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### Radical Polymerization of n-BMA Using a Di-Site Phase Transfer Catalyst

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## Radical Polymerization of n-BMA Using a Di-Site Phase Transfer Catalyst

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*The di-site phase transfer catalyzed radical polymerization of butyl methacrylate with the phase transfer catalyst  $N,N'$ -diheptyl- $N,N,N',N'$ -tetramethyl-1,2-ethanediammonium dibromide (DHTMEDADB) was carried out in an aqueous-organic biphasic system at  $60 \pm 1^\circ\text{C}$  under nitrogen atmosphere at fixed pH and ionic strength. A suitable kinetic scheme has been proposed and its significance was discussed. The polymers obtained were investigated and characterized (FTIR,  $^1\text{H-NMR}$  and XRD studies).*

**Keywords:** phase transfer catalysis, polymerization of n-BMA, radical polymerization

### INTRODUCTION

Catalytic applications in chemical industries have an ostensible impact in the rapid development of the economy. Many desirable reactions which cannot be brought about because of the crucial difficulty in bringing the inaccessible reactants together have been carried out by phase transfer catalysis [1–4]. Even though addition of a solvent that is both aqueous- and organic-like (eg. ethanol which derives the hydrophilic nature from its hydroxyl group and lipophilic nature from the ethyl group) can make the reactants accessible, rate acceleration is minimal due to the excessive solvation of the nucleophile [5,6].

An alternate method of adding expensive polar aprotic solvents, such as DMF or DMSO, has been used but that suffered from the disadvantage of being difficult to separate from the reaction mixture. As a

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result, an industrially successful and feasible method was developed over the last quarter century which, by means of employing phase transfer agents that are able to pass through the phase barriers and transfer reactive anions from the aqueous or solid phase into the organic phase where the reaction occurs [7–11]. Researchers have discussed the various involvements of phase transfer catalysts in the field of chemistry and engineering [12–16].

Quaternary ammonium salts, crown ethers, cryptands and polyethylene glycols are all some of the commonly used catalysts. In general, a reaction mixture consists of two phases: an organic phase having monomer in water-insoluble solvent and an aqueous phase containing the free radical initiator and the phase transfer catalyst. The preferred adducts have the general formula  $[Q^+]_n X^{n-}$  where  $Q^+$  represents an organically soluble residue of a phase transfer agent and  $X^{n-}$  represents the anionic residue of the initiator which is capable of producing free radicals and  $n$  is an integer usually 1 or 2 [17]. In this work, the kinetics of free radical polymerization of n-BMA involving a di-site PTC and potassium peroxydisulphate initiator is studied and a suitable mechanism is proposed. The polymers obtained were characterized by spectral techniques (FT-IR,  $^1H$ -NMR and XRD studies). Excellent performance, simplicity, safety and ecofriendliness are all some of the characteristics of a phase transfer catalysed reactions and this prompted us to make an investigation in the application of the lipophilic di-site phase transfer catalyst (DHTMEDADB) that has an ability in the transfer of anions from the aqueous to organic phase, which is confirmed by the polymerization reactions carried out and the yield of the polymers.

## MATERIALS AND METHODS

The monomer butyl methacrylate, potassium peroxydisulphate initiator, methanol, butanone and ethylacetate were purified by standard procedures and used for the reactions. The phase transfer catalyst, N,N'-diheptyl-N,N',N',N'-tetramethyl-1,2-ethanediammonium dibromide, synthesized in one laboratory [18], was involved in the free radical polymerization of n-BMA.

### Procedure for Polymerization

The polymerization was carried out in an oxygen-free  $N_2$  atmosphere under undisturbed condition at  $60 \pm 1^\circ C$  with equal volumes of aqueous and organic phases (10 ml each). PTC, initiator, potassium bisulphate (for maintaining ionic strength) and sulphuric acid

(for maintaining uniform acid strength) in aqueous phase and the monomer dissolved in solvent was in the organic phase. The polymerization reaction was initiated by adding initiator of known concentration to the reaction mixture. As soon as the initiator was added, polymerization started and precipitation of polymer was observed. The reaction was arrested by pouring the reaction mixture into ice-cold methanol. In case of colloidal polymer formation, the polymer was coagulated by the controlled addition of a few drops of concentrated HCl. The polymers formed were then filtered quantitatively through a G-4 sintered crucible, washed several times with distilled water followed by anhydrous methanol and finally dried at 50°C in a vacuum oven to constant weight.

