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Phase transfer catalyst aided radical polymerization of *n*-butyl acrylate in two-phase system: a kinetic study

Vajjiravel Murugesan[1] · M. J. Umapathy[2]

Abstract The kinetics of radical polymerization of butyl acrylate initiated by potassium peroxydisulphate and cetyltrimethylammonium bromide as phase transfer catalyst (PTC) was carried out under inert and unstirred conditions at constant temperature of $60 \pm 2\ ^{\circ}\mathrm{C}$ in ethyl acetate–water biphase media. The polymerization reactions were relatively fast in the two-phase systems with phase transfer agent whereas extremely sluggish in the system without PTC. Use of PTC accelerates the reaction effectively if the reactants located in two phase. The effects of rate of polymerization (R_p) on various experimental conditions such as different concentrations of monomer, initiator, phase transfer catalyst, temperature, and different ionic strength of the medium were explored. The order with respect to monomer, initiator and phase transfer catalyst was found to be unity. The R_p is independent of ionic strength and pH of the medium. However, an increase in the polarity of solvent has slightly increased the R_p value. Based on the results obtained, a plausible mechanism has been proposed for the polymerization reaction. The obtained polymer was confirmed by FT-IR analysis.

Keywords Kinetics · Phase transfer catalyst · Rate of polymerization · Radical polymerization · Two-phase system

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Introduction

The growth and use of phase transfer catalyst (PTC) in the field of chemistry such as organic chemistry [1], inorganic chemistry [2], analytical applications [3], electrochemistry [4–8], photochemistry [9, 10] and in polymer chemistry [11–15] has become increasingly popular within industrial and academic arenas, because it is a potent and versatile technology which offers (1) less dependence on organic solvents, (2) excellent scalability and inherent compatibility with moisture, (3) enhancement of reactivity, which permits shortened reaction times and increased yields, (4) ability to substitute inconvenient reagents [like lithium diisopropylamide (LDA)] and (5) to control enantioselective variants and eco-friendliness. The efficient source of PTC technology in synthesis of polymers offers important technical rewards compared to other conventional polymerization methods [16]. PTC technique make easy of the reactions that are heterogeneously located in an immiscible phases by operating through the transfer of an anionic species from an aqueous (or solid) phase to the organic phase, thus polymerization and organic reactions will take place.

The acrylic esters such as *n*-butyl acrylate (*n*-BA) are commercially attractive and important functional monomers for the synthesis of acrylic resins. Because of their optical clarity, mechanical properties, adhesion and chemical stability, acrylic resins have many applications in paints, adhesives and coatings [17, 18]. Radical polymerization is one of the most widely facilitated commercial processes for the synthesis of polymers with high molecular weight. The rewards of radical polymerization are obvious: it can be applied to almost all vinyl monomers under mild reaction conditions over a wide temperature range, it is water tolerant and its cost is relatively low. The

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development of a new kinetic model for the polymerization of acrylic monomers, particularly *n*-butyl acrylate (*n*-BA), using efficient catalyst at moderate (low) temperature is one of the best approaches to an industrial perspective [19].

The growth of novel catalysts and efficient kinetic methodologies for the synthesis of polymers is an important target of research. Recently, phase transfer-catalyzed polymerization of vinyl monomers was gaining remarkable interest [20–34]. Inspired by the versatile application of PTC, herein, we report the systematic kinetic study of radical polymerization of *n*-butyl acrylate using cetyltrimethylammonium bromide (CTMAB) as phase transfer catalyst and potassium peroxydisulphate (PDS) as water-soluble initiator in an ethyl acetate–water two-phase system. The various kinetic parameters on the rate of polymerization were ascertained and based on the experimental observation plausible mechanism has been derived and its significance was discussed. Moreover, the resultant kinetics was evaluated with the reported radical polymerization of *n*-BA using different catalyst [35].

