

Kinetics of Radical Polymerization of Glycidyl Methacrylate Initiated by Multi-Site Phase Transfer Catalyst–Potassium Peroxydisulfate in Two-Phase System

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ABSTRACT: The kinetics of radical polymerization of glycidyl methacrylate, initiated by the free radicals formed *in situ* in the multi-site phase transfer catalyst (PTC), 1,1,2,2-tetramethyl-1-benzyl-2-*n*-propylethylene-1,2-diammonium bromide chloride–potassium peroxydisulfate system was studied in an aqueous–organic two-phase media at $60^{\circ}\text{C} \pm 1^{\circ}\text{C}$ under inert and unstirred condition. The rate of polymerization (R_p) was determined at various concentrations of the monomer, initiator, catalyst, and volume fraction of aqueous phase. The effect of acid, ionic strength, and water-immiscible organic solvents on the R_p was examined. The temperature dependence of the rate was studied, and activation parameters were calculated. R_p increased

with an increase in the concentrations of monomer, initiator, multi-site PTC, and increase in the polarity of solvent and temperature. The order with respect to monomer, initiator, and multi-site PTC was found to be 0.50. A feasible free-radical mechanism consistent with the experimental data has been proposed, and its significance was discussed. The synthesized polymer was confirmed by Fourier transform infrared spectral analysis. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1794–1799, 2011

Key words: kinetics; multi-site phase transfer catalyst (MPTC); radical polymerization; potassium peroxydisulfate (PDS); glycidyl methacrylate (GMA)

INTRODUCTION

Acrylate-containing copolymers have received significant attention over other various polymeric raw materials because of their excellent properties, such as ageing resistance, light stability, and good adhesion to various types of substrates.¹ Glycidyl methacrylate (GMA) is a commercially fascinating functional monomer with extensive range of industrial applications. This monomer is used to prepare homogeneous and heterogeneous polymer networks, which play an important role in polymer science and technology, for instance, in coatings, matrix resins, and adhesives.^{2,3} The best advantage of polymer supports based on GMA is because the reactivity of the oxirane ring toward various nucleophiles is helpful for the chemical modification of the basic polymer for various novel end-use applications. In addition, such polymers have recently gained special interest in application of biosensors^{4–6} and drug and bimolecular binding.⁷

The growth and use of phase transfer catalyst (PTC) in polymerization and organic reactions is gaining remarkable progress in recent and past^{8–10};

they have been used in polycondensation,¹¹ anionic polymerization,¹² free-radical¹³ and graft copolymerization,¹⁴ and synthesis and modification of polymers,¹⁵ and also several reports are existing in literature regarding the use of commercially available PTC in free-radical polymerization of various hydrophobic vinyl monomer in aqueous–organic two-phase system.^{16–23} In this technique, polymerization is initiated by the free radical arising from decomposition of complex of quaternary ammonium dication coupled with peroxy anion (QS_2O_8) in organic phase extracted from aqueous phase, propagation occurs subsequently, and termination takes place by combination of the growing polymer chain radicals.

The first report published on multi-site PTC was by Idoux et al.,²⁴ and they have synthesized phosphonium and quaternary onium ions containing more than one active site per molecule. The significant consideration of “multi-site” type of onium salts compared with single-site salts include facile synthesis, low energy consumption, and high reactivity in a particular organic and polymerization reactions under mild experimental conditions. The application of the multi-site PTC in radical polymerization reactions is limited compared with commercially available PTC. However, we reported multi-site PTC-assisted radical polymerization of acrylonitrile,^{25,26} methyl methacrylate,²⁷ ethyl methacrylate,²⁸ and *n*-butyl methacrylate²⁹ in an aqueous–organic two-phase system.

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Consequently, this inspired us to work on kinetics of free-radical polymerization of GMA using $K_2S_2O_8$ (potassium peroxydisulfate, PDS) as water-soluble initiator in the presence of newly synthesized multi-site PTC³⁰ (1,1,2,2-tetramethyl-1-benzyl-2-*n*-propylethylene-1,2-diammonium bromide chloride, TMBPEDBC) in cyclohexane–water two-phase system.

