Comparative investigation on radical polymerization of methyl and ethyl methacrylate under multi-site phase-transfer catalytic conditions

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Abstract

Methyl and ethyl methacrylate was polymerized in heterogeneous system with the help of newly synthesized multi-site phase-transfer catalyst and using water-soluble initiator at 60 ± 1 °C under unstirred inert atmospheric condition. Polymer yield was increased with increasing molar concentrations of monomer, initiator, catalyst and temperature. Polymerization follows first-order kinetics with respect to monomer and half-order with respect to catalyst and initiator, respectively. PTC has myriads of applications in the synthesis of various organic and polymeric materials because of its fast reaction and high yield in short period of time. Without addition of PTC, polymerization did not occur; this indicates that catalyst plays the pivotal role on initiation of polymerization. It extracts the reactive radical anion from aqueous phase and transfers to the organic phase where acrylates were polymerized. Polymerization reactivity of methyl and ethyl methacrylate under PTC conditions was studied by various parameters. The activation energy (E_a) and other thermodynamic parameters were calculated. The E_a value supports the reactivity of acrylates. The results obtained from this investigation were used for inferring the radical mechanism of phase-transfer-catalyzed polymerization. The obtained polymers were analyzed by spectral and thermal analyses.

Keywords Kinetics · Multi-site phase-transfer catalyst · Rate of polymerization · Two-phase system · Methyl and ethyl methacrylate

Introduction

Acrylates containing polymers have potential applications in industries like textile, surface coating, automotive, aerospace, biomedical to optics and microelectronics, etc. because of their surface-free energy properties and water/oil repellence, etc. [1, 2]. Synthesis of acrylates polymers with controlled molecular weight distributions and low polydispersity index (PDI) is one of the key parameters to realize any kind of applications and synthesis of such acrylates polymers has attracted remarkable attention between polymer chemists and industrial community. Among the various polymerization techniques, free radical polymerization is one of the simplest and well-known best techniques for

synthesizing poly (alkyl acrylates/alkyl methacrylates) with different composition, structures, and functionalities and with low dispersity, as this polymerization can be carried out at room and or moderately high temperature with less-stringent reaction condition compared to anionic polymerization [3–9].

The discovery and establishment of nitroxide-mediated stable free radical polymerization (NMP) [3, 7], radical addition fragmentation chain transfer polymerization (RAFT) [5, 8], atom transfer radical polymerization (ATRP) [4, 6] and degenerative chain transfer polymerization [10, 11] contributed an incredible advancement in the area of controlled living radical polymerization of alkyl acrylates/alkyl methacrylates for the past few decades. Consequently, in the verge of these polymerization techniques, phase-transfer-catalyzed polymerization is one of the recognized and established techniques for the polymerization of alkyl methacrylates in heterogeneous condition using water-soluble initiator. PTC is the most important innovative technique for promoting reactions between lipophilic and hydrophilic reactants. In

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which one reactant is lipophilic and the other is hydrophilic, high rates of reaction can be attained by adding PTC and it helps to overcome the immiscibility of the reactants during the reaction. In this technique, the monomer (acrylates) was dissolved in the organic solvent and initiator (PDS) is dissolved in water, these mixtures are immiscible in nature and then by adding PTC, polymerization reaction occur through the transport of one reactant into the other phase. The advantages of PTC are well documented in the literature [12–15].

There are several reports on polymerization of various alkyl methacrylates was reported using different PTC [16–27]. According to these reports, the comparative and reactivity of methyl and ethyl methacrylate under multi-site phase-transfer catalytic conditions is limited. In this context, herein we report the polymerization of methyl and ethyl methacrylate under multi-site phase-transfer catalytic conditions. In this study, we observe that the reactivity of EMA is faster than MMA on the rate of polymerization and it was supported by Arrhenius plot. Further, the influence of various reaction parameters on the rate of polymerization (R_p) of methyl and ethyl methacrylate was studied and discussed in detail.

Experimental

Reagents and solvents

Methyl methacrylate (MMA) and ethyl methacrylate (EMA) supplied by Lancaster, India were purified by washing with 5 wt% of sodium hydroxide to remove inhibitor and then dried with calcium chloride overnight and distilled over calcium hydride under reduced pressure prior to use. The initiator potassium peroxydisulphate (PDS, Aldrich, India) was purified twice by recrystallization in cold water. The multi-site phase-transfer catalyst (TMBPEDBC as multi-site PTC) was synthesized by adopting reported procedure [24, 25]. All the solvents were of reagent grade and were purchased from Finar, Avra, India. The double distilled water is used to make an aqueous phase.