Experimental

Materials and solvents

Butyl acrylate (*n*-BA, Lancaster, India) was purified by washing three times with a 10 % sodium hydroxide solution then washing three times with de-ionized water, drying over calcium carbonate and finally distilling under reduced pressure, no more than 24 h prior to use. The initiator potassium peroxydisulphate (PDS, Merck, India) was purified twice by recrystallization in cold water. The cetyltrimethylammonium bromide (CTMAB, SRL, India) was used without further purification. The solvents, benzene, ethyl acetate and acetone (SRL, India) was used as received. The double-distilled water was used to make an aqueous phase.

Polymerization procedure

A polymerization experiment was carried out in annular glass ampoules with dimensions of 30 and 26 mm for outer and inner diameter, respectively, and 120 mm height. These ampoules have a surface area/volume ratio large enough for the heat transfer necessary to maintain the isothermal conditions during the polymerization. The polymerization ampoule consists of equal volumes of aqueous and organic phase (10 mL each). The monomer (*n*-BA) in ethyl acetate was the organic phase and the catalyst, sodium bisulfate (for adjusting the ionic strength [μ]) and sulphuric acid (maintaining the [H^+]), was in the aqueous phase. The ampoule was degassed using nitrogen

gas continuously about 15 min after which it was sealed. Polymerizations were performed by placing the ampoules in a constant water bath at 60 ± 2 °C and the ampoules were removed from the water bath after a recorded time interval. The polymer were precipitated into a tenfold excess of methanol, filtered and dried at high vacuum until a constant weight was reached.

The rate of polymerization (R_p) was calculated from the gravimetric determination of the polymer formed in a given time of polymerization. The R_p was calculated from the weight of polymer obtained using the formula: $R_p = 1000 \, W/V \times t \times M$; where W is the weight of the polymer in gram; V is the volume of the reaction mixture in mL; t is the reaction time in seconds; M is the molecular weight of the monomer in g/mol. The kinetic experiment was carried out by changing the concentration of monomer, initiator, catalyst, temperature, etc., by adopting above-stated polymerization procedure.

Viscosity measurements

The viscosity average molecular weight of the polymer was determined in acetone at 30 ± 1 °C using Ostwald viscometer with the values of Mark–Houwink constant [36] using $[\eta] = K \, (M_v)^{\alpha}$. From the molecular weight of the polymer, the degrees of polymerization (P_n) values were calculated.

Kinetic model

The incompatible reactants dissolve in the different phases, that is, the ionic reactant [QX (phase transfer catalyst) and KY (initiator)] in the aqueous phase and the organic compound (monomer) in the organic phase and the reaction can take place at the interface between the two phases. Usually, this kind of situation in two-phase approach, because of a small interface, generally causes low reaction rate. This situation can be dramatically improved with the help of phase transfer catalysis (PTC). Phase transfer agent (PTA), a quaternary ammonium or phosphonium salt (QX salt) or a crown ether is added to the two-phase system. These PTAs have the ability to carry the ionic reactant into the organic phase. Once in the organic phase, the reactant becomes highly reactive because the degree of solvation is low; thus, the anion behaves like a 'naked' ion. Therefore, the reaction in the aqueous phase produces QY at the interface between the two phases where it was decomposed and produced the radical ions which initiate the polymerization at 60 ± 2 °C. The simple reaction kinetic model is shown in Schemes 1 and 2. A similar type of kinetic model was reported for phase transfer-catalyzed reactions [37–39].

Scheme 1 Phase transfer-catalyzed radical polymerization of *n*-butylacrylate (*n*-BA) in two-phase system

n-Butyl acrylate

CTMAB (PTC)