EXPERIMENTAL

Materials

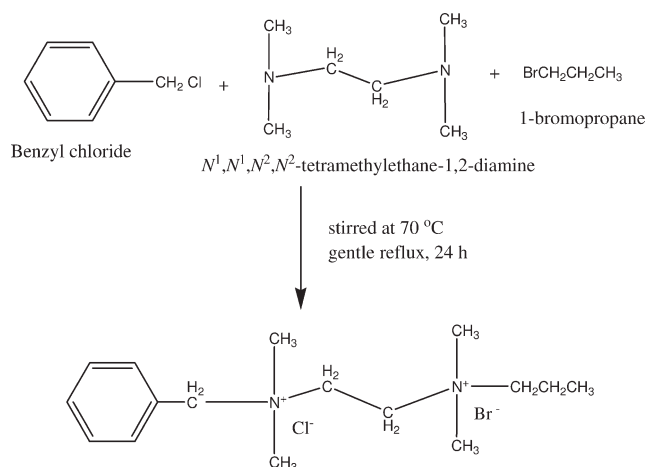
GMA (Lancaster, Chennai, India), N^1,N^1,N^2,N^2 -tetramethylethane 1,2-diamine (Lancaster), *n*-propyl bromide, benzyl chloride (SRL, Mumbai, India), PDS (Merck, Mumbai, India), and methanol (SRL) were used as received. The distilled water and cyclohexane were used as solvents for two-phase system. The multi-site PTC, TMBPEDBC, was synthesized by the following procedure.

Synthesis of multi-site PTC (TMBPEDBC)

N^1,N^1,N^2,N^2 -tetramethylethane 1,2-diamine (0.01 mol) was dissolved in ethanol (10 mL), taken in a two-necked round-bottom flask stirred at 70°C. The *n*-propyl bromide (0.01 mol dissolved in ethanol) was added drop wise. After 1 h, a solution of benzyl chloride (0.01 mol dissolved in ethanol) was slowly added to the reaction mixture. The reaction mixture was gently refluxed and stirred for 24 h. After that, the mixture was cooled to room temperature, and the solvent was evaporated. The precipitate of TMBPEDBC was obtained. It was purified by dissolving minimum amount catalyst in ethanol and diffused over hexane; pure white precipitate was collected and dried.³⁰ The melting point of the catalyst was 210°C (Scheme 1).

Polymerization procedure: Poly(glycidyl methacrylate)

The polymerization reaction tube consists of equal volumes of aqueous phase and organic phase (10 mL each). The monomer in cyclohexane was the organic phase. The catalyst, sodium bisulfate (for adjusting the ionic strength), and sulfuric acid (for maintaining $[H^+]$) was taken in the aqueous phase. The reaction mixture was thoroughly de-aerated for 30 min. Subsequently, the reaction tube was placed in the water bath at a constant temperature $60^\circ\text{C} \pm 1^\circ\text{C}$ under unstirred condition. A known concentration of PDS was added to the reaction mixture, polymerization occurred, and poly(glycidyl methacrylate) precipitated continuously for 40 min. After, the stipulated time period, the reaction was arrested by pouring the reaction mixture into excess of ice-cold methanol.



Scheme 1 Synthesis of multi-site PTC: 1,1,2,2-tetramethyl-1-benzyl-2-*n*-propylethylene-1,2-diammonium bromide chloride (TMBPEDBC).

The precipitated polymer was filtered through a sintered glass crucible, washed with plenty of methanol and distilled water, and then dried in vacuum oven at 50°C until constant weight was obtained. The polymer was used for the characterization without further purification. The R_p was determined by gravimetric method. The R_p was calculated from the weight of the polymer obtained using the formula:

$$R_p = \frac{1000}{V \times t \times M}$$

where, W = weight of the polymer in gram, V = volume of the reaction mixture in milliliter, t = reaction time in seconds, and M = molecular weight of the monomer.

RESULTS AND DISCUSSION

The polymerization of GMA initiated by MPTC-PDS in cyclohexane–water two-phase system was studied under different experimental conditions to evaluate the various parameters that influence the R_p . From the qualitative point of view, it was noted that PDS alone does not initiate polymerization under de-aerated (absence of oxygen) experimental conditions. However, there was an initiation of polymerization under aerated (presence of oxygen) condition. Thus, it was evident that the polymerization was initiated by free radicals generated *in situ* by the decomposition of multi-site PTC-PDS (QS_2O_8) complex in organic phase.

