

# Synthesis and Characterization of New Soluble Multisite Phase Transfer Catalysts and Their Catalysis in Free Radical Polymerization of Methyl Methacrylate Aided by Ultrasound—A Kinetic Study

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**ABSTRACT:** Four different soluble phase transfer catalysts (PTCs) containing single, di, tri, and tetra active sites have been prepared and proved by FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, mass, elemental analysis, and conductivity measurement. The presence of the number of active sites in each catalyst was also been confirmed by determining their rate of polymerization of methyl methacrylate (MMA) using potassium peroxydisulfate (PDS) as a water soluble initiator in biphasic medium. The comparative study reveals that the  $R_p$  of MMA determined in the presence of PTC combined with ultrasound has shown twofold enhancement in the activity than PTC alone. The observed order

of activity was found to be of single-site < di-site < tri-site < tetra-site. Further, the thorough kinetic study of free radical polymerization of MMA has been investigated using superior tetra site viz., HBTAMPDTC and by varying the experimental parameters such as [MMA],  $[\text{K}_2\text{S}_2\text{O}_8]$ , [MPTC], and the temperature. Based on the observed kinetic results and activation parameters, a suitable mechanism was proposed. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 263–273, 2012

**Key words:** phase transfer catalysis; FT-IR; radical polymerization; catalysts; degree of polymerization (DP)

## INTRODUCTION

In the early period, the immiscible substrate reaction has been performed by agitating the solution, supplying the temperature, addition of co-solvents (both protic and nonprotic), surfactants, and soluble single-site phase transfer catalyst (PTC). All the said means has their own demerits which often hindered their commercialization. Of course, phase transfer catalysis (PTC) has been recognized as a convenient and highly useful synthetic tool in all branches of chemistry because of its simplicity, high conversion, and high selectivity under very mild reaction condition, safety considerations, and environmental concern. Due to these salient features, PTC is proved to be an important one to carry out the reactions between immiscible lipophilic and hydrophilic reactants. Therefore, the study of PTC technique was well explored and documented by numerous researchers.<sup>1–3</sup> The well-known PTCs such as quaternary onium salts, crown ethers, cryptands, etc. are exploited extensively to carry out the various

organic transformations. The combination of PTC/ peroxydisulfate (PDS) has been used effectively as an alternative tool to the conventional initiators like AIBN and BPO for catalysis of free radical polymerization of vinyl monomers. Because, this PTC/PDS initiated polymerization has provided certain advantages including more stable, eliminate the storage and handling problems which are normally associated with the organic soluble initiators. Besides, Rasmussen and Smith<sup>4</sup> reported the copolymerization of isooctyl acrylate and acrylic acid with 10-fold increase in shear strength of the copolymers with PTC/PDS catalyzed polymerization and these cannot be observed in the other initiators.

The first study on phase transfer catalyzed free radical polymerization was reported by Rasmussen and Smith.<sup>5,6</sup> They reported the polymerization of butyl acrylate with different crown ethers as a PTC and potassium peroxydisulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) as a water soluble initiator. Jayakrishnan and Shah<sup>7,8</sup> studied the free radical polymerization of acrylonitrile and methyl methacrylate (MMA) in the presence of ammonium peroxydisulfate and hexadecylpyridinium chloride as PTC in ethyl acetate-water medium. It was shown that quaternary onium salts coupled with peroxydisulfates are better initiators for vinyl polymerizations in biphasic medium than common

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organic initiators like AIBN or benzoyl peroxide. Gupta and Mandal studied the free radical polymerization of MMA and styrene using  $K_2S_2O_8$  as the initiator and  $Bu_4N^+Br^-$  as the PTC.<sup>9,10</sup> Choi and Lee investigated the kinetics of bulk free radical polymerization of MMA using 18-crown-6 as catalyst and  $K_2S_2O_8$  as a water soluble initiator.<sup>11</sup> Balakrishnan et al. reported the kinetics of free radical polymerization of MMA using  $K_2S_2O_8$  as a water soluble initiator and triethylbenzylammonium chloride (TEBAC) as a PTC in toluene-water biphasic media<sup>12</sup> and similarly, free radical polymerization of acrylonitrile (AN) initiated by potassium peroxomonosulfate (PMS) coupled with tetrabutylphosphonium chloride (TBPC) in ethyl acetate/water biphasic media have also studied.<sup>13</sup> Although various soluble single-site PTCs are widely used for free radical polymerization<sup>14</sup> and organic reactions, but again because of its inseparability, its usage is often limited. In order to recover the catalyst for reuse, the soluble single active site PTC was immobilized onto the inorganic/organic matrices and thus derived their respective insoluble heterogeneous single-site PTC. However, because of its lower activity and diffusion limitation the applicability of insoluble heterogeneous single-site PTC has always received poor attention among the stakeholders. Subsequently, in order to improve the catalytic efficiency, soluble form of multisite PTC has been synthesized and used for various organic transformations especially in biphasic medium. In fact, several researchers have devoted their attention for the development of new soluble and insoluble multisite PTCs for the simple reason is that they can accelerate the reactions between immiscible lipophilic and hydrophilic reactants more effectively even under mild reaction condition. Further, nowadays much emphasis has been given to economy of scale and efficiency of onium salts particularly for the industrial scale preparation of organic compounds. The first report published on multisite PTC was by Idoux et al. and they have synthesized phosphorus and quaternary onium ions containing more than one site per molecule.<sup>15</sup> Vajiravel et al. reported the kinetics of free radical polymerization of vinyl monomers using multisite PTC as a catalyst and  $K_2S_2O_8$  as the water soluble initiator in organic-water two-phase system.<sup>16,17</sup> In our laboratory also, we have synthesized and reported different multisite PTCs for various organic reaction.<sup>18-27</sup>