PDS (Initiator) 60 °C

Ethyl acetate

Poly(n-butyl acrylate)
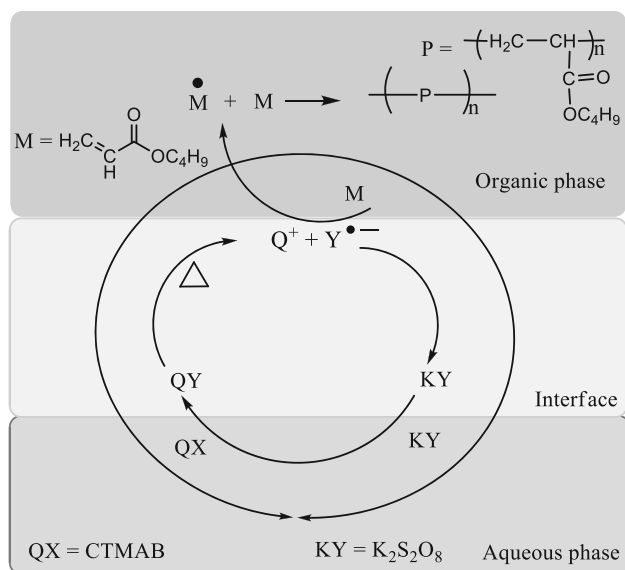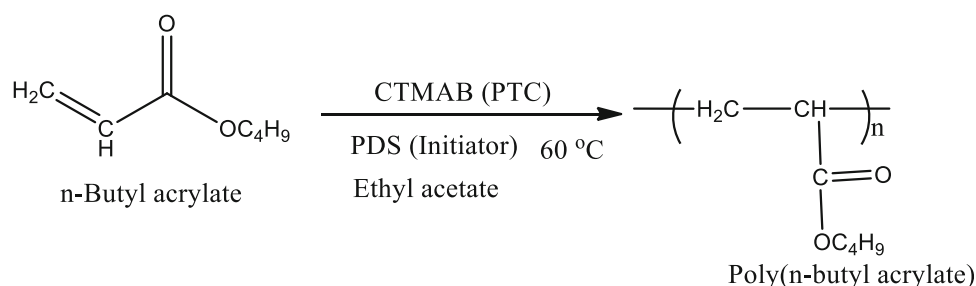
Scheme 2 Simple kinetic model of phase transfer catalyst aided polymerization of *n*-BA

Fig. 1 Steady-state rate of polymerization. Polymerization condition: [BA]: 2.0 mol dm^{-3}; [K$_2$S$_2$O$_8$]: 2.0 × 10^{-2} mol dm^{-3}; [CTMAB]: 2.0 × 10^{-2} mol dm^{-3}; [H$^+$]: 0.5 mol dm^{-3}; [μ]: 0.2 mol dm^{-3}; temp: 60 ± 2 °C

Results and discussion

The radical polymerization of *n*-butyl acrylate initiated by PDS–PTC in an ethyl acetate–water two-phase system was studied under different experimental conditions to evaluate the various parameters, which influence the rate of polymerization reaction.

Steady-state rate of polymerization

The steady-state rate of polymerization for the *n*-butyl acrylate was studied by determining R_p at different intervals of time. A plot of R_p versus time shows an increase to some extent and then reaches constant. The steady-state rate of polymerization of the *n*-butyl acrylate was fixed at 40 min (Fig. 1).

Effect of [BA] on the rate of polymerization (R_p)

The effect of *n*-butyl acrylate [*n*-BA] on the rate of polymerization (R_p) has been carried out at 60 ± 2 °C using

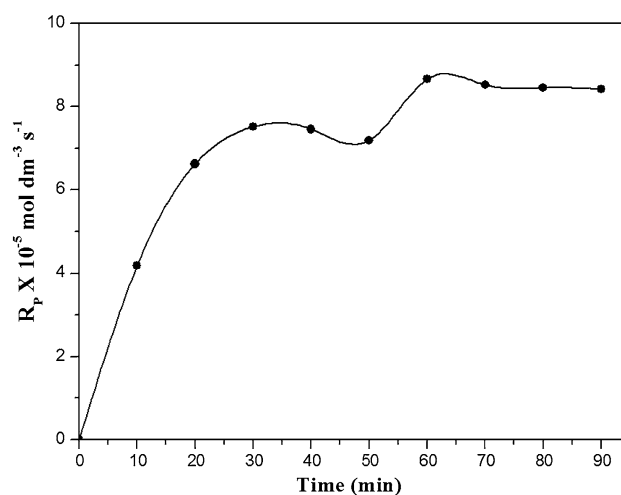fixed concentration of PTC, PDS, ionic strength and pH of aqueous phase, the monomer concentrations ranging from 1.0 to 2.1 mol dm^{-3}. The R_p increase with an increase in the concentration of the monomer was noticed. The reaction order with respect to monomer concentration was determined from the slope of $6 + \log R_p$ versus $3 + \log$ [BA] and the reaction order with respect to the monomer concentration was found to be 0.91, it is approximately equal to order of unity. Also the plot of R_p versus [BA] passing through the origin confirms the above observations with respect to [BA] (Fig. 2). The monomer reaction order of unity has been reported for the phase transfer catalyst and PDS-aided polymerization of various vinyl monomers [26, 28, 30, 34].

