

Toxic solvent-free: Radical polymerizations of vinyl monomers using a di-site phase-transfer catalyst – a kinetic approach

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Free radical polymerizations of vinyl monomers, namely methyl methacrylate and ethyl methacrylate, were performed using 1,1,4,4-tetramethyl-1,4-dioctylethylenediammonium bromide (TDEDDB) which is a newly synthesized di-site phase-transfer catalyst (PTC), in ethyl acetate/water as a biphasic medium. The catalyst was characterized by Fourier-transform infrared, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectroscopies along with C, H, and N elemental analyses. Polymerization was initiated using the water-soluble potassium peroxydisulfate initiator at a constant temperature of 60 ± 1 °C. The competency of TDEDDB was examined in a kinetic study. The reaction orders with respect to the monomer, PTC and initiator were determined. The effect of ionic and acid strengths and solvent polarity were also investigated. A suitable mechanism was proposed on the basis of the experimental conditions. The molecular weights of the poly(methyl methacrylate) and poly(ethyl methacrylate) were determined by gel permeation chromatography.

Keywords: Di-site phase-transfer catalyst; 1,1,4,4-Tetramethyl-1,4-dioctylethylenediammonium bromide; Mechanism; Radical polymerization; Potassium peroxydisulfate

INTRODUCTION

Reactions between inaccessible reactants present in heterogeneous phases are made possible through the use of phase-transfer catalysts (PTCs) which are powerful tools. The introduction to these highly active, interface-penetrating PTCs by Starks [1] in 1971 led to tremendous transformations in synthetic chemistry. This versatile and reliable synthetic methodology has garnered attention in chemical industries because of its affordability, trivial reaction conditions, high conversions or yields, lack of byproducts, purging of excessive and dangerous non-ecofriendly solvents that dissolve the reactants in a single phase, solvent-selection flexibility, and ability to easily treat wastewater streams [2–4]. Hence, these robust catalysts have emerged as an area of research thrust, especially in organic synthesis and polymer chemistry. Phase-transfer-catalyzed polymerization reactions have facilitated the use of water and reduced or eliminated the usage of non-ecofriendly organic solvents. The transportation of aqueous-phase-soluble inorganic reactants across the boundary in a heterogeneous aqueous–organic solvent system using a PTC was first reported by Makosza [5]. This motivated the researchers to investigate the use of single-site and multi-site PTCs, especially in the free radical polymerizations of vinyl monomers in aqueous–organic biphasic media [6–18]. Success in this chemistry motivated us to investigate the competency of a newly synthesized di-site PTC in

the radical polymerizations of methyl and ethyl methacrylates, which were analyzed in a kinetic study using a water-soluble potassium peroxydisulfate initiator.

EXPERIMENTAL

Materials and Methods

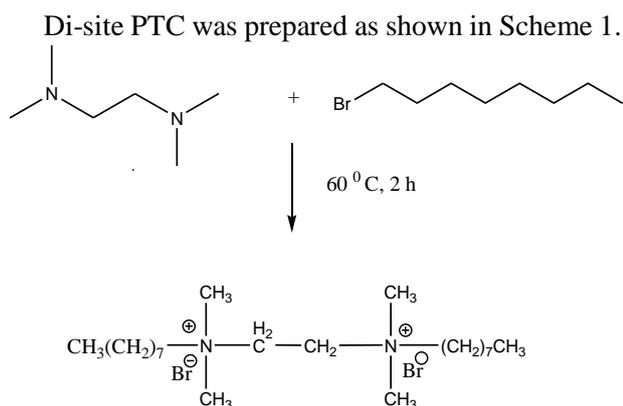
Methyl methacrylate (MMA) and ethyl methacrylate (EMA) (Merck, Mumbai) were distilled at reduced pressure prior to use. The PDS water-soluble initiator (SRL, Mumbai), was used as received. Methanol (SRL, Mumbai) and ethyl acetate (SRL, Mumbai) were distilled before use. Doubly distilled water was used as the solvent in the biphasic system.

Instrumentation

The FT-IR spectra were recorded on a Perkin Elmer Spectrum RX I spectrometer in the 4400–400 cm^{-1} spectral region using the KBr-disc method. High-resolution $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on Bruker 500 MHz and DRX 125.77 MHz FT-NMR spectrometers at room temperature using D_2O as the solvent. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) using a Waters 501 instrument, with styragel column and tetrahydrofuran as the eluent. Polystyrene standards were employed for calibration.