Steady-state R_p

The steady-state R_p for GMA was studied by determining R_p at different intervals of time. The plot of R_p versus time shows an increase to some extent, decreased thereafter, and then reached the constant

TABLE I
Steady State Rate of Polymerization

Time (min)	R_p ($\times 10^5$ mol dm $^{-3}$ s $^{-1}$)
10	1.5470
20	8.2950
30	5.4910
40	4.4260
50	3.7284
60	3.1363
70	3.1416

Reaction condition: [GMA], 2.0 mol dm $^{-3}$; [K $_2$ S $_2$ O $_8$], 2.0×10^{-2} mol dm $^{-3}$; [TMBPEDBC], 2.0×10^{-2} mol dm $^{-3}$; [H $^+$], 0.5 mol dm $^{-3}$; [μ], 0.2 mol dm $^{-3}$; temperature: 60°C \pm 1°C.

value of R_p . At the beginning, there is an increase in R_p due to low viscosity of the medium, and then the R_p decreases as the medium becomes more viscous with gradually increasing time and, thereafter, R_p reaches constant value. The steady-state R_p reaction time was fixed at 40 min to carry out the experiments with different reaction conditions (Table I, Fig. 1).

Effect of monomer concentration

The R_p increases with increase in monomer concentration in the range 4.5–9.5 mol dm $^{-3}$ while keeping the concentration of PDS, MPTC, ionic strength, and pH constant. From the plot of $(6 + \log R_p)$ versus $(3 + \log [\text{GMA}])$, the order of the reaction with respect to monomer concentration is found to be 0.50 in aqueous–organic two-phase system. The plot of R_p versus [GMA] passing through the origin confirms the above observations (Fig. 2). At higher monomer concentration, the R_p reaches the constant value; this may due to increase in viscosity of the medium and diffusion of the ions through the medium becomes difficult.

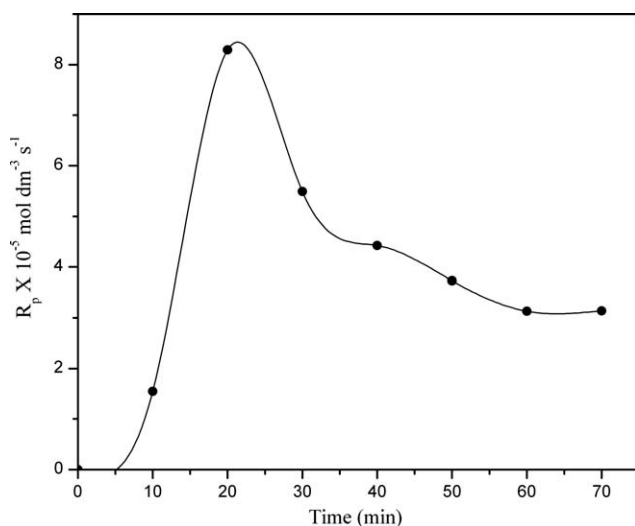


Figure 1 Steady state rate of polymerization. Reaction condition: [GMA], 2.0 mol dm $^{-3}$; [K $_2$ S $_2$ O $_8$], 2.0×10^{-2} mol dm $^{-3}$; [TMBPEDBC], 2.0×10^{-2} mol dm $^{-3}$; [H $^+$], 0.5 mol dm $^{-3}$; [μ], 0.2 mol dm $^{-3}$; temperature: 60°C \pm 1°C.

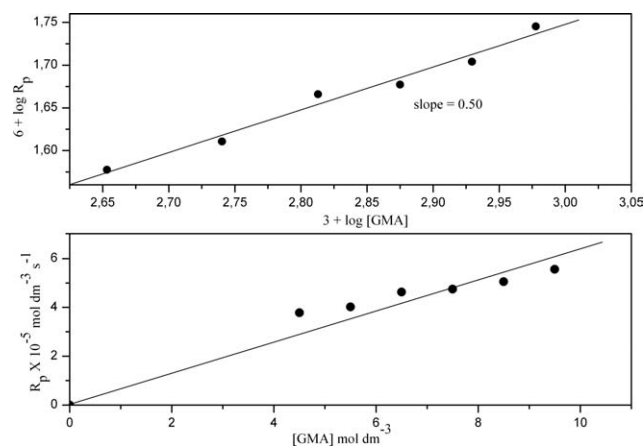


Figure 2 Effect of monomer concentration. Reaction condition: [K $_2$ S $_2$ O $_8$], 2.0×10^{-2} mol dm $^{-3}$; [TMBPEDBC], 2.0×10^{-2} mol dm $^{-3}$; [H $^+$], 0.5 mol dm $^{-3}$; [μ], 0.2 mol dm $^{-3}$; temperature: 60°C \pm 1°C.