Effect of [PDS] on the rate of polymerization (R_p)

At fixed concentrations of monomer, catalyst and volume ratio of aqueous to organic phase, the effect of concentration of PDS on the rate of polymerization of *n*-butyl acrylate was studied by varying the concentrations in the range of 1.5–6.5 mol dm^{-3}. The R_p was found to an

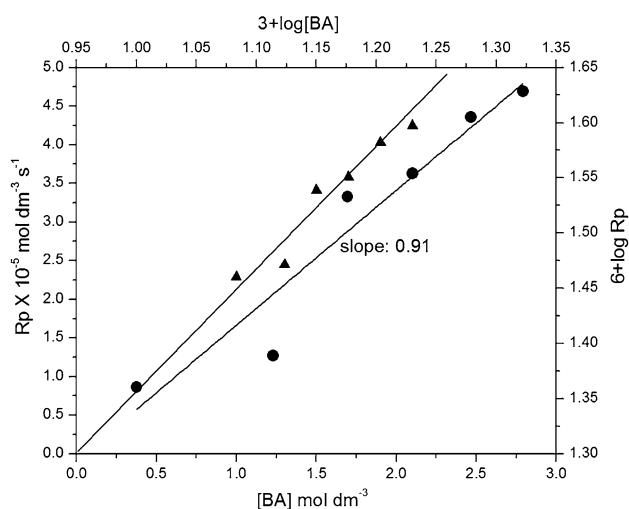**Fig. 2** Effect of [BA] on the R_p. Polymerization condition: [PDS]: 2.0×10^{-2} mol dm^{-3}; [CTMAB]: 2.0×10^{-2} mol dm^{-3}; [H$^+$]: 0.5 mol dm^{-3}; [μ]: 0.2 mol dm^{-3}; temp: 60 ± 2 °C; time: 40 min
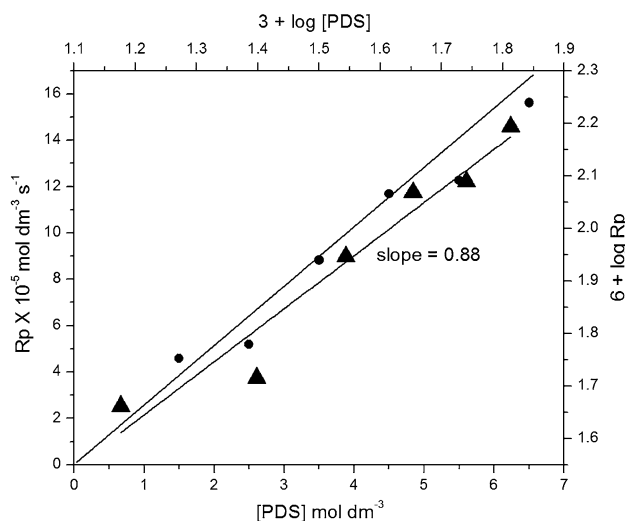
Fig. 3 Effect of [PDS] on the R_p. Polymerization condition: [BA]:2.0 mol dm^{-3}; [CTMAB]: 2.0×10^{-2} mol dm^{-3}; [H$^+$]:0.5 mol dm^{-3}; [μ]: 0.2 mol dm^{-3}; temp: 60 ± 2 °C; time: 40 min