In the recent past, the ultrasound irradiations have been employed in various chemical reactions due to its effective role for enhancement of chemical reaction rates and selectivity. Especially, it has been considered as a convenient and useful technique in organic synthesis because of its advantages such as higher yield, shorter reaction times, and milder conditions and environmentally benign. Recently

reported studies reveals that the ultrasonic technique combined with PTC are proved to be an effective one in organic transformations.<sup>28-34</sup> However, the combination of multisite PTC with ultrasonic technique for free radical polymerization of vinyl monomers have not been reported so far, especially, the effects of new soluble multisite PTC with ultrasound in free radical polymerization are not studied. In view of these backgrounds, in this study, we are reporting the synthesis of four different new soluble multisite PTCs containing single-site, di-site, tri-site, and tetra-site via simplified experimental procedures using low cost starting materials. The activity of these catalysts have been explored by conducting the free radical polymerization of MMA using  $K_2S_2O_8$  as a water soluble initiator in ethyl acetate-water biphasic media at  $60 \pm 1^\circ C$  in association with ultrasound wave energy (42 kHz and 100 W). The catalytically superior tetra-site PTC was employed again for thorough kinetics of free radical polymerization of MMA.

## EXPERIMENTAL

### Materials

The following chemicals were used as received: 2,2-dimethyl-1-propanol (Alfa aesar), 2,2-dimethyl-1,3-propandiol (Alfa aesar), 1,1,1-tris(hydroxymethyl)ethane (Alfa aesar), pentaerythritol (Alfa aesar), phosphorous trichloride (CDH), dichloromethane (SRL), triethylamine (SRL), acetonitrile (SRL), MMA (Alfa aesar), potassium peroxydisulfate (SDF), ethyl acetate (SRL), and methanol (SRL).

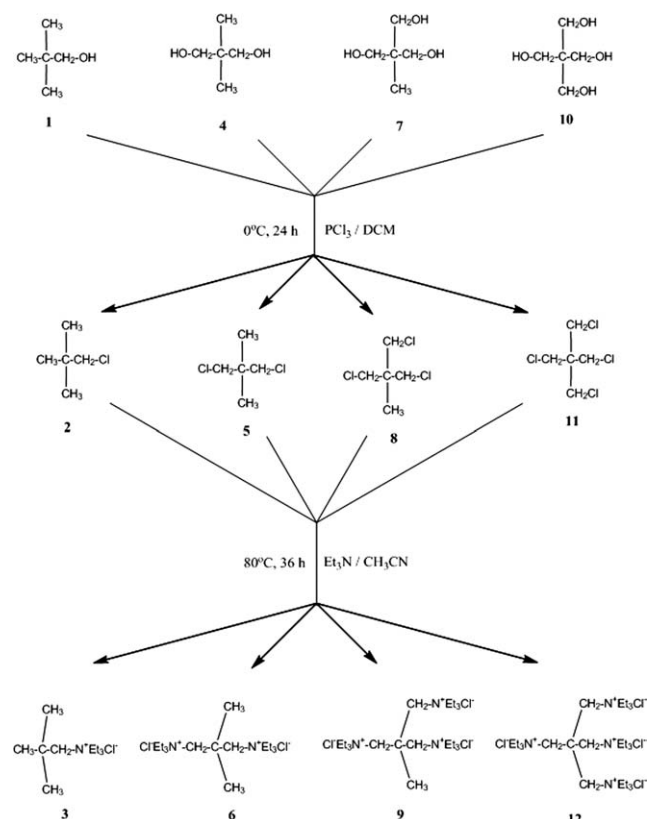
### Instrumentation

The FT-IR spectra were recorded on a Bruker-Tensor 27 FT-IR spectrophotometer. The  $^1H$  NMR and  $^{13}C$  NMR spectra were recorded on Bruker 500 MHz and 125 MHz spectrometers. The mass spectra were recorded on a JEOL GCmate mass spectrometer. Elemental analysis was performed on a Perkin-Elmer 240B elemental analyzer. The conductance of PTCs were measured by using the Elico conductivity bridge of model CM 185. The ultrasonic cleaner apparatus (model RZ-08895-22) was used for enhancing the rate of polymerization.

### Preparation of different soluble multisite PTCs (MPTCs)

Synthesis of N,N,N-triethyl-2,2-dimethylpropan-1-aminium chloride (TEDMPAC 3) (single-site PTC)

The compound 2,2-dimethyl-1-propanol (**1**) (3 g, 34.03 mmol) was dissolved in 30 mL of dichloromethane and placed in a 100-mL round bottom flask



**Scheme 1** Synthesis of TEDMPAC (single-site), HEDMPDADC (di-site), HMTAMPDTC (tri-site), and HBTAMPDTC (tetra-site) PTCs.

and then it was kept in ice bath. To this ice-cold solution, 15 mL (excess) of phosphorus trichloride ( $\text{PCl}_3$ ) was added slowly in drop wise at  $0^\circ\text{C}$ . After the addition, the reaction mixture was stirred at room temperature for 24 h. The excess solvent and unreacted reactant was removed and thus obtained halogenated product viz., 1-chloro-2,2-dimethylpropane (2). Further, it was dissolved in acetonitrile (50 mL) using 100 mL two necked round bottom flask and to that excess triethylamine (20 mL) was added for quaternization, the whole mixture was stirred at  $80^\circ\text{C}$  for 36 h in inert atmosphere. The excess solvent available in the mixture was removed by vacuum evaporator, the resulting white precipitate viz., *N,N,N*-triethyl-2,2-dimethylpropan-1-aminium chloride (TEDMPAC 3) was washed with ether, dried, and stored in desiccators (Scheme 1). Yield was 79%. FT-IR (KBr,  $\text{cm}^{-1}$ ): 1172 (C–N stretching), 2936 (aliphatic C–H str.), 1392 and 1473 (aliphatic C–H bending);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.893 (s, 9H,  $-\text{CH}_3$ ), 1.395–1.424 (t, 9H,  $J = 7.25$  Hz,  $-\text{CH}_3$ ), 3.086–3.130 (q, 6H,  $J = 7.25$  Hz,  $-\text{CH}_2-$ ), 3.282 (s, 2H,  $-\text{CH}_2-$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.61, 26.02, 32.59, 45.84; 73.30; EI-MS [ $\text{M}^+$ ] = 207.54; Elemental analysis Calc. C, 63.58; H, 12.61; N, 6.74. Found: C, 63.42; H, 12.35; N, 6.59.

