stationary state hypothesis to the radical species, the rate law for this mechanism can be determined as

$$R_p = K_p \frac{k_d K^{0.5}}{(k_t)} \frac{[M][S_2O_8^{2-}]^{0.5}[Q^+]_{Total}}{1 + K[Q^+]_w[S_2O_8^{2-}]_w}$$

TABLE 8 Dependence of \bar{P}_n on $[K_2S_2O_8]$

$[K_2S_2O_8] \times 10^3$ mol.dm ⁻³	$[K_2S_2O_8]^{1/2} \times 10^2$ (mol.dm ⁻³) ^{1/2}	$\bar{P}_n \times 10^{-3}$	$1/\bar{P}_n \times 10^3$
0.5	2.20	2.92	0.34
1.0	3.16	2.49	0.40
1.5	3.87	2.25	0.44
2.0	4.47	1.78	0.56
2.5	5.00	1.50	0.66
3.0	5.48	1.46	0.68

[MMA]: 2.0×10^{-2} mol.dm⁻³; [PPBDMAC]: 2.0×10^{-2} mol.dm⁻³; [H⁺]: 0.2 mol.dm⁻³; μ : 0.5 mol.dm⁻³; Temp: 60°C.

Degree of Polymerization

The degree of polymerization of MMA with varying concentrations of $K_2S_2O_8$ was evaluated from the intrinsic viscosity data obtained from the viscosity measurements of polymers. The degree of polymerization decreases with increasing $K_2S_2O_8$ concentration. A plot of $1/\bar{P}_n$ versus $[K_2S_2O_8]^{1/2}$ gives a straight line passing through the origin (Table 8).

The expression for the degree of polymerization is given by

$$\bar{P}_n = \frac{R_p}{R_t} = \frac{k_p[M][M]}{k_t[M]^2}$$

$$\bar{P}_n = \frac{k_p[M]}{2(k_1k_dK)^{0.5}[Q^+][S_2O_8^2]^{0.5}}$$

$$1/\bar{P}_n = \frac{(k_1k_dK)^{0.5}[Q^+][S_2O_8^2]^{0.5}}{k_p[M]}$$

It is found that plot of $1/\bar{P}_n$ versus $[K_2S_2O_8]^{0.5}$ gives a straight line passing through the origin.

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