increase with an increasing concentration of PDS in this system. From the plot of $6 + \log R_p$ versus $3 + \log$ [PDS], the slope (0.88) is almost equal to unity. As expected, a plot of R_p versus [PDS] is linear passing through the origin supporting the above deduction (Fig. 3). Similar order of reaction with respect to initiator concentration has been reported for the polymerization of other vinyl monomers [29, 31, 32, 40] using different phase transfer catalyst initiated by PDS. The higher order of polymerization in the case of initiator variation may be either due to gel effect or diffusion-controlled termination rate constant [40].

Effect of [PTC] on the rate of polymerization (R_p)

The effect of concentration of phase transfer catalyst (PTC), cetyltrimethylammonium bromide (CTMAB), on the rate of polymerization was studied by varying its concentration in the range of 1.5–6.5 mol dm^{-3} at definite concentrations of other parameters. The rate of polymerization (R_p) was increased with an increasing concentration of PTC for *n*-butyl acrylate system. The order with respect to the concentration of the PTC was found to be around unity (0.97) from the plot of $6 + \log R_p$ versus $3 + \log$ [PTC]. Also the plot of R_p versus [PTC] passing through origin confirms that the observations with respect to [PTC] (Fig. 4). The polymerization did not occur in the absence of catalyst even after several minutes.

Effect of ionic strength (μ) and [H$^+$] variation

The effect of ionic strength was observed by varying the ionic strength in the range of 0.40–0.60 mol dm^{-3}. The variation of ionic strength was found to exert no significant change in the rate of polymerization. In addition, the effect of [H$^+$] variation was observed by varying the acidic concentration in the range of 0.10–0.30 mol dm^{-3}. The variation of [H$^+$] is found to exert no significant change in the rate of polymerization. This kind of common observations was reported in polymerization of different acrylate monomer using various phase transfer catalyst [20–23].
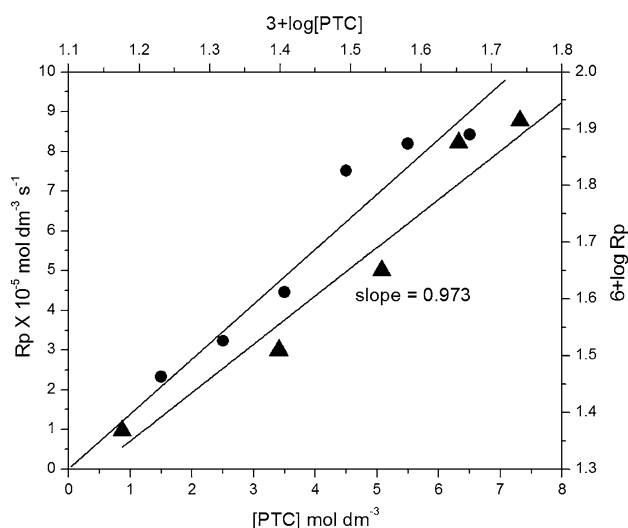

Fig. 4 Effect of PTC concentration on the R_p. Polymerization condition: [BA]: 2.0 mol dm^{-3}; [PDS]: 2.0×10^{-2} mol dm^{-3}; [H$^+$]: 0.5 mol dm^{-3}; [μ]: 0.2 mol dm^{-3}; temp: 60 ± 2 °C; time: 40 min