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Synthesis of Di-site PTC: 1,1,4,4-Tetramethyl-1,4-dioctylethylenediammonium bromide



Scheme 1. Synthesis of TDEDB

A solution of 0.01 M N,N,N',N'-tetramethylethylenediamine and 0.02 M 1-bromooctane was introduced into a 250-mL flask. The mixture was gently refluxed at 60 °C for 2 h. The resulting white 1,1,4,4-tetramethyl-1,4-dioctylethylenediammonium bromide (TDEDB) precipitate was collected by filtration, dried and then purified by dissolving it in a minimal amount of acetone/ethanol. The melting point of the prepared TDEDB was found to be 173 °C.

FT-IR Spectral Analysis of TDEDB

The FT-IR spectrum of TDEDB (Fig. 1) displays the following signals: 3112 cm⁻¹ (C–H stretches of the methyl groups attached to the positively charged nitrogen atoms), 2966 and 2838 cm⁻¹ (symmetric and asymmetric stretches of the methyl and methylene groups, respectively), 1488 and 1397 cm⁻¹ (CH₂–N and CH₃–N stretches, respectively), and 932 cm⁻¹ (CH₂-group rocking).

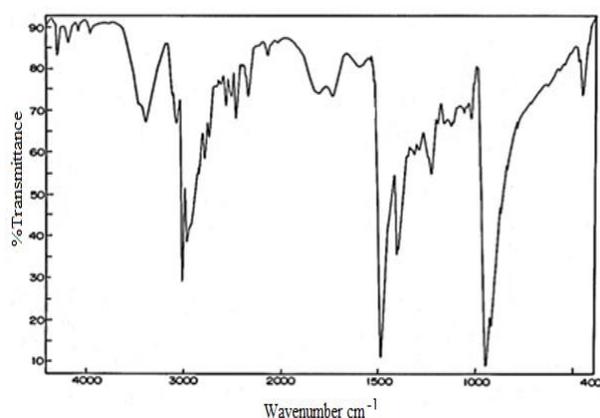


Fig. 1. FT-IR spectrum of TDEDB

¹H-NMR Spectrum of TDEDB

The ¹H NMR spectrum of TDEDB is shown in

Fig. 2 and exhibits the following signals: 2.78 ppm (ethylene protons), 2.45 ppm (methylene protons of the octyl groups attached to the nitrogen atoms), 2.21 ppm (protons of the methyl groups attached to the nitrogen atoms), 1.79 and 1.18 ppm (remaining methylene protons of the octyl groups), and 0.99 ppm (methyl protons of the octyl groups).

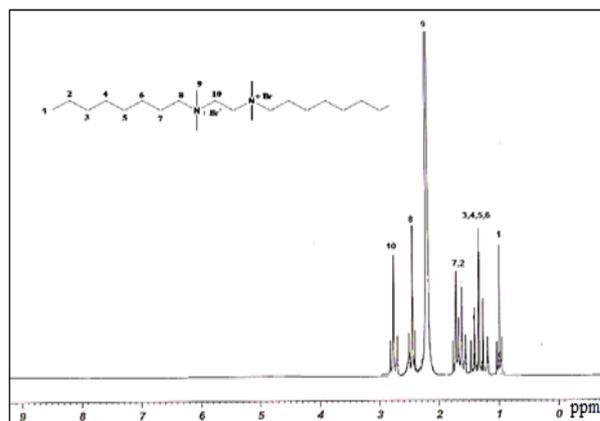


Fig. 2. ¹H NMR spectrum of TDEDB

¹³C-NMR Spectrum of TDEDB

The ¹³C-NMR spectrum of TDEDB is presented in Fig. 3, which displays the following signals: 61.55 and 61.49 ppm (methylene carbons of the octyl groups and those of the ethylene groups attached to the nitrogen atoms, respectively), 46.06 ppm (methyl carbons attached to the nitrogen atoms), 14.02 ppm (methyl carbons of the octyl groups), and 32.53, 30.02, 28.32, 27.24, and 23.13 ppm (remaining methylene carbons of the octyl groups).