### Degree of Polymerization

Viscosity measurements of the polymers were made using Ubbelohde viscometer, provided with a large reservoir for dilution to be made in the viscometer itself. The polymer samples were purified by repeated precipitation from a suitable solvent. A 0.4 percent solution was prepared and filtered through sintered glass funnels (G-4) to remove any suspended impurities. The following equation was used to calculate the molecular weight of the polymers obtained.

For poly (*n*-BMA) in butanone at 30°C [19]

$$\log \bar{P}_n = 1.408 \log[\eta_i] + 3.659$$

### Rate Measurements

Rate of polymerization ( $R_p$ ) was calculated from the weight of the polymer obtained in each experiment by the equation.

$$R_p = 1000 * W/V.t.M$$

where, W is the weight of the polymer in g, M is the molecular weight of the monomer, V is the volume of the reaction mixture in ml, and t is the reaction time in seconds.

## RESULTS AND DISCUSSION

### Kinetics of Free Radical Polymerization

The kinetics of free radical polymerization of *n*-BMA using PDS with DHTMEDADB has been studied as follows:

### Steady State Rate of Polymerization

Polymerization reactions have been carried out at  $60 \pm 1^\circ\text{C}$  with n-BMA dissolved in ethylacetate solvent as organic phase and the initiator and PTC in aqueous phase. The induction period was found to be negligible. By the determination of  $R_p$  at different time intervals and by keeping the concentrations of monomer, initiator and the phase transfer catalyst constant, the steady state rate of polymerization was ascertained. In Figure 1, a sharp increase in  $R_p$  was observed initially which then reached a maximum, slightly decreased and thereafter remained constant. The time taken to attain the steady state rate of polymerization to carry out further experiments with variation in other parameters was found to be 40 min.

### Monomer Concentrations

At fixed concentration of all the parameters, the effect of monomer on  $R_p$  was studied in the range of  $0.9\text{--}1.9\text{ mol dm}^{-3}$ .  $R_p$  increased with increase in [n-BMA]. Order with respect to the monomer was found to be 0.5 from the graph plotted against  $6 + \log R_p$  vs.  $3 + \log [\text{n-BMA}]$  and the observation was confirmed by plotting  $R_p$  vs. [n-BMA] in Figure 2. A plot of  $R_p$  vs.  $[\text{n-BMA}]^{0.5}$  was also found to be linear and passing through the origin. The free radicals precipitate from the liquid phase before termination.

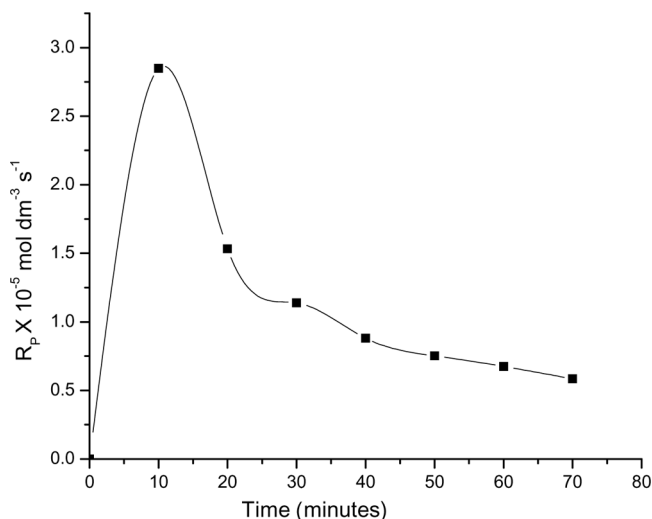