Effect of temperature on R_p

The effect of variation of temperature from 45 to 60 °C on the rate of polymerization was studied by keeping the variables such as n-BA, PDS, PTC, ionic strength and pH constant. The rate of polymerization increases with an increase in temperature. The overall activation energy of polymerization (E_a) obtained from plot of log R_p versus $1/T$ is 66.36 kJ/mol for n-butyl acrylate system (Fig. 5). The higher E_a (91.35 kJ/mol) value was reported for the polymerization of n-BA using di-site PTC [ref]. From the activation energy value we can conclude that current study has more efficiency than reported [35]. The thermodynamic parameters such as entropy of activation ($\Delta S^{\#}$), enthalpy of activation ($\Delta H^{\#}$) and free energy of activation ($\Delta G^{\#}$) have been calculated and reported in Table 1.
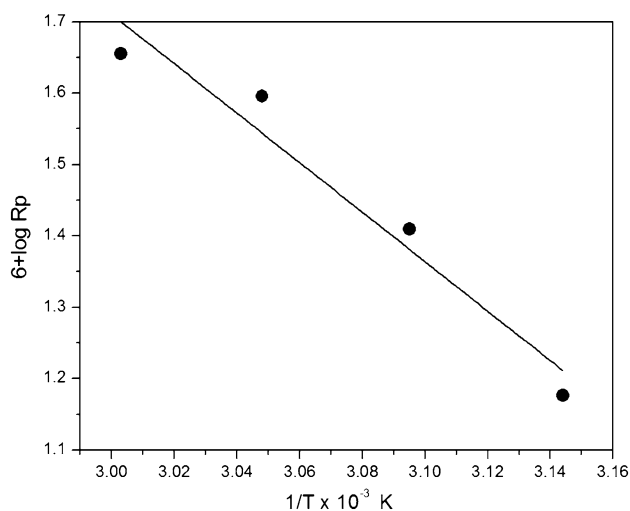

Fig. 5 Effect of temperature on the R_p. Polymerization condition: [BA]: 2.0 mol dm^{-3}; [PDS]: 2.0×10^{-2} mol dm^{-3}; [CTMAB]: 2.0×10^{-2} mol dm^{-3}; [H$^+$]: 0.5 mol dm^{-3}; [μ]: 0.2 mol dm^{-3}; time: 40 min

Table 1 Thermodynamic parameters

E_a (kJ/mol)	$\Delta G^{\#}$ (kJ/mol)	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (EU)
66.36	55.24	176.72	−95.75

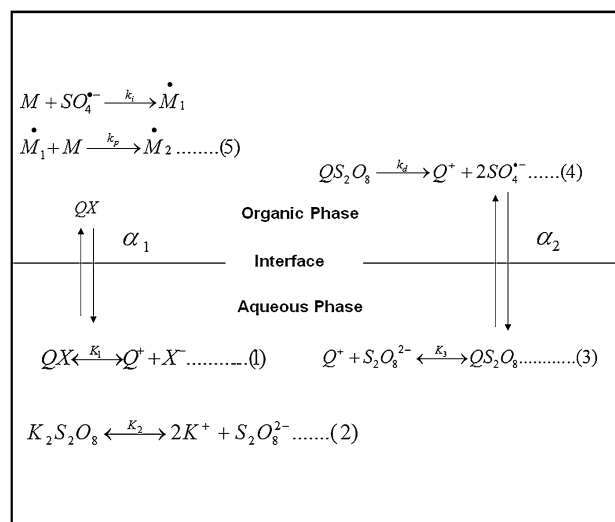## Effect of organic solvent polarity on R_p

The effect of organic solvents on R_p was examined by carrying out the polymerization of n-butylacrylate in three solvents, cyclohexane, ethylacetate and cyclohexanone having the dielectric constants 2.02, 6.02 and 18.03, respectively. It was found that the R_p decreased in the following order:

Cyclohexanone > Ethylacetate > Cyclohexane

An increase in the rate of polymerization may be due to an increase in polarity of the medium which makes easy transfer of more species of peroxydisulfate to the organic phase [41] (Table 2).