Effect of initiator concentration

An increase in the R_p occurs with an increase in initiator concentration (K $_2$ S $_2$ O $_8$) in the range 1.5–2.5 mol dm $^{-3}$ when other reaction parameters are fixed. This is attributed to an increased concentration of active species in organic phase. The reaction shows a fractional (one-half) order dependence on initiator concentration as shown by the slope of the plot of $(6 + \log R_p)$ versus $(3 + \log [\text{K}_2\text{S}_2\text{O}_8])$. The plot of R_p versus [K $_2$ S $_2$ O $_8$] is linear passing through the origin, supporting the above deduction (Fig. 3).

Effect of multi-site PTC concentration

The R_p increases with increase in concentration of multi-site PTC (TMBPEDBC) in the range 1.5–2.5 mol dm $^{-3}$ when other reaction conditions are fixed. From the plot of $(6 + \log R_p)$ versus $(3 + \log$

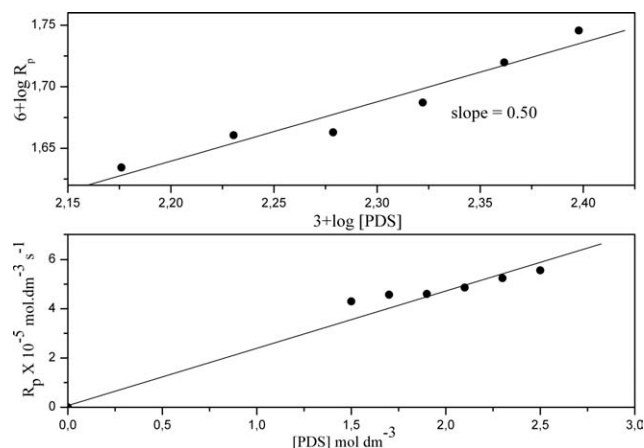


Figure 3 Effect of initiator concentration. Reaction condition: [GMA], 2.0 mol dm $^{-3}$; [TMBPEDBC], 2.0×10^{-2} mol dm $^{-3}$; [H $^+$], 0.5 mol dm $^{-3}$; [μ], 0.2 mol dm $^{-3}$; temperature: 60°C \pm 1°C.

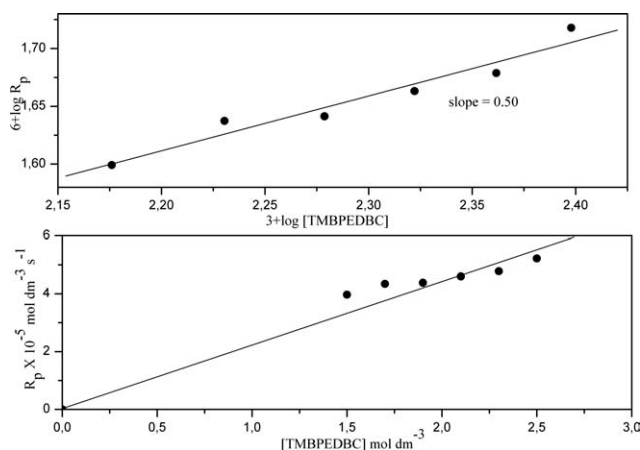


Figure 4 Effect of multi-site phase transfer catalyst concentration. Reaction condition: [GMA], 2.0 mol dm^{-3} ; $[\text{K}_2\text{S}_2\text{O}_8]$, $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+]$, 0.5 mol dm^{-3} ; $[\mu]$, 0.2 mol dm^{-3} ; temperature: $60^\circ\text{C} \pm 1^\circ\text{C}$.