Synthesis of multi-site phase-transfer catalyst (TMBPEDBC)

N, N, N', N'-tetramethylethylenediamine (0.01 mol) was dissolved in ethanol (10 mL), taken in a two-necked round-bottom flask and stirred at 70 °C. The *n*-propyl bromide (0.01 mol dissolved in ethanol) was added dropwise. After 1 h, a solution of benzyl chloride (0.01 mol dissolved in ethanol) was added slowly 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 white precipitate of 1, 1, 2,

2-tetramethyl-1-benzyl-2-*n*-propylethylene-1, 2-diammonium bromide chloride (TMBPEDBC) was obtained. It was purified by dissolving a minimum amount of catalyst in ethanol and diffusing over hexane; pure white precipitate was collected and dried [24, 25]. The yield and melting point of the catalyst were 78% and 210 °C, respectively (Scheme 1).

Polymerization of methyl and ethyl methacrylate

Polymerization experiments were carried out in a specially designed borosil glass tube with dimensions of 30 and 26 mm for outer and inner diameter, respectively, and 120 mm height. The polymerization glass tube consists of equal volume of organic and aqueous phase. The monomer in ethyl acetate was the organic phase and aqueous phase containing specified concentrations of initiator, catalyst and acid (for maintaining pH). The tube containing above mixture was bubbled by passing nitrogen gas for 20 min to remove dissolved oxygen completely from polymerization system and then it was sealed. The reaction tube was then placed in a temperature-controlled water bath at 60 ± 1 °C (Fig. 1). After the stipulated time, polymerization was terminated by pouring reaction mixture into cold methanol. Finally, the resultant polymer was filtered (Fig. 2) and dried in vacuum oven at 60 °C.

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; and M is the molecular weight of the monomer in g/mol. The kinetic experiments were carried out by changing the concentration of monomer, initiator, catalyst and temperature, etc. by adopting aforementioned polymerization procedure as depicted in Scheme 2.

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

Fig. 1 Polymerization reaction setup: **a** Temperature-controlled water bath, **b** Polymerization reaction tube consists of equal volume of aqueous and organic phase

Fig. 2 Differences in the rate of precipitations of **a** poly (methyl methacrylate) and **b** poly (ethyl methacrylate)

Scheme 2 Multi-site phase transfer catalyzed radical polymerization of methyl and ethyl methacrylate in two-phase system

Instruments

The FT-IR spectrum of poly (alkyl methacrylate) was recorded on an FT-IR spectrometer (JASCO) in the spectral region from 3500 to 500 cm^{-1} . A pellet of polymer samples was made with KBr on recording of spectrum. The thermal analyses of poly(methyl methacrylate) and poly (ethyl methacrylate) were carried out using TA (DSC Q10, TGA Q600)

instruments; Pyris diamond DSC/TGA analyzer; sample weight 3.0540 mg of PMMA and 4.9055 mg of PEMA at heating rate 15°C per minutes with the temperature range of 30–600 °C. The wide-angle X-ray diffraction was recorded using PAN Analytical Xpert PRO instrument operated at the Cu K α radiation wavelength of 1.54 Å at 45 mA and 40 kV.

Reaction model

In heterogeneous reactions, the rate of reaction depends on the interaction and diffusion between two phases. The reaction between two immiscible reactants is low due to less collision between them. The common way to address such difficulty is to carry out the reaction at high temperature and using a co-solvent. However, such conditions are generally limited because of side reactions and complexity in choosing co-solvent. Generally, in a heterogeneous medium the rate of reaction dramatically enhanced with the help of phase-transfer catalyst (PTC). PTC is capable of extracting and transferring ionic reactants of aqueous and or solid phase into organic phase, where the reaction will take place. An extraction mechanism was presumed for the polymerization process, the quaternary ammonium salt (QX) is dissolve well in the aqueous phase and react with initiator (KY), then produces radical anion (QY) at the interface between the phases. Subsequently, PTC transfers the radical anion (QY) from the aqueous phase into organic phase where the polymerization occurs at 60 ± 1 °C. A typical phase-transfer-catalyzed radical polymerization cyclic process is shown in Scheme 3.

Results and discussion

In an attempt to verify the reaction kinetics model and explore the role of monomers, initiator, catalyst, temperature and aqueous phase variation on the rate of polymerization (R_p) were investigated in cyclohexane–water two-phase systems at 60 ± 1 °C.