Radical mechanism of n-BA–PTC–PDS in two-phase system

Scheme 3 represents the reactions characterizing the polymerization of n-butyl acrylate (M) initiated by PDS/ PTC in ethyl acetate/water two-phase systems. It is assumed that dissociation of QX and K$_2$S$_2$O$_8$, formation of QS$_2$O$_8$ in aqueous phase, and initiation of monomer in

Scheme 3 Polymerization pathways of n-BA–PTC–PDS in an aqueous organic two-phase system

Table 2 Effect of solvents

Experimental conditions	$R_p \times 10^{-5}$ mol dm^{-3} s^{-1}		
	Cyclohexanone (18.3)	Ethylacetate (3.91)	Cyclohexane (1.13)
[BA]: 2.0 mol dm^{-3} [PDS]: 2.0×10^{-2} mol dm^{-3} [PTC]: 2.0×10^{-2} mol dm^{-3} [H$^+$]: 0.5 mol dm^{-3} [μ]: 0.2 mol dm^{-3}; temp: 60 ± 2 °C	2.50	1.65	1.08

organic phase occur along the reactions shown in 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 QX and QS_2O_8 are defined as follows, respectively,

$$K_1 = \frac{[Q^+]_w[X^-]_w}{[QX]_w} \tag{6}$$

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

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

$$\alpha_1 = \frac{[Q^+X^-]_w}{[QX]_o} \tag{9}$$

$$\alpha_2 = \frac{[Q^+S_2O_8^{2-}]_w}{[QS_2O_8]_o}. \tag{10}$$

The initiation rate (R_i) of radical SO_4^- in Eq. (4) may be represented as follows, f is initiator efficiency

$$R_i = \frac{d[SO_4^{0-}]}{dt} = 2K_d f K_3[Q^+]_w[S_2O_8^{2-}]_w. \tag{11}$$

The growth of polymer chain is according to the reaction in Eq. (5), the propagation step is represented as follows

$$\overset{0}{M}_1 + M \overset{K_p}{\longrightarrow} \overset{0}{M}_n \tag{12}$$

$$\cdots \quad \cdots \quad \cdots$$
$$\cdots \quad \cdots \quad \cdots$$

$$\overset{0}{M}_{n-1} + M \overset{K_p}{\longrightarrow} \overset{0}{M}_n \tag{13}$$

The rate of propagation (R_p) step in the reaction in Eq. (12) is given as

$$R_p = k_p\overset{0}{[M]}[M] \tag{14}$$

$$\overset{0}{[M]} = \frac{R_p}{k_p[M]} \tag{15}$$

The termination occurs by the combination of two growing polymer chain radicals, it can be represented as

$$2\overset{0}{M}_n \longrightarrow k_t\text{polymer} \tag{16}$$

The rate equation of termination (R_t) process according to the Eq. (16)

$$R_t = 2k_t\overset{0}{[M]}^2 \tag{17}$$

The steady state prevails, the rate of initiation equals to rate of termination, i.e.,

$$R_i = R_t \tag{18}$$

$$2K_d f K_3[Q^+]_w[S_2O_8^{2-}]_w = 2k_t[M^0]^2 \tag{19}$$

$$\overset{0}{[M]}^2 = \frac{K_d f K_3[Q^+]_w[S_2O_8^{2-}]_w}{k_t} \tag{20}$$

$$\overset{0}{[M]} = \left[\frac{K_d f K_3[Q^+]_w[S_2O_8^{2-}]_w}{k_t}\right]^{1/2} \tag{21}$$

Using Eqs. (15) and (21), the rate of polymerization is represented as follows

$$R_p = k_p\left[\frac{k_d K_3 f}{k_t}\right]^{1/2}[Q^+]_w^1[S_2O_8^{2-}]_w^1[M]^1 \tag{22}$$

The above equation satisfactorily explains all the experimental observations. The expression for the degree of polymerisation is

$$\bar{P}_n = \frac{R_p}{R_t} \tag{23}$$

$$\overline{P_n} = \left[\frac{K_p[M]}{2(K_3k_tk_df)^{1/2}[Q^+]_w^1[S_2O_8]_w^1}\right] \tag{24}$$

This Eq. (24) for the degree of polymerization $\bar{P}_n$ is directionally proportional to [M] ^{1}. It is found that a plot of $\bar{P}_n$ versus [M]^1 gives straight line passing through the origin for n-butyl acrylate system (Fig. 6). This observation supports the proposed mechanism.