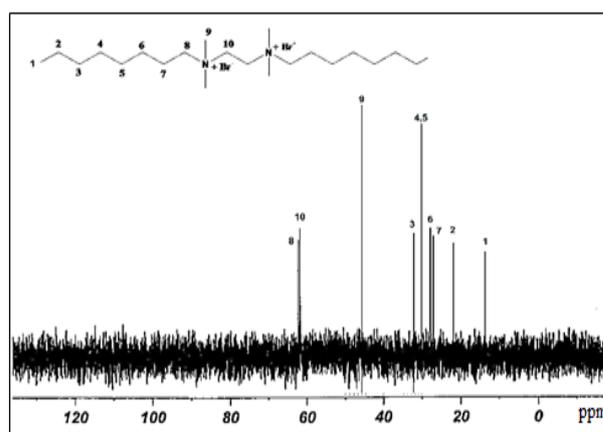


Fig. 3. ¹³C-NMR spectrum of TDEDB

Elemental Analysis of TDEDB

The C, H, and N contents of TDEDB were determined and found to be very close to the theoretical values. Molecular formula: C₂₂H₅₀Br₂N₂;

Mol. wt. 502; Elemental analysis (%): C: 52.52 (found): 52.59 (calculated), H: 10.09 (found): 10.03 (calculated), N: 5.54 (found): 5.58 (calculated).

Polymerization Procedure

Methyl methacrylate and ethyl methacrylate (RMA) were polymerized in a classic manner in thick-walled, long, sealed Pyrex tubes without stirring in an inert atmosphere at 60 ± 1 °C. The reaction mixture was composed of the monomer in 10 mL of the organic phase (ethyl acetate), the phase-transfer catalyst (TDEDDB), sodium bisulfate (0.5 M) to control the ionic strength, and sulfuric acid (0.2 M) to control the pH of the 10-mL aqueous phase. Polymerization was initiated by the addition of PDS to the reaction mixture. After the stipulated period of time, the reaction was terminated by pouring the reaction mixture into ice-cold methanol [6-10,11,14]. The precipitated polymer was collected by filtration using a sintered glass crucible, washed several times with doubly distilled water and methanol, and then dried in an oven (60 ± 0.1 °C) to constant weight. The rate of polymerization (R_p) was calculated using equation (1):

$$R_p = \frac{1000 \times W}{V \times t \times M} \quad (1)$$

where R_p is the rate of polymerization, W is the weight of the polymer (g), V is the volume of the reaction mixture, t is the reaction time (s), and M is the molecular weight of the monomer.

RESULTS AND DISCUSSION

Kinetics of Free Radical Polymerization

Polymerization is discussed in terms of the kinetics of the free radical polymerizations of methyl and ethyl methacrylate using TDEDDB as the catalyst and PDS as the initiator in ethyl acetate/water as the biphasic medium under the experimental conditions described below.

Steady-state Polymerization Rates

The rates of monomer polymerization were determined at monomer concentrations of 2.0 M and a PDS concentration of 0.02 M in a total volume (aqueous + organic phase) of 10 mL; sulfuric acid (0.2 M), and sodium bisulfate (0.5 M) were also added. Furthermore, polymerization was initiated by adding 0.1 M TDEDDB into the aqueous phase. Fig. 4 displays the relationships between polymerization rates and time. The steady-state rates of polymerization were determined from these plots at 50 min for both MMA and EMA with TDEDDB as the PTC.

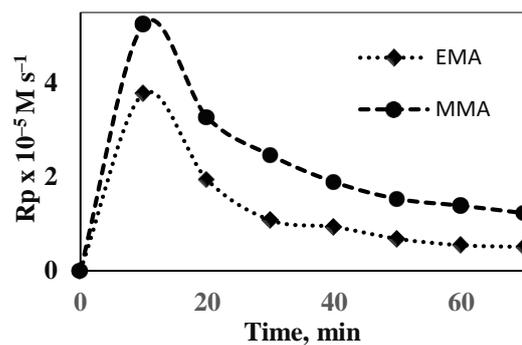


Fig. 4. Steady-state rates of polymerization (R_p) catalyzed by TDEDDB as functions of time.