Steady-state rate of polymerization

The plot of R_p versus time for the polymerization of methyl and ethyl methacrylate (RMA) using initiator (PDS), multi-site PTC (TMBPEDBC) and with the fixed concentrations of all other parameters is shown in Fig. 3. The rate of polymerization (R_p) increases nicely to some extent, slightly decreases thereafter and reaches the constant value [22]. The steady-state rate of polymerization of RMA was arrived at 50 min. The role of various reaction parameters on the rate of polymerization was studied at steady-state time.

Scheme 3 Reaction model for the polymerization of alkyl methacrylate in two-phase system

Fig. 3 Steady-state rate of polymerization. Reaction condition: [RMA]: 2.0 mol dm^{-3} ; [PDS]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; [TMBPEDBC]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+]$: 0.50 mol dm^{-3} ; $[\mu]$: 0.20 mol dm^{-3} ; Temperature: $60 \pm 1^\circ \text{C}$

Role of [RMA] on R_p

Generally, most of the polymerization rate is first-order dependence with respect to monomer concentration. We have studied polymerization rate of the methyl and ethyl methacrylate concentrations in the range of $4.5\text{--}9.5 \text{ mol dm}^{-3}$ by keeping other parameters constant. R_p increases with an increase in the concentration of the monomers. We observed that the polymerization rate is higher for EMA as compared to MMA is may attributed to possession electron donating group in EMA. Figure 4 shows the half-order relationship for the polymerization of methyl and ethyl methacrylate. The plot of R_p versus [RMA] passing through the origin confirms the above observations with respect to [RMA]. The deviation from the first-order relationship is due to the dependence of initiation rate on the monomer concentration. The half-order with respect to concentration of monomer

Fig. 4 Role of [RMA] on the R_p . **a** Plot of $6 + \log R_p$ versus $3 + \log [RMA]$. **b** Plot of R_p versus [RMA]. Reaction condition: [PDS]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; [TMBPEDBC]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+]$: 0.50 mol dm^{-3} ; $[\mu]$: 0.20 mol dm^{-3} ; Temperature: $60 \pm 1^\circ \text{C}$; Time: 50 min

has been reported for the polymerization of n-butyl methacrylate and ethyl methacrylate with other multi-site PTC using potassium peroxydisulphate as initiator [24, 26, 27].

Role of [PDS] on R_p

To check the role of initiator on polymerization rate, we conducted the polymerization using the initiator concentrations in the range of 1.5–2.5 mol dm⁻³ at fixed concentrations of other parameters. It was observed that the rate of polymerization increases with rise of initiator concentration. Figure 5a shows initiator dependence order value of 0.59 and 0.80 for MMA and EMA, respectively. It was obtained from the plot of $6 + \log R_p$ versus $3 + \log [\text{PDS}]$. As expected, the plot of R_p versus [PDS] is linear passing through the origin supporting the above deduction in Fig. 5b. Generally, polymerization rate is to be dependent on the square root of the initiator concentration. The deviation of square root relationship of initiator is due to the termination occurring by combination of primary radicals and gel effect or diffusion-controlled termination constant [16].

Role of [TMBPEDBC] on R_p

Polymerization rate was explored using multi-site PTC (TMBPEDBC) in the concentration range of 1.5–2.5 mol dm⁻³ at fixed other parameters. It was found that the rate of polymerization of MMA and EMA increases with increasing concentration of catalyst. The amount and formation of QS₂O₈ (quaternary ammoniumperoxydisulphate complex) are increased with increasing catalyst (dual active-site) concentration. The highly concentrated QS₂O₈ complex is decomposed and produces more radical anion which accelerates the polymerization fast and it may lead to increase in the polymerization rate. As shown in Fig. 6a, the plot of $6 + \log R_p$ versus $3 + \log [\text{TMBPEDBC}]$, the order with respect to catalyst was found to be 0.63 and 0.42 for MMA and EMA. The observed order was confirmed by the plot of R_p versus [TMBPEDBC] as shown in Fig. 6b. To establish the role of catalyst in this polymerization system, we performed the blank experiment: First of all, we observed that the PDS alone did not initiate the polymerization in two-phase system under our reaction conditions. The changes in the appearance of two-phase media was observed (slight turbid) but while pouring the reaction mixture into methanol it was disappeared. The polymerization did not occur in the absence of catalyst even after several minutes. This observation was the proof for role of catalyst on the polymerization reaction.