### Synthesis of $\text{N}^1, \text{N}^1, \text{N}^1, \text{N}^3, \text{N}^3, \text{N}^3$ -hexaethyl-2,2-dimethylpropan-1,3-diaminium dichloride (HEDMPDADC 6) (di-site PTC)

The 2,2-dimethyl-1,3-propanediol (4) (3 g, 28.80 mmol) was taken into the 250 mL round bottom flask and dissolved in 30 mL of dichloromethane. The flask was kept in ice bath at  $0^\circ\text{C}$  and then excess quantity of phosphorus trichloride (20 mL) was slowly added in drop by drop with continuous stirring. Once the addition was over, the whole solution was stirred at room temperature for 24 h, then the excess solvent was removed by distillation. The resulting halogenated liquid product i.e. 1,3-dichloro-2,2-dimethylpropane (5) was dissolved again in acetonitrile (50 mL) using 100 mL double necked round bottom flask, then the mixture was deaerated and then triethylamine (excess) was added, refluxed, and stirred continuously for 36 h by keeping the reaction vessel on an oil bath maintained at a temperature of  $80^\circ\text{C}$ . The available solvent was removed by vacuum evaporator; the obtained white precipitate viz.,  $\text{N}^1, \text{N}^1, \text{N}^1, \text{N}^3, \text{N}^3, \text{N}^3$ -hexaethyl-2,2-dimethylpropan-1,3-diaminium dichloride (HEDMPDADC 6) was repeatedly washed with ether solvent ( $3 \times 10$  mL) and dried (Scheme 1). The yield was 81%. FT-IR (KBr,  $\text{cm}^{-1}$ ): 1173 (C–N stretching), 2938 (aliphatic C–H str.), 1394 and 1474 (aliphatic C–H bending);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.78 (s, 6H,  $-\text{CH}_3$ ), 1.277–1.331 (m, 18H,  $-\text{CH}_3$ ), 3.029–3.076 (m, 12H,  $-\text{CH}_2-$ ), 3.296 (s, 4H,  $-\text{CH}_2-$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.65, 26.04, 36.55, 46.09, 69.87; EI-MS [ $\text{M}^+$ ] = 342.99. Elemental analysis Calc. C, 59.46; H, 11.74; N, 8.16. Found: C, 59.28; H, 11.65; N, 8.08.

### Synthesis of $\text{N}^1, \text{N}^1, \text{N}^1, \text{N}^3, \text{N}^3, \text{N}^3$ -hexaethyl-2-methyl-2-((triethylammonio)methyl)propan-1,3-diaminium trichloride (HMTAMPDTC 9) (tri-site PTC)

In a 100-mL round bottom flask, 3 g of 1,1,1-tris(hydroxymethyl) ethane (7) (24.97 mmol) dissolved in 50 mL of dichloromethane, to that 20 mL of phosphorus trichloride ( $\text{PCl}_3$ ) was added slowly in drop wise at  $0^\circ\text{C}$  then the reaction mixture was stirred at room temperature for 24 h, as a result, the hydroxyl groups of  $-\text{CH}_2\text{OH}$  present in 1 were converted into  $-\text{CH}_2\text{Cl}$ . The solvent dichloromethane was removed by distillation. This chlorinated product viz., 1,1,1-tris(chloromethyl)ethane (8) was further dissolved in 50 mL of acetonitrile and quaternized by stirring with excess of triethylamine (30 mL) for about 36 h at  $80^\circ\text{C}$  in an inert atmosphere ( $\text{N}_2$ ). Once the stipulated time was over, the solvent and unreacted triethylamine were removed under vacuum and the resulting quaternary onium salt was repeatedly washed with ether solvent ( $3 \times 10$  mL) and thus obtained white precipitate of tri-site PTC



viz.,  $N^1,N^1,N^1,N^3,N^3,N^3$ -hexaethyl-2-methyl-2-((triethylammonio) methyl) propane-1,3-diaminium trichloride (HMTAMPDTC, **9**) which was stored in a  $\text{CaCl}_2$  desiccators (Scheme 1). Yield was 75%. FT-IR (KBr,  $\text{cm}^{-1}$ ): 1173 (C–N stretching), 2936 (aliphatic C–H stretching), 1393 and 1474 (aliphatic C–H bending);  $^1\text{H}$  NMR (500 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  0.74 (s, 3H,  $-\text{CH}_3$ ), 1.16–1.19 (t, 27H,  $J = 7.5$  Hz,  $-\text{C H}_2-\text{CH}_3$ ), 3.07–3.12 (q, 18H,  $J = 7.5$  Hz,  $-\text{CH}_2-$ ), 3.26 (s, 6H,  $-\text{CH}_2-$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  8.30, 20.43, 36.38, 46.69, 68.04; EI-MS [ $\text{M}^+$ ] = 478.51; Elemental analysis Calc. C, 57.66; H, 11.36; N, 8.77. Found: C, 57.54; H, 11.28; N, 8.62.