Impact of Monomer Concentration on the Rate of Polymerization

The dependence of polymerization rate on monomer concentration was determined by varying its concentration from 0.8 to 1.8 M while maintaining the concentration of PDS at 0.02 M and of TDEDDB at 0.1 M, with the ionic strength maintained at 0.5 M at a constant pH. We observed that R_p increased with increasing monomer concentration. The reaction orders with respect to the MMA and EMA monomer concentrations are almost one half, which contrasts with the first-order reactions observed for vinyl monomers. The observed deviation from first order [19-21] has been attributed to primary-radical termination and occlusion phenomena, or gelation effects during the initiation step. But in the present case, deviation may be due to the formation of a charge-transfer complex with the oxygen of PDS, hence this would have hampered the reactivity of the monomer. The increase in viscosity of the medium also restricted the diffusion of ions [22, 23]. Fig. 5 shows the plots of R_p as a function of monomer concentration raised to suitable powers such that the straight lines pass through the origin in each case; these plots confirm the above observations with respect to [RMA].

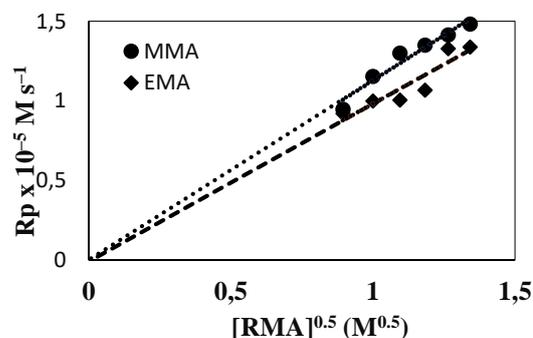


Fig. 5. Rate of polymerization (R_p) as a function of $[RMA]^{0.5}$

Effect of TDEDB Concentration on the Rate of Polymerization

By keeping the concentration of the other factors constant, the effect of TDEDB on R_p was determined in the 0.015–0.025 M concentration range. The plot of $\log R_p$ vs. $\log [TDEDB]$ is linear with a slope of 0.5 for EMA, signifying a half-order dependence. However, for the polymerization of MMA, the order is almost equal to unity under the same catalyst conditions. The plots of R_p vs. $[TDEDB]$ (Figs. 6 and 7) are linear and pass through their respective origins, which supports the above observations. The results show a lack of polymerization in the absence of the catalyst even after several hours. Moreover, the first-order

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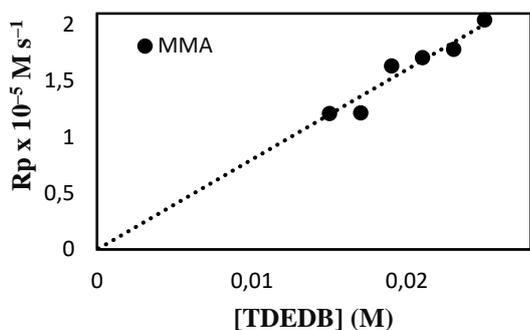


Fig. 6. Rate of polymerization (R_p) as a function of $[TDEDB]$ for MMA

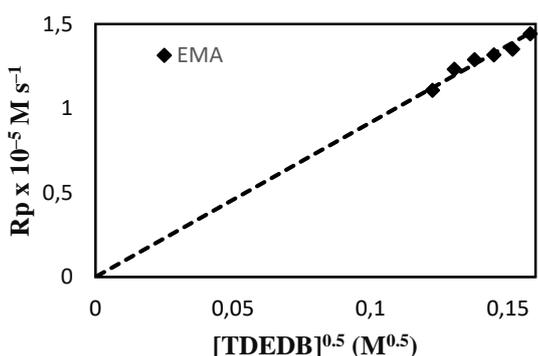


Fig. 7. Rate of polymerization (R_p) as a function of $[TDEDB]^{0.5}$ for EMA

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Effect of Initiator Concentration on the Rate of Polymerization

The effect of concentration of $K_2S_2O_8$ on the rate of polymerization of RMA was studied by varying the concentration of $K_2S_2O_8$ in the range of 0.015 to 0.025 M by keeping other concentrations constant. As the concentration of PDS was increased, R_p was found to increase. The plot of $\log R_p$ versus $\log [PDS]$ and the order of reaction are found to be nearly unity for MMA and nearly half-order for EMA. Figs. 8 and 9 show that the plot of R_p versus $[PDS]$ raised to suitable power passes through the origin, supporting the above observation. The normal half-order dependence of the rate on initiator concentration which is observed in most of the free radical polymerization has been deviated for MMA.