Fig. 5 Role of [PDS] on the R_p . **a** Plot of $6 + \log R_p$ versus $3 + \log [\text{PDS}]$. **b** Plot of R_p versus [PDS]. Reaction condition: [RMA]: 2.0 mol dm⁻³; [TMBPEDBC]: 2.0×10^{-2} mol dm⁻³; [H⁺]: 0.50 mol dm⁻³ [μ]: 0.20 mol dm⁻³; Temperature: 60 ± 1 °C; Time: 50 min

Role of temperature on R_p

The role of temperature (T) on the polymerization reaction was varied from 50 to 65 °C. The plot of $\log R_p$ versus $1/T$ is shown in Fig. 7. The gradual increase in R_p with varying temperature was observed. An increase in the rate of polymerization is attributed to fast formation rate of radicals and intensive nucleation which are responsible for accelerating the polymerization process promptly and, thereby, the rate of polymerization was increased significantly. The Arrhenius equation with activation energy of polymerization (E_a) was found to be 10.20 and 8.59 k J/mol for MMA and EMA, respectively. The lower value of E_a of EMA suggested that the polymerization reaction occurs quickly as compared with MMA under multi-site phase-transfer catalytic condition. The thermodynamic parameters such as entropy of activation ($\Delta S^\ddagger$), enthalpy of activation ($\Delta H^\ddagger$) and free energy

Fig. 6 Role of [TMBPEDBC] on the R_p . **a** Plot of $6 + \log R_p$ versus $3 + \log [\text{TMBPEDBC}]$. **b** Plot of R_p versus [TMBPEDBC]. Reaction condition: [RMA]: 2.0 mol dm^{-3} ; [PDS]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+]$: 0.50 mol dm^{-3} ; $[\mu]$: 0.20 mol dm^{-3} ; Temperature: $60 \pm 1^\circ\text{C}$; Time: 50 min

of activation ($\Delta G^\ddagger$) have been calculated and presented in Table 1. The comparison of E_a value for different alkyl methacrylate under phase-transfer catalytic polymerization was reported [20, 28, 29]. The overall activation energy of 72.80 kJ/mol was reported for the polymerization of MMA using diphenyldisulphide and Cu (II) ion system [33].

Role of organic solvents polarity on R_p

The role of organic solvents polarity on the R_p was examined under aforementioned conditions. The organic solvents involved in the investigation are 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 > ethyl acetate > cyclohexane. An increase in the rate of polymerization was attributed to the increase in the polarity of the solvents,

Fig. 7 Role of temperature on the R_p Reaction condition: [RMA]: 2.0 mol dm^{-3} ; [PDS]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; [TMBPEDBC]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+]$: 0.50 mol dm^{-3} ; $[\mu]$: 0.20 mol dm^{-3} ; Time: 50 min

Table 1 Thermodynamic parameters of RMA

Monomer	$E_a \text{ kJ/mol}$	$\Delta G^\ddagger \text{ kJ/mol}$	$\Delta H^\ddagger \text{ kJ/mol}$	$\Delta S^\ddagger \text{ kJ/mol}$
MMA	10.20	40.96	4.118	-110.68
EMA	8.59	43.89	3.28	-121.98

Table 2 Role of organic solvents polarity on R_p

Solvents	Dielectric constant (ϵ)	$R_p \times 10^5 \text{ mol L}^{-1} \text{ s}^{-1}$ (MMA)	$R_p \times 10^5 \text{ mol L}^{-1} \text{ s}^{-1}$ (EMA)
Cyclohexanone	18.3	3.04	2.83
Ethyl acetate	3.91	2.90	1.96
Cyclohexane	2.02	2.02	1.09

[RMA]: 2.0 mol L^{-1} ; [PDS]: $2.0 \times 10^{-2} \text{ mol L}^{-1}$; [TMBPEDBC]: $2.0 \times 10^{-2} \text{ mol L}^{-1}$; $[\text{H}^+]$: 0.5 mol L^{-1} ; $[\mu]$: 0.2 mol L^{-1} ; Temperature: $60 \pm 1^\circ\text{C}$; Time: 50 min

which facilitates greater transfer of peroxydisulfate ion from aqueous phase to organic phase [27–29] (Table 2).