Synthesis of  $N^1,N^1,N^1,N^3,N^3,N^3$ -hexaethyl-2,2-bis((triethylammonio) methyl) propane-1,3-diaminium tetrachloride (HBTAMPDTC **12**) (tetra-site PTC)

In a 250-mL round bottom flask, 3 g of pentaerythritol (**10**) (22.03 mmol) dissolved in dichloromethane was taken and kept at  $0^\circ\text{C}$  in an ice bath, 20 mL of phosphorous trichloride (excess) was slowly added in drop wise and then the solution was stirred at room temperature for 24 h. Then the solvent was removed by distillation and thus yielded halogenated white precipitate of 1,3-dichloro-2,2-bis(chloromethyl)propane (**11**). This in turn was dissolved in excess of dry acetonitrile (50 mL) using 100 mL double necked round bottom flask and then the solution was deaerated by passing nitrogen gas to maintain the inert atmosphere, to that, 50 mL triethylamine (excess) was added and the mixture was gently refluxed and stirred continuously for 36 h by keeping the reaction vessel on an oil bath maintained at a temperature of  $80^\circ\text{C}$ . After the reaction time, the excess solvent was removed by vacuum evaporator, and thus formed tetra-site PTC viz.,  $N^1,N^1,N^1,N^3,N^3,N^3$ -hexaethyl-2,2-bis((triethylammonio) methyl)-propane-1,3-diaminium tetrachloride (HBTAMPDTC **12**) and this in turn was repeatedly washed with ether solvent ( $3 \times 10$  mL) and dried and thus yielded the white precipitate with yield of 73% (Scheme 1). FT-IR (KBr,  $\text{cm}^{-1}$ ): 1173 (C–N stretching), 2937 (aliphatic C–H stretching), 1395 and 1473 (aliphatic C–H bending);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.338–1.389 (t, 36H,  $J = 7.5$  Hz,  $-\text{CH}_3$ ), 3.059–3.100 (q, 24H,  $J = 8$  Hz,  $-\text{CH}_2-$ ), 3.619 (s, 8H,  $-\text{CH}_2-$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.64, 45.87, 46.62, 65.99; EI-MS [ $\text{M}^+$ ] = 613.10; Elemental analysis Calc. C, 56.66; H, 11.15; N, 9.11. Found: C, 56.57; H, 11.04; N, 9.06.

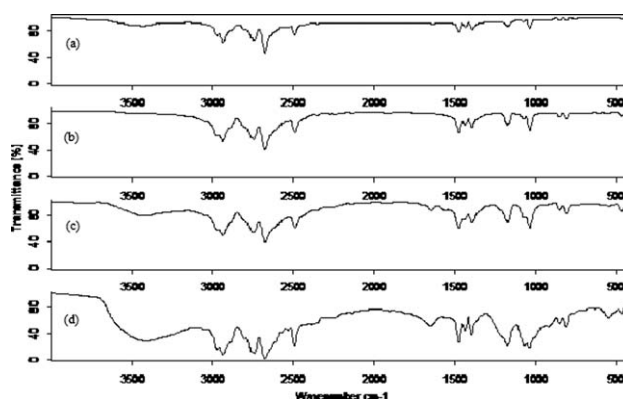
#### Sample preparation for FT-IR Analysis

For FT-IR analysis, the specimens for four different new PTCs such as TEDMPAC (single-site), HEDMPDADC (di-site), HMTAMPDTC (tri-site),

and HBTAMPDTC (tetra-site) were prepared individually into a pellet by disc technique and were employed for quantitative measurements (Fig. 1). Since the recorded FT-IR spectra were planned to use for quantitative study (semiquantitative), adequate care was taken to prepare the pellets. That is, known weights of KBr and the respective test substances viz., TEDMPAC (single-site), HEDMPDADC (di-site), HMTAMPDTC (tri-site), and HBTAMPDTC (tetra-site) were taken individually with 1 : 1 ratio and were made into pellets. The thickness of the pellets (i.e. pellets prepared from single-site PTC to tetra-site PTC with KBr) was kept uniform by measuring the surface thickness through dial micrometer at several points. The respective prepared pellets were employed for analysis, from the observed spectrum, the intensity of the characteristic peaks such as C–Cl and C–N stretching's were measured quantitatively at  $700\text{ cm}^{-1}$  and  $1173\text{ cm}^{-1}$  so as to quantify the amount of chloride and ammonium ions available in the respective catalyst and thus established the number of active-site (quaternary onium groups) in each catalyst.

#### Conductivity measurement

The structures of newly synthesized PTCs, especially, the number of quaternary ammonium groups present in each catalyst were confirmed further by measuring the conductance of the respective catalysts. The equimolar solution (0.1M) of all the four catalysts such as single-site TEDMPAC, di-site HEDMPDADC, tri-site HMTAMPDTC, and tetra-site HBTAMPDTC were prepared separately and the conductance of the respective catalysts were measured by Elico conductivity bridge (model CM 185). The obtained conductivity results were shown in Table I.



**Figure 1** FT-IR spectrum of (a) TEDMPAC, (b) HEDMPDADC, (c) HMTAMPDTC, and (d) HBTAMPDTC.

**TABLE I**  
**Comparative Study of Catalytic Activity of Phase Transfer Catalysts**

Catalysts	Conductance ( $\times 10^3$ S $\text{cm}^{-1}$ )	$R_p \times 10^5$ mol $\text{l}^{-1}$ $\text{s}^{-1}$	
		Without ultrasound	With ultrasound
TEDMPAC	7.2	3.21	6.30
HEDMPDADC	15.4	7.43	13.65
HMTAMPDTC	20.6	10.11	19.86
HBTAMPDTC	29.7	13.37	25.98