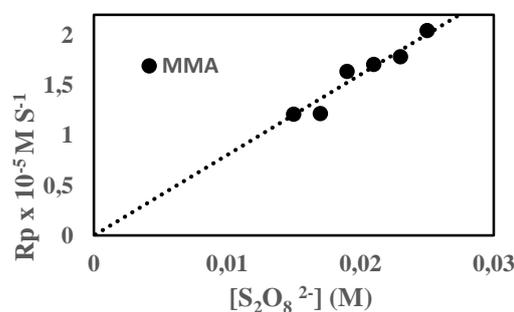


Fig. 8. Rate of polymerization (R_p) as a function of $[S_2O_8]$ for MMA

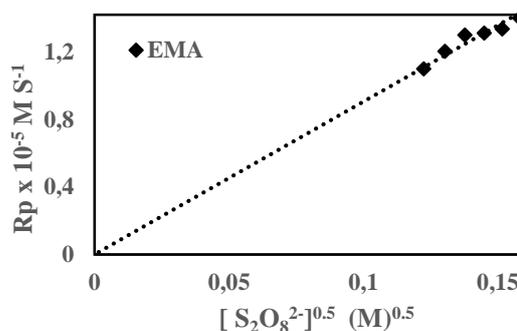


Fig. 9. Rate of polymerization (R_p) as a function of $[S_2O_8]^{0.5}$ for EMA

In the case of free radical polymerization of vinyl monomers, the order with respect to initiator is found to be a square root of initiator concentration when the polymer radical terminates by mutual bimolecular reaction. The higher order of polymerization in the case of MMA may be due

either to the induced decomposition of the initiator or to the decrease in termination rate constant. The induced decomposition of peroxydisulphate in the presence of oxidizable organic compounds is well known. The decomposition of PDS in water was greatly enhanced [26-28] in the presence of methanol, ethanol, ethyl acetate, etc.

Effect of Ionic Strength and Acid Strength

The effect of ionic strength varied in the range from 0.4 to 0.6 M and acid strength from 0.1 to 0.3 M on the rate of polymerization was studied by maintaining constant concentrations of monomer, initiator, PTC and solvent. It was observed that there were no significant changes in the rate of polymerization [11, 13-15, 29].

Effect of Solvent Polarity on the Rate of Polymerization

MMA and EMA were polymerized using three different solvents, namely cyclohexane, ethyl acetate, and cyclohexanone, whose dielectric constants are 2.02, 6.02, and 18.03, respectively. The rates of polymerization were found to increase in the order:

cyclohexane < ethyl acetate < cyclohexanone.

Fig. 10 displays the influence of the polarity (dielectric constant) of the solvent on the rate of polymerization. We observed that the dielectric constant of the medium increases the rate of polymerization, which is attributable to the greater migration of sulfate ions into the organic phase with increasing solvent polarity [12,14, 30].

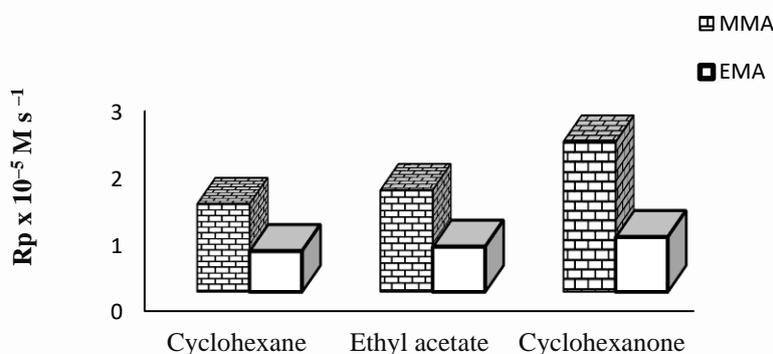


Fig. 10. Effect of solvent polarity on Rp

Table 1. Mn, Mw, and Mw/Mn of polymers

1. Polymer	M _n	M _w	M _w /M _n
PMMA – L	37276	57685	1.547
PMMA – H	53437	102534	1.919
PEMA – L	17212	27815	1.616
PEMA – H	37805	62118	1.643

Determining the Molecular Weights of the Poly(alkyl methacrylate)s

The molecular weights of the polymers were established by gel permeation chromatography. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (M_w/M_n) of each polymer are presented in Table 1. The molecular weights of the polymers which were synthesized at low monomer concentrations and fixed concentrations of the PTC and PDS are referred to as “poly(alkyl methacrylate - L)”, while those synthesized at higher monomer concentrations and fixed initiator and PTC concentrations are referred to as “poly(alkyl

methacrylate - H)”. The polydispersity index values of both poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) suggest that chains are terminated predominantly through disproportionation [30–32]. The molecular weight of PMMA was found to consistently be higher than that of PEMA, which is attributable to chain-propagation difficulties during the polymerization of EMA compared to MMA. In this study, we observed that the molecular weights of the polymers increased with increasing monomer concentration.