[TMBPEDBC]), the order of reaction with respect to catalyst concentration was found to be 0.50. The plot of R_p versus [TMBPEDBC] passing through origin confirms the above observations (Fig. 4). The half-order with respect to catalyst concentration has already been reported in the phase transfer catalyzed radical polymerization of vinyl monomers.^{25–29} In the absence of multi-site PTC, no polymerization reaction occurred, which confirmed the role of multi-site PTC in the reaction.

Effect of volume fraction of aqueous phase

The effect of volume fraction of aqueous phase on the R_p was studied in the range of $V_w/V_0 = 0.29$ – 0.90 mol dm^{-3} at fixed concentrations of all other

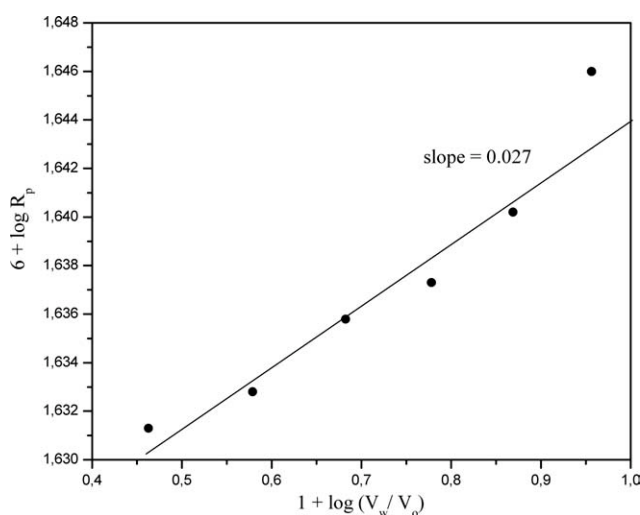


Figure 5 Effect of volume fraction of aqueous phase. Reaction condition: [GMA], 2.0 mol dm^{-3} ; $[\text{K}_2\text{S}_2\text{O}_8]$, $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; [TMBPEDBC], $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+]$, 0.5 mol dm^{-3} ; $[\mu]$, 0.2 mol dm^{-3} ; temperature: $60^\circ\text{C} \pm 1^\circ\text{C}$.

TABLE II
Effect of Volume Fraction of Aqueous Phase

V_w/V_0	$1 + \log (V_w/V_0)$	$R_p (\times 10^5 \text{ mol dm}^{-3} \text{ s}^{-1})$	$6 + \log R_p$
0.29	0.4628	4.2795	1.6313
0.37	0.5789	4.2941	1.6328
0.48	0.6825	4.3234	1.6358
0.60	0.7781	4.3381	1.6373
0.73	0.8687	4.3674	1.6402
0.90	0.9565	4.4260	1.6460

Reaction condition: [GMA], 2.0 mol dm^{-3} ; $[\text{K}_2\text{S}_2\text{O}_8]$, $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; [TMBPEDBC], $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+]$, 0.5 mol dm^{-3} ; $[\mu]$, 0.2 mol dm^{-3} ; temperature: $60^\circ\text{C} \pm 1^\circ\text{C}$.

parameters. It is observed that there is slight increase in the R_p with an increase in volume fraction of aqueous phase ratio. Initially, at certain volume of aqueous phase is enhance the transfer of quaternary ammonium peroxydisulfate (QS_2O_8) complex from aqueous phase to organic phase; therefore, slight increase in R_p was observed. When the volume of aqueous phase is increased, the concentration of quaternary ammonium peroxydisulfate (QS_2O_8) complex decreases, and also migration of complex from aqueous phase to organic phase becomes feeble. Hence, the R_p becomes constant. From the plot of $(6 + \log R_p)$ versus $1 + \log (V_w/V_0)$ in Figure 5, the reaction order with respect to (V_w/V_0) was found to be 0.027 (Table II).

Effect of temperature

The R_p increases with increase in the temperature range of 50 – 65°C at fixed reaction parameters. The increase in R_p with increasing temperature is due to an increase in the decomposition of the initiator in organic phase, and transportation of initiator from aqueous phase to organic phase also accelerated at high temperature, which leads to increase in R_p . The values for activation energy (E_a) and other activation parameters, such as entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger), and free energy of activation (ΔG^\ddagger), were obtained from plot of $6 + \log R_p$ versus $1/T$ and are presented in Table III and Figure 6.