### Comparative catalysis of four different new MPTCs through free radical polymerization of MMA

The catalytic activities of these four different new MPTCs were examined under identical reaction condition taking equal mole of [catalyst] using free radical polymerization of MMA as a model reaction. The polymerization of MMA was carried out in Pyrex glass tubes (5 cm  $\times$  20 cm) of 100 mL capacities with a provision of inlet and outlet for deaeration of nitrogen gas. Generally, the polymerization was carried out individually with 10 mL of aqueous phase contains 1 mL of respective PTC ( $2 \times 10^{-2}$  mol  $\text{L}^{-1}$ ), 1 mL of potassium peroxydisulfate ( $2 \times 10^{-2}$  mol  $\text{L}^{-1}$ ), 1 mL of potassium sulfate (0.2 mol  $\text{L}^{-1}$ ), 1 mL of sulfuric acid (0.5 mol  $\text{L}^{-1}$ ), and 6 mL of water. Organic phase (10 mL) consists of 5.4 mL MMA (2.5 mol  $\text{L}^{-1}$ ) and 4.6 mL of ethyl acetate and this mixture in turn were flushed with purified nitrogen gas so as to eliminate the dissolved  $\text{O}_2$  before initiating the polymerization. Then the respective polymerization reaction was performed under nitrogen atmosphere by adding the initiator viz., 1 mL of potassium peroxydisulfate ( $2 \times 10^{-2}$  mol  $\text{L}^{-1}$ ) at zero time. The reaction tube containing each catalyst mixture was suspended at the center of the ultrasonic cleaning bath for 50 min to get the maximum ultrasound energy. The reaction was arrested by pouring the respective reaction mixture into ice-cold methanol containing traces of hydroquinone. The polymers obtained from catalyst were filtered on a G-4 sintered glass crucible, washed repeatedly with water and methanol, and then dried in vacuum oven at 60°C until it reaches to constant weight. The rate of polymerization ( $R_p$ ) catalyzed by each MPTC catalyst was calculated from the weight of the polymer obtained. The conversion was restricted to less than 10% in all kinetic studies.

The rate of polymerization ( $R_p$ ) was calculated from the weight of the polymer formed by using the following equation:

$$R_p = 1000W/MVt$$

where  $W$  is the weight of polymer in grams,  $V$  is the total volume of the polymerization reaction mixture

in mL,  $t$  is the reaction time in seconds, and  $M$  is the molecular weight of the monomer.

## RESULTS AND DISCUSSION

The preparation of new soluble multisite PTC is essentially an emerging area of current interest. Many researchers devoted their attention to synthesis newer MPTCs to meet the demands to carry out immiscible substrate reactions. Especially, preparation of low molecular weight homopolymers through catalysis of MPTCs aided with peroxydisulfate and ultrasound is an active area of study. To fulfill this demand, soluble form of new single-site PTC viz.,  $N,N,N$ -triethyl-2,2-dimethylpropan-1-ammonium chloride (TEDMPAC) and other three different types of soluble multisite MPTCs including di-site- $N^1,N^1,N^1,N^3,N^3,N^3$ -hexaethyl-2,2-dimethylpropan-1,3-diaminium dichloride (HEDMPDADC), tri-site- $N^1,N^1,N^1,N^3,N^3,N^3$ -hexaethyl-2-methyl-2-((triethylammonio) methyl) propane-1,3-diaminium trichloride (HMTAMPDTC), and tetra-site- $N^1,N^1,N^1,N^1,N^3,N^3,N^3$ -hexaethyl-2,2-bis((triethylammonio) methyl)-propane-1,3-diaminium tetrachloride (HBTAMPDTC) were prepared by adopting the simplified chlorination/quaternization reactions. The presence of the number of quaternary ammonium groups (catalytic site) in each catalyst was established with FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, mass spectra, and elemental analysis. The observed spectral and elemental analysis results in each technique were given in the Experimental section and these results have strongly supported the formation of single-site, di-site, tri-site, and tetra-site in TEDMPAC, HEDMPDADC, HMTAMPDTC, and HBTAMPDTC catalysts, respectively. Apart from these results, the number of active sites present in each PTCs was also confirmed by measuring their conductance. The observed result reveals that the conductance for single-site PTC was  $7.2 \times 10^{-3}$  S  $\text{cm}^{-1}$ , which is relatively lower than other MPTCs. That is, the order of conductivity was found to be single-site < di-site < tri-site < tetra-site ( $7.2 \times 10^{-3}$  to  $29.7 \times 10^{-3}$  S  $\text{cm}^{-1}$ ). This shows that, on increasing the number of quaternary onium ions in a molecule, the conductance was also parallelly increased (Table I). Murugan et al. measured conductivity for the amphiphilic poly(propyleneimine) based dendrimers and correlated the number of quaternary onium groups in a molecule.<sup>35</sup> In other words, although the number of quaternary onium group (active site) in each catalyst was proved beyond the doubt through spectral and conductance techniques, but again, its presence in a molecule should also be proved through catalytic activity. To examine the catalytic activity of these newer soluble MPTCs, they were employed individually for the catalysis of free radical polymerization of MMA under identical

pseudo-first-order reaction condition using potassium peroxydisulfate as a water soluble initiator. The number of catalytic site present in each catalyst, the influence of peroxydisulfate and ultrasound energy has been studied based on the observed  $R_p$  values (Table I).

### Comparative kinetic study for polymerization of MMA with new soluble multisite PTCs

The pseudo-first-order rate constants for the polymerization of MMA have been determined for all the catalysts by fixing equal mole [catalyst] and keeping under identical reaction condition with ultrasound wave energy of 42 kHz, output power of 100 W conditions. From the observed values (Table I), it infers that the rate of polymerization of MMA was increased on par with number of quaternary onium groups available in a molecule. That is, the activity lies in the order of single-site < di-site < tri-site < tetra-site, and the same trend was also followed in the case of catalyst with ultrasound energy (Table I). These results reveals that the  $R_p$  was gradually increases from single-site PTC (TEDMPAC) to tetra-site PTC (HBTAMPDTC) due to the enhancement of number of quaternary onium group and thus confirmed the presence of number of active site in the respective catalyst. It is a known fact that the  $R_p$  of monomers used to depend on the number of catalytic site present in the MPTCs and in fact we reported analogue study earlier.<sup>20-26</sup> Similarly, the same catalyst has also shown twofold enhancements in  $R_p$  in the presence of ultrasound energy. This observation has strongly supported that the number of quaternary onium ions has linearly promoted the catalytic activity, at the same time, when the respective catalyst was joined with ultrasound energy they doubled the  $R_p$  of MMA and due to their cooperative action. The effect of ultrasound for the promotion of polymerization of MMA was caused by the generation of intense local conditions due to cavitations bubble dynamics, i.e., the nucleation, formation, disappearance, and coalescence of vapor or gas bubbles in the ultrasonic field.<sup>36-38</sup> However, in PTC reactions, rate enhancement are typically due to mechanical effects, mainly through an enhancement in mass transfer. In liquid-liquid bi-phase system, the presence of ultrasound used to disrupts the interface by cavitation collapse near the liquid-liquid interface and impels jets of one liquid into other, forming fine emulsions and it leads to a dramatic enhancement in the interfacial contact area through which transfer of species can take place.<sup>39,40</sup> Therefore, the combination of quaternary onium ions and ultrasound energy has proved to be a best benign catalytic method to conduct the homopolymerization of MMA. Further, it is worth to state that