Role of variation of aqueous phase on R_p

The role of aqueous (liquid) phase is playing the pivotal role in the phase-transfer-catalyzed reactions. The role of aqueous phase on the rate of polymerization of MMA and EMA under phase-transfer catalytic conditions was explored in polymerization and the reactions were conducted with a constant volume of organic phase and changing the volumes of aqueous phase ($V_w/V_o = 0.29\text{--}0.90$) at fixed concentrations of all other parameters for MMA and EMA (Fig. 8). The

Fig. 8 Role of aqueous phase on the R_p . Reaction condition: [RMA]: 2.0 mol dm^{-3} ; [PDS]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; [TMBPEDBC]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[H^+]$: 0.50 mol dm^{-3} ; $[\mu]$: 0.20 mol dm^{-3} ; Time: 50 min; Temperature: $60 \pm 1^\circ\text{C}$

variation of aqueous phase was found to exert no significant change in the rate of polymerization for both alkyl methacrylates. It has been reported that the variation of aqueous phase on R_p was not affected significantly on phase-transfer-catalyzed polymerization studies [18–27].

Role of ionic strength and pH on R_p

The role of ionic strength and pH is an important parameter in the polymerization reaction. The pH may influence the polymerization rate by coagulating the dispersed phase and affecting the initiation step. The adding and presented ions may cause a change in the ionic strength of the medium and it leads to a change in the initial and limiting conversion rate in polymerization. In this investigation, ionic strength

and pH of the medium do not influence much on the polymerization rate. A similar kind of behavior was reported in phase-transfer-catalyzed polymerization of vinyl monomers [19–25].

Relative reactivity of methyl and ethyl methacrylate on R_p

Generally, acrylate monomers can be polymerized either by free radical or ionic methods. The type of polymerization depends on the nature of reactive functional moiety present in monomer molecules. Most of the monomers will undergo polymerization with a radical initiator at varying rates. Methyl and ethyl methacrylate containing carbon–carbon double bond is responsible for polymerization and its carbonyl group is not prone to polymerization by radical initiators because of its polarized nature. However, the type of substitute on the C=C double bond of acrylate monomers determines the reactivity and rate of polymerization. From the investigation, we observed that the rate of polymerization of EMA is greater compared to MMA (Table 3; Fig. 2). These trends can be explained in terms of inductive effect and steric effects. An increase in the rate from methyl to ethyl is attributed to the greater electron-donating tendency of ethyl ($-\text{CH}_2\text{CH}_3$ of EMA) as compared with methyl group ($-\text{CH}_3$ group of MMA) [30]. An increased electron-donating tendency (of EMA) is facilitating the easy opening of the double bond and in this way increases the rate of addition of monomer to the polymer radical. The steric differences between MMA and EMA become insignificant in the rate of polymerization (steric effects may become important with more substituent) [31, 32]. The vinyl monomers such as MMA, EMA, n-BMA, styrene and acrylonitrile were polymerized using DPDS and Cu (II) system [33]. Among these monomers, EMA was polymerized easily compared to other monomers. The order of ease of

Table 3 Comparison of the relative reactivity of RMA

Parameters	Methyl methacrylate (MMA)	Ethyl methacrylate (EMA)
Structure		
R_p value ($\text{mol L}^{-1} \text{s}^{-1}$)	3.0241×10^{-5}	1.7885×10^{-5}
E_a (kJ/mol)	10.20	8.59
Inductive effect (electron-donating power)	Less because of possessing methyl group	More because of possessing ethyl group
Steric effect (atom of molecules occupies space)	Insignificant	Insignificant

polymerization is as follows: EMA > MMA > n-BMA > styrene > AN. This reported observation and the above explanation clearly support the polymerization reactivity of EMA and MMA under phase-transfer catalyst condition.

Polymerization reaction mechanism

On the basis of the observed experimental conditions, the polymerization reaction mechanism for alkylmethacrylates in the presence of multi-site PTC (TMBPEDBC) and potassium peroxydisulphate was proposed as shown in Scheme 4. Initially, the formation of QS_2O_8 took place in the aqueous phase on reaction between multi-site PTC (QX_2) and initiator ($K_2S_2O_8$). The intermediate (QS_2O_8) complex is decomposed and forms a radical anion at the interface which initiates the polymerization reaction.