Effect of acid (H^+) and ionic strength (μ)

The variation of acid and ionic strength has no significant change in the R_p because there is no ionizable group in GMA; therefore, it will not susceptible to increase of pH by neutralization and ionic strength.

TABLE III
Activation Parameters

E_a (kJ/mol)	ΔG^\ddagger (kJ/mol)	ΔH^\ddagger (kJ/mol)	ΔS^\ddagger (J/K mol)
46.31	70.63	43.16	–84.04

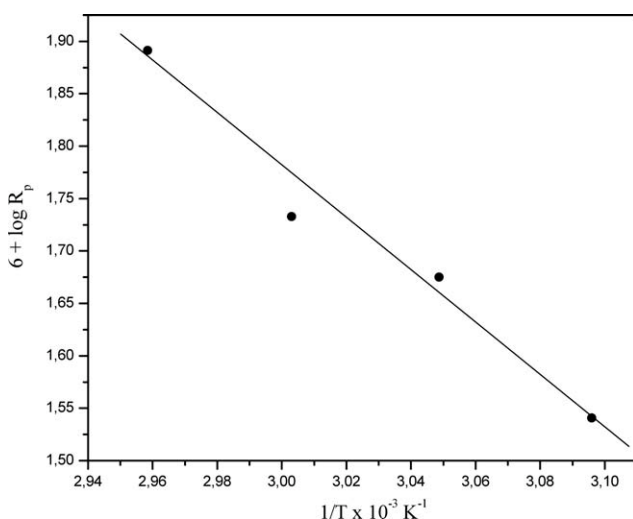


Figure 6 Effect of temperature. Reaction condition: [GMA], 2.0 mol dm⁻³; [K₂S₂O₈], 2.0 × 10⁻² mol dm⁻³; [TMBPEDBC], 2.0 × 10⁻² mol dm⁻³; [H⁺], 0.5 mol dm⁻³; [μ], 0.2 mol dm⁻³; temperature: 60°C ± 1°C.

Effect of water-immiscible organic solvents

Water-immiscible organic solvents such as cyclohexanone, ethyl acetate, and cyclohexane are found to increase the R_p . This could be explained by the fact that these solvents have high dielectric constants and polarity, which facilitates to increase the transfer of peroxydisulfate from aqueous phase to organic phase. The R_p decreases in the following order: cyclohexanone > ethyl acetate > cyclohexane (Table IV).

Polymerization mechanism and scheme

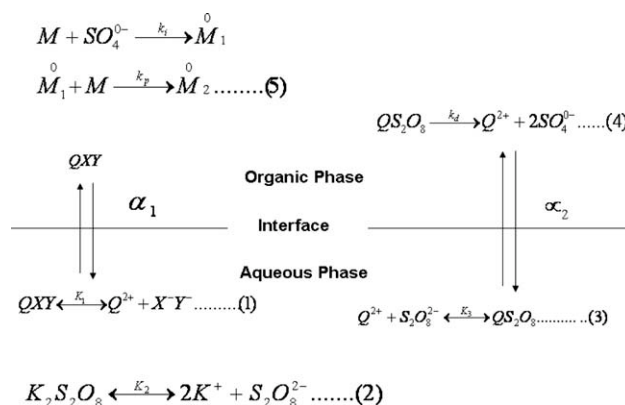
Scheme 2 represents the reactions characterizing the polymerization of GMA (M) initiated by K₂S₂O₈/multi-site PTC in cyclohexane–water two-phase systems. It is assumed that dissociation of QXY and K₂S₂O₈, formation of QS₂O₈ in aqueous phase, and initiation of monomer in organic phase occur along the reactions such as eqs. (1)–(5). The equilibrium constants (K_1 and K_2) in the reactions in eqs. (1)–(3) and distribution constants (α_1 and α_2) of QXY and QS₂O₈ are defined as follows, respectively.

$$K_1 = \frac{[Q^{2+}]_w [XY]_w}{[QXY]_w} \quad (6)$$

TABLE IV
Effect of Water-Immiscible Organic Solvents

$R_p (\times 10^5 \text{ mol dm}^{-3} \text{ s}^{-1})$		
Cyclohexanone	Ethyl acetate	Cyclohexane
5.46	4.57	4.05

Reaction condition: [GMA], 2.0 mol dm⁻³; [K₂S₂O₈], 2.0 × 10⁻² mol dm⁻³; [TMBPEDBC], 2.0 × 10⁻² mol dm⁻³; [H⁺], 0.5 mol dm⁻³; [μ], 0.2 mol dm⁻³; temperature: 60°C ± 1°C.