since the multisite viz., HBTAMPDTC contains four quaternary onium active sites and hence it is able to accelerate the polymerization of MMA more effectively than the single-site PTCs viz., TEDMPAC even under equal mole [catalyst] and identical reaction condition and thus produced four times enhanced polymer yield than single-site PTC yield. Therefore, thorough kinetics for polymerization of MMA was studied by using the superior tetra-site viz., HBTAMPDTC catalyst in association with ultrasound by varying the experimental parameters such as [MMA],  $[K_2S_2O_8]$ , [MPTC], and the temperature.

### Steady state rate of polymerization

The steady state rate for polymerization ( $R_p$ ) of MMA was ascertained first by carrying out the experiments at regular intervals of time and it has been observed that there is no induction period for the polymerization of monomer. The rate increases sharply to some extent, slightly decreases thereafter, and then remains constant value. The plot of  $R_p$  versus time shows that the steady state rate of polymerization of MMA was attained at 50 min. Hence, the reaction time was fixed at 50 min to carry out the experiments with variation in other parameters (Fig. 2).

### Effect of [initiator] on rate of polymerization ( $R_p$ )

To find out the effect of concentration of peroxydisulfate on the  $R_p$  of MMA, the parameters including [monomer], [catalyst], acid strength, ionic strength, and temperature were kept constant and the concentration of  $K_2S_2O_8$  was varied in the range from  $1 \times 10^{-2}$  mol L<sup>-1</sup> to  $4 \times 10^{-2}$  mol L<sup>-1</sup> in combined with ultrasound wave (42 kHz and 100 W). The observed result reveals that the rate of polymerization has found to be linearly increased on increasing the concentration of potassium peroxydisulfate.

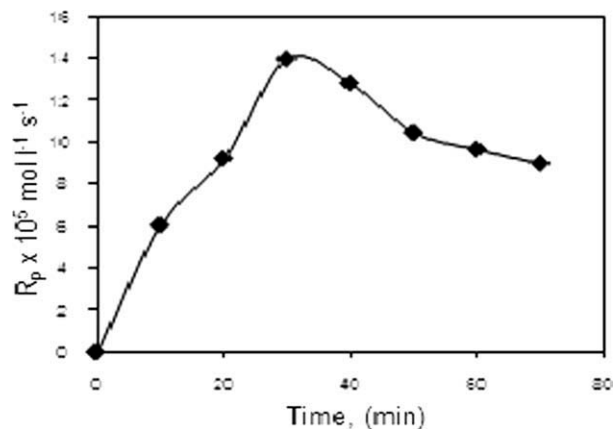


Figure 2 Steady state rate of polymerization.



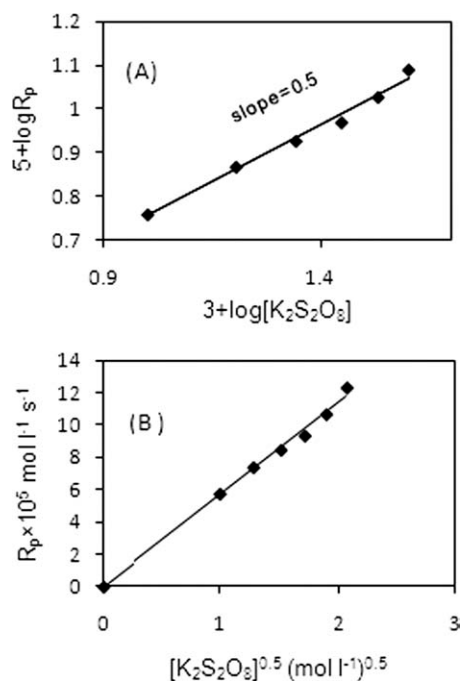


Figure 3 Effect of [initiator] on  $R_p$ .

A bilogarithmic plot of  $3 + \log[\text{K}_2\text{S}_2\text{O}_8]$  versus  $5 + \log R_p$  has found to be linear with a slope of 0.5 [Fig. 3(A)]. This indicates that the polymerization reaction proceeds with half order and it is quite common one, similar studies have already been reported with this order.<sup>7,9</sup> A linear plot of  $[\text{K}_2\text{S}_2\text{O}_8]^{0.5}$  versus  $R_p$  shows that the line passing through the origin has again supported the above order [Fig. 3(B)]. The order with respect to initiator is observed to be 0.5 whenever termination is bimolecular in the free radical polymerization process. It also suggests that the monomer-induced decomposition of  $\text{Q}_2\text{S}_2\text{O}_8$  is absent, where  $\text{Q}_2\text{S}_2\text{O}_8$  is the complex formed between the PTC ( $\text{Q}^+$ ) and the initiator peroxydisulfate ( $\text{S}_2\text{O}_8^{2-}$ ).