The equilibrium constants (K_1 and K_2) in the reactions in Eq. (1) to (3) and distribution constants (α_1 and α_2) of QX and QS_2O_8 are defined as follows, respectively:

$$K_1 = \frac{[Q^{2+}]_w [X^-]_w^2}{[QX]_w} \quad (6)$$

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

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

$$\alpha_1 = \frac{[Q^{2+}X_2^-]_w}{[QX]_o} \quad (9)$$

Scheme 4 Polymerization reaction mechanism of RMA-TMB-PEDBC-PDS in two-phase system

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

Applying general principles of free radical polymerization and steady-state hypothesis to radical species, the rate law for this mechanism can be derived [22, 28] as follows:

$$R_p = k_p \left[\frac{k_d K_3 f}{k_t} \right]^{1/2} [Q^{2+}]_w^{0.50} [S_2O_8^{2-}]_w^{0.60} [M]^{0.50} \quad (11)$$

Analysis of poly (alkyl methacrylates)

FT-IR analysis of poly (alkyl methacrylate)

Figure 9 depicts the FT-IR spectrum of obtained PMMA and PEMA. The observed frequency confirms an ester functional stretching band of poly (methyl methacrylate) and poly (ethyl methacrylate) at 1732 and 1734 cm^{-1} , respectively. The following bands were also observed in the spectra of PMMA (cm^{-1}): 1128–1262 (C–O–C stretching band), 1458 (C–H deformation), 2952 (C–H stretching band) and PEMA (cm^{-1}): 1260 (C–O–C stretching band), 1470 (C–H deformation), 3042 (C–H stretching band). All the characteristics bands corresponding to the synthesised poly (alkyl acrylates) were in good agreement with their pristine polymers [34–36].

TG-DSC analysis of poly (alkyl methacrylate)

TGA analysis is mainly used to examine thermal stability and degradation temperature of polymers. The thermal stabilities of poly (alkyl methacrylate) were studied by TG analysis. Figure 10 shows the TG curve of both polymers. The thermogram of PMMA and PEMA showed no weight

Fig. 9 FT-IR spectral analysis of poly (alkyl methacrylate)

loss up to 150 and 200 °C, respectively. PMMA showed a weight loss of about 17% in the range of 250–375 °C and in the third stage PMMA has a weight loss about 80.50% due to 375–420 °C and the remaining left as a residue. In PEMA thermogram, the first weight loss of the polymer is about 5.57% at 200–215 °C is may bedue to absorbed water. In the second stage, the weight loss of 15.17% observed at 215–485 °C. The extensive degradation of polymer occurs at 485–576 °C with loss of 80% and then finally leaves residue of the polymer of the sample.

DSC analysis was carried out to observe the changes like fusion, glass transition temperature (T_g) and crystallization of polymers. The glass transition of amorphous polymers or amorphous domains of semi-crystalline polymers marks the change from a glassy to a rubbery state. The softening physical nature of the polymers was characterized by T_g . Further, T_g depends on tacticity, molecular weight and solvent used. Figure 11 depicts the DSC thermogram curve of synthesised PMMA and PEMA. The glass transition temperature (T_g) was estimated at the inflection point between the onset and end set temperature. The glass transition temperature (T_g) value of PMMA and PEMA was observed at 107 and 65 °C, respectively [37].

XRD analysis of poly (alkyl methacrylate)

The XRD is generally used to delineate nature of polymers that is amorphous or crystalline in nature, etc. The d-spacing is determined from the peak position using Bragg's law: $n\lambda = 2d\sin\theta$, where λ is the wavelength of the X-rays and n is positive integer. Figure 12 shows the XRD pattern of the synthesised PMMA and PEMA. The diffraction patterns of both polymers show very broad diffraction peak at low angle in the range of 10° to 30°. A typical amorphous material exhibits few band of low intensities centred at 30° and 42° [38]. It revealed that both polymers have predominated amorphous nature.

Fig. 10 Thermo gravimetric analysis of poly (alkyl methacrylate)

Fig. 11 DSC analysis of poly (alkyl methacrylate)

Conclusions

The new multi-site phase-transfer catalyst (TMBPEDBC) was synthesized and employed in polymerization of MMA and EMA using water-soluble initiator. The relative reactivity of MMA and EMA was explored under phase-transfer catalytic conditions by various reaction parameters. The results showed that the reactivity of EMA is faster than MMA. Increases in the rates from MMA to EMA are attributed to the greater electron-donating power of the ethyl group as compared with methyl. The steric difference between methyl and ethyl is probably unimportant. In addition to that, the reactivity of alkyl methacrylate was well supported by the activation energy of polymerization reaction. The obtained poly (alkyl methacrylate) was analyzed by thermal and spectral analyses. Herein the reported

Fig. 12 XRD analysis of poly (alkyl methacrylate)

polymerization process was followed half order with respect to monomer, initiator and catalyst. Phase-transfer catalyst showed great potential applications for synthesis of polymers and organic compounds. We believe that the integration of PTC with other technologies may pave a facile and promising avenue for obtaining high yield in heterogeneous system.

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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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