Characterization of polymer: FT-IR analysis

The FT-IR spectrum of poly(n-butyl acrylate) was recorded with a Perkin-Elmer RXI spectrophotometer in the spectral region from 4500 to 500 cm^{-1}. The pellets of about 25 mg of polymer in KBr powder containing grained powder of sample were made before recording. The FT-IR
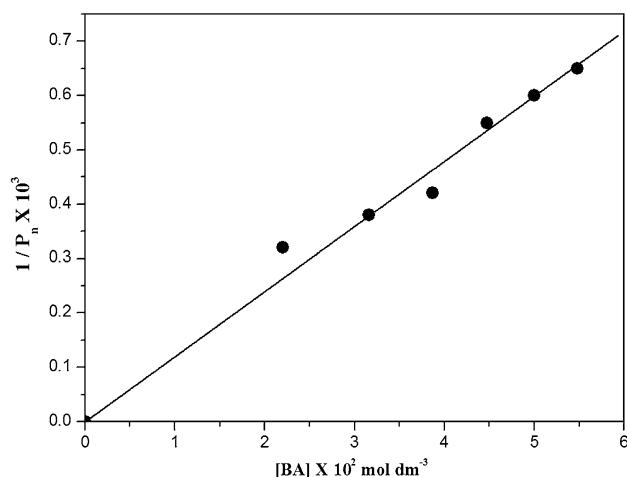
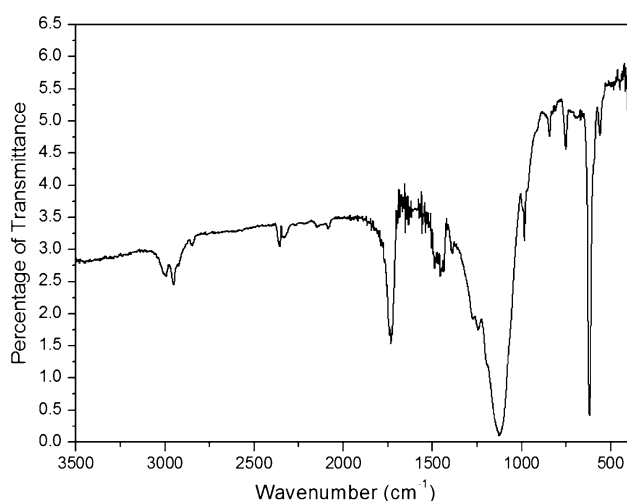**Fig. 6** n-BA–PTC–PDS system dependence of P_n on [n-BA]

Fig. 7 FT-IR spectral analysis of poly(*n*-butylacrylate)

spectroscopy confirms a band of 1732 cm^{-1} of ester group of poly(butylacrylate) (Fig. 7). The following bands were observed in the spectra 1125–1260 cm^{-1} (C–O–C stretching band), 1455 cm^{-1} (C–H deformation), 2950 cm^{-1} (C–H stretching band).

Conclusions

The present work shows that the radical polymerization of *n*-butylacrylate was successfully performed with the help of PTC–PDS in two-phase system. The kinetic features, the rate of polymerization (R_p) of *n*-butylacrylate, were increased with an increasing concentration of monomer, initiator and catalyst. The hydrogen ion concentration and ionic strength of the medium do not show any appreciable effect on the R_p. The reaction rate increases with an increasing temperature. The phase transfer-catalyzed polymerization of *n*-butylacrylate follows the order of unity with respect to monomer, initiator and catalyst. Based on the results obtained, a suitable mechanism has been proposed. The obtained results showed that the rate of polymerization was more efficient than the reported. The polymer obtained by free-radical polymerization of butylacrylate was confirmed by FT-IR spectral analysis. The versatile nature and use of PTC resulted in high reaction rate in heterogeneous (two-phase) system. This could be a practical interest in the preparation of polymers and organic compounds in which reagents incompatibility problem often occurs and in which PTC is frequently used as a way to bring the reactant together.

Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest regarding the publication of this article.

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