Generally, the rate of polymerization is proportional to the square root of [initiator] at a condition that the termination is bimolecular. In case, if the termination takes place by combination with primary radicals, the obtained order on varying the initiator is expected to deviate from 0.5 and approach a value very close to zero. However, in this study, the initiator exponent was found to be 0.5 for the catalyst HBTAMPDTC. A square-root relationship between  $R_p$  and  $[\text{K}_2\text{S}_2\text{O}_8]$  was also observed by Choi and Lee<sup>11</sup> in the free radical polymerization of MMA with  $\text{K}_2\text{S}_2\text{O}_8/18\text{-crown-6}$  and Gupta and Mandel<sup>9,10</sup> in the solution polymerization of MMA with trioctylmethylammonium-peroxydisulfate initiator system. Similarly, Balakrishnan et al. have also observed similar order with respect to [initiator] in PTC-assisted free radical polymerization of MMA<sup>12</sup> and acrylonitrile.<sup>13</sup>

#### Effect of [monomer] on rate of polymerization ( $R_p$ )

The effect of [MMA] on the rate of polymerization ( $R_p$ ) was studied by varying the concentration in the range  $1 \times 10^{-2} \text{ mol L}^{-1}$  to  $4 \times 10^{-2} \text{ mol L}^{-1}$ , by keeping the other parameters as constant along with ultrasound wave energy. The observed results suggested that the rate of polymerization ( $R_p$ ) increases on par with [monomer]. The order of the reaction with respect to monomer concentration was deduced from a plot of  $3 + \log [\text{MMA}]$  versus  $5 + \log R_p$  [Fig. 4(A)]. The order of the reaction with respect to the [monomer] was found to be 1.8 ( $\approx 2$ ) and this indicates that the reaction proceeded with second-order dependence of  $R_p$  on [MMA]. A linear plot of [MMA] versus  $R_p$  has found to be passing through the origin and hence it confirms the observed second-order with respect to [MMA] [Fig. 4(B)]. A reaction order greater than unity is not uncommon among the polymerization of vinyl monomers,<sup>41–44</sup> Balakrishnan and Jayachandramani observed a second-order dependence of  $R_p$  on monomer concentration in the polymerization of MMA using  $\text{K}_2\text{S}_2\text{O}_8$  and TEAB as PTC.<sup>12</sup> Generally, in most free radical polymerization of vinyl monomers, the order with respect to monomer was found to be unity. The deviation from the first-order on monomer may be attributed to any one of these factor such as occlusion phenomenon, primary radical termination, initiation rate dependence [monomer], and gel effect.<sup>45,46</sup> The incidence of occlusion is almost nil when the polymerization reaction is carried out at  $60^\circ\text{C}$ . Since this polymerization reaction was

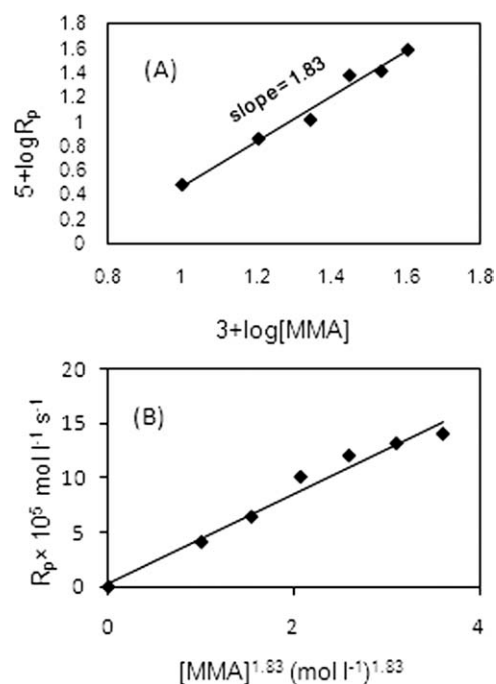


Figure 4 Effect of [monomer] on  $R_p$ .

performed at 60°C, the incidence of occlusion is negligible<sup>47</sup> and thereby occlusion cannot account for the higher monomer order. The half order with respect to initiator instead of zero order rules out the possibility of primary radical termination. Therefore, the higher monomer order observed in this study can be attributed to the dependence of initiation rate on [monomer]. Further, the monomer order may be significantly influenced by the variation in diffusion controlled termination rate constant.<sup>13,14</sup> Either or both of these factors could have contributed to the higher reaction order of 1.8 with respect to monomer concentration of MMA.

### Effect of [catalyst] on rate of polymerization ( $R_p$ )

The effect of concentration of MPTC viz., HBTAMPDTC on the rate of polymerization of MMA was studied by varying the concentration range from  $1 \times 10^{-2}$  mol L<sup>-1</sup> to  $4 \times 10^{-2}$  mol L<sup>-1</sup> and by keeping the rest of the parameters as constant and combined with ultrasound energy. The observed results reveal that the  $R_p$  was linearly proportional to the [HBTAMPDTC]. A bilogarithmic plot of  $3 + \log$  [HBTAMPDTC] versus  $5 + \log R_p$  gives a linear plot with the slope of 0.5 [Fig. 5(A)]. From the observed slope value, it is inferred that it obeys half-order dependence on [HBTAMPDTC]. Also, the plot of [HBTAMPDTC] versus  $R_p$  passing through the origin again confirms the above observation with respect to concen-

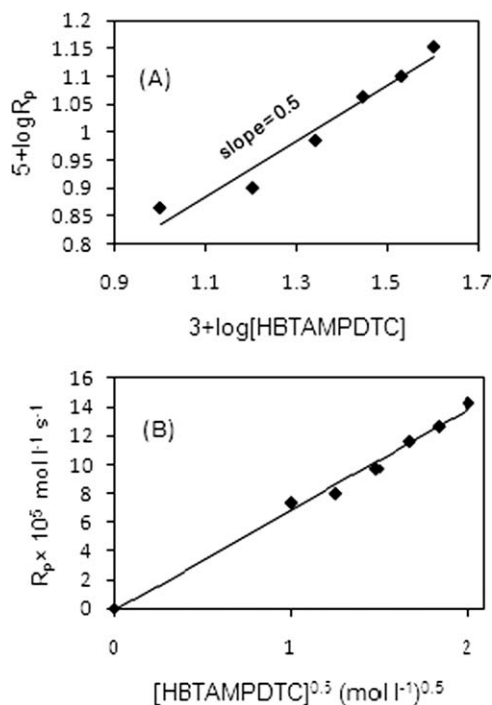
tration of catalyst [Fig. 5(B)]. In the earlier study also, the  $R_p$  to the square root of [PTC] in the polymerization of MMA using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>-18-crown-6 system found by Choi and Lee<sup>11</sup> are on par with our observation of HBTAMPDTC catalyst system. That is, the observed order for HBTAMPDTC catalyst is 0.5 and it is not uncommon one and similar inference have already been reported by Balakrishnan et al. in the polymerization of MMA in toluene/water media using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/TEBA system<sup>12</sup> and in the free radical polymerization of acrylonitrile using PMS/TBPC system in ethyl acetate–water biphasic media.<sup>13</sup> Vajjiravel and Umapathy have already observed the similar order with respect to catalyst in the PTC-assisted free radical polymerization of vinyl monomers.<sup>48–50</sup>

### Effect of acid strength, ionic strength, and temperature on $R_p$

The effect of variation of ionic strength and acid strength on the rate of polymerization was investigated by varying the ionic strength from 0.2 mol L<sup>-1</sup> to 0.8 mol L<sup>-1</sup> and acid strength in the range of 0.4 mol L<sup>-1</sup> to 1.6 mol L<sup>-1</sup> independently at constant [monomer], [initiator], [catalyst], and temperature in association with ultrasonic effect. The variation in either ionic strength or acid strength of the medium was found to exert no significant changes in the rate of polymerization. Similarly, the effect of temperature on the rate of polymerization of MMA was carried out at four different temperatures viz., 50, 55, 60, and 65°C using the catalyst viz., HBTAMPDTC and keeping the other experimental parameters as constant. These observed value indicates that the  $R_p$  was increased with increasing the temperature along with ultrasonic effect.<sup>51</sup> This may be due to the fact that at higher temperature, the rate of initiator decomposition was increased and thus yield more radicals which in turn accelerate the rate of polymerization. From the Arrhenius plot derived from  $\log R_p$  versus  $1/T$  (Fig. 6), the overall activation energy ( $E_a$ ) for the polymerization reaction was calculated 37.85 kJ mol<sup>-1</sup>. The other thermodynamic parameters such as entropy of activation ( $\Delta S^\ddagger$ ), enthalpy of activation ( $\Delta H^\ddagger$ ), and free energy of activation ( $\Delta G^\ddagger$ ) were determined as  $-227.52$  J K<sup>-1</sup> mol<sup>-1</sup>, 35.08 kJ mol<sup>-1</sup>, and 126.79 kJ mol<sup>-1</sup>, respectively.

### Effect of solvent on $R_p$

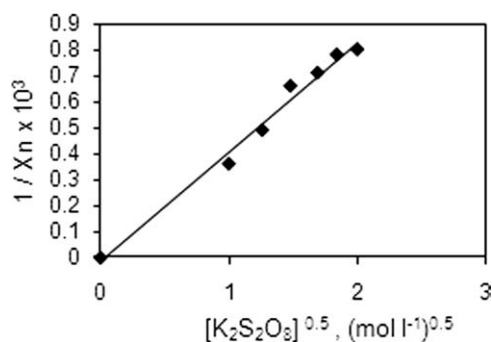
The effect of solvent on rate of the polymerization was determined by carrying out the polymerization of MMA with three different solvents, such as cyclohexane, ethyl acetate, and cyclohexanone under ultrasound irradiation condition. The dielectric constants of the solvents are 2.02, 6.02, and



**Figure 5** Effect of [catalyst] on  $R_p$ .







**Figure 7** MMA-HBTAMPDTC- $K_2S_2O_8$  system dependence of  $1/\bar{X}_n$  on  $[K_2S_2O_8]$ .

### CONCLUSION

Four different soluble PTCs such as TEDMPAC (single-site), HEDMPDADC (di-site), HMTAMPDTC (tri-site), and HBTAMPDTC (tetra-site) were synthesized by simplified routes. The presence of number of quaternary ammonium groups in each catalyst was proved through FT-IR,  $^1H$  NMR,  $^{13}C$  NMR, mass spectra, elemental analysis, and conductivity measurement. Especially, the experimental results and their observations such as increases in conductance, gradual enhancement in peak intensity of C-N stretching frequency noticed in FT-IR noticed from single-site to tetra-site has indicated the number of quaternary onium groups in the respective catalysts. Similarly, in  $^1H$  NMR analysis, the quaternized *N*-ethyl group consisting of methyl and methylene proton peaks were appeared as triplet and quartet and in  $^{13}C$  NMR, the methyl and methylene carbon showed a high intense peak and these results has shown strong support for the formation of number of active site in the respective PTCs. Further, the catalytic activity of these catalysts were ascertained from the rate of polymerization of MMA individually as well as combined with ultrasonic waves. That is, in the comparative study the  $R_p$  determined without ultrasound energy was found in the order of single-site < di-site < tri-site < tetra-site, and this in turn proves the number of quaternary ammonium groups in the respective MPTCs. Similarly, the  $R_p$  determined in the presence of respective MPTC and ultrasound energy has also shown the same order of activity with two-fold enhancements in the  $R_p$ . That is, the rate of polymerization was dramatically enhanced to two-fold than with catalyst alone, this is because of the combination of MPTC with ultrasound energy. Further, the superior tetra-site MPTC viz., HBTAMPDTC has been studied for the thorough kinetics of polymerization of MMA. The rate of polymerization was increased on increasing the [monomer], [initiator], [catalyst], and temperature.

From the Arrhenius plot, energy of activation ( $E_a$ ) and other thermodynamic parameters such as entropy of activation ( $\Delta S^\ddagger$ ), enthalpy of activation ( $\Delta H^\ddagger$ ), and free energy of activation ( $\Delta G^\ddagger$ ) have also been calculated. On the basis of the kinetic results, a suitable mechanism has been proposed.

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