Scheme 2 Polymerization pathways using multi-site phase transfer catalyst (multi-site PTC) in an aqueous-organic two-phase system.

$$K_2 = \frac{[K^+]_w^2 [S_2O_8^{2-}]_w}{[K_2S_2O_8]_w} \quad (7)$$

$$K_3 = \frac{[QS_2O_8]_w}{[Q^{2+}]_w [S_2O_8^{2-}]_w} \quad (8)$$

$$\alpha_1 = \frac{[Q^{2+}XY]_w}{[QXY]_o} \quad (9)$$

$$\alpha_2 = \frac{[Q^{2+}S_2O_8^{2-}]_w}{[QS_2O_8]_o} \quad (10)$$

Applying the general principles of free-radical polymerization and stationary state hypothesis to the radical species, the rate law for this mechanism can be derived as (for detailed mechanism see the Ref. 26)

$$R_p = k_p \left[\frac{k_d K_3 f}{k_t} \right]^{1/2} [Q^{2+}]_w^{0.5} [S_2O_8^{2-}]_w^{0.5} [M]^{0.5} \quad (11)$$

The above equation satisfactorily explains all the experimental observations. The R_p is directionally proportional to GMA, PDS, and multi-site PTC. R_p increases with an increase in the concentrations of monomer, initiator, and catalyst.

Characterization of the polymer by Fourier transform infrared spectroscopy

The Fourier transform infrared (FTIR) spectrum of poly(glycidyl methacrylate) was recorded with a Perkin–Elmer (Waltham, MA) RX I FTIR spectrometer in the spectral region from 3500 to 500 cm⁻¹. Pellets of about 100 mg of KBr powder containing polymer sample were made before the recording. The FTIR spectroscopy confirms a band at 1732 cm⁻¹ together with the stretching band range of 1130–1273 cm⁻¹, which suggests an ester group. The stretching band at 909 cm⁻¹ corresponds to the epoxy group (Fig. 7).

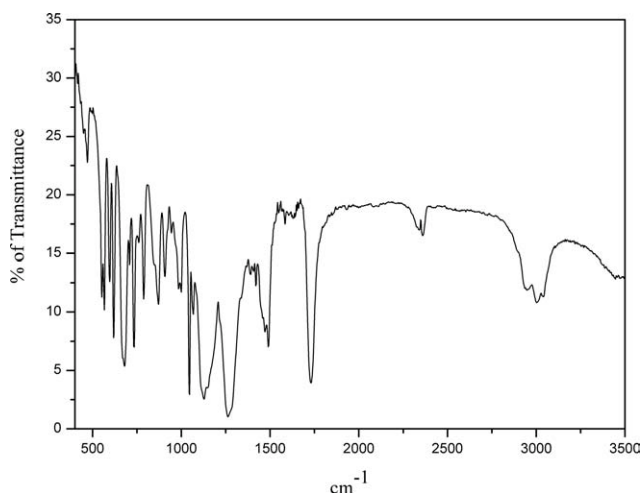


Figure 7 FTIR spectral analysis of poly(glycidyl methacrylate).

CONCLUSIONS

GMA was successfully polymerized by multi-site PTC coupled with PDS (water soluble initiator) in cyclohexane–water two-phase system at $60^{\circ}\text{C} \pm 1^{\circ}\text{C}$ under inert atmosphere nitrogen via free-radical mechanism. The polymerization reaction order with respect to monomer, initiator, and catalyst was found to be 0.50. The R_p increases with increase in temperature and polarity of water-immiscible organic solvents. There was no significant change in the R_p in variation of acid and ionic strength of medium. Based on the experimental results, a plausible multi-site phase transfer catalyzed free-radical mechanism has been proposed. The obtained polymer was confirmed by FTIR spectral analysis.

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