Product Analysis

The FT-IR spectra of the products obtained by the phase-transfer polymerization of MMA and EMA revealed the absence of the peak at 1635 cm⁻¹ originally present in the FT-IR spectra of the monomers. This suggests that the olefinic double bond was involved in the polymerization process, and that the products are PMMA and PEMA, respectively.

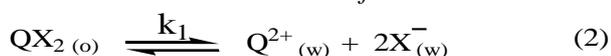
Mechanism

The following observations were made during the free radical polymerizations of the alkyl methacrylates using K₂S₂O₈ as the initiator and the di-site quaternary ammonium salt, TDEDDB, as the PTC:

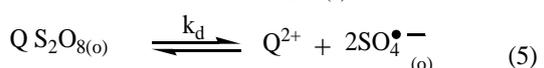
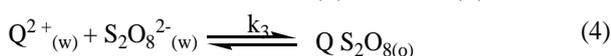
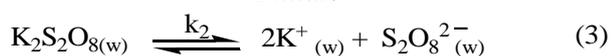
- The reaction exponent with respect to [monomer] = 0.5–1;
- The reaction order with respect to [TDEDDB] = 0.5–1;
- The reaction order with respect to [K₂S₂O₈] = 0.5 to 1;
- R_p increases with increasing solvent polarity;
- The rate of polymerization is independent of ionic strength (μ) and [H⁺].

We propose an appropriate mechanism to explain the above-mentioned experimental observations. Scheme 2 displays a pathway for the polymerization of an alkyl methacrylate (M) initiated by K₂S₂O₈/PTC in an ethyl acetate/water biphasic system. Subscripts (w) and (o) refer to aqueous and organic phases, respectively, while k₁, k₂ and k₃ are equilibrium constants of equations (2) to (4); k_d is the dissociation constant of equation (5); k_i, k_p, and k_t are the rates of initiation, propagation, and termination, respectively, and QX₂ represents the PTC.

Phase Transfer:



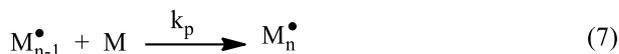
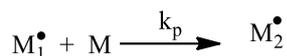
Initiator:



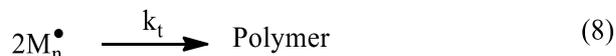
Initiation:



Propagation:



Termination:



Scheme 2. Mechanism proposed for the polymerization of an alkyl methacrylate initiated by K₂S₂O₈/PTC in an ethyl acetate/water biphasic system.

Based on this mechanism, the rate of polymerization for RMA catalyzed by TDEDDB can be derived to be:

$$R_p = k_p \left[\frac{k_d K}{k_t} \right]^{1/2} [Q^{2+}]^{0.5} [S_2O_8^{2-}]^{0.5} M^{0.5}$$

This derived expression sufficiently explains all experimental observations.

CONCLUSION

The kinetics of the free radical polymerizations of alkyl methacrylates initiated by K₂S₂O₈ was studied using a newly synthesized di-site PTC in an ethyl acetate/water biphasic medium under inert conditions. The rates of polymerization were evaluated by increasing the concentrations of the monomer, PTC and initiator. The reaction orders were found to be 0.5 with respect to monomers, 0.5–1 with respect to initiator and di-site PTC. Based on the results obtained, a suitable mechanism was proposed. The effects of ionic and acid strengths, as well as of solvent polarity were also determined. Insignificant changes were observed by the increase of ionic and acidic strengths but polarity of the solvents played a significant role in increasing the rate of polymerization. The molecular weight of polymers was found to be higher at higher monomer concentrations and at fixed initiator and PTC concentrations. Hence, the synthesized PTC promotes higher polymerization rates in the ethyl acetate/water biphasic system using a water-soluble initiator. In addition, the newly synthesized PTC is expected to be applied to organic reactions, such as alkylation, oxidation, reduction, hydrolysis, etherification, and esterification, among others; hence the hidden potential of this PTC needs to be further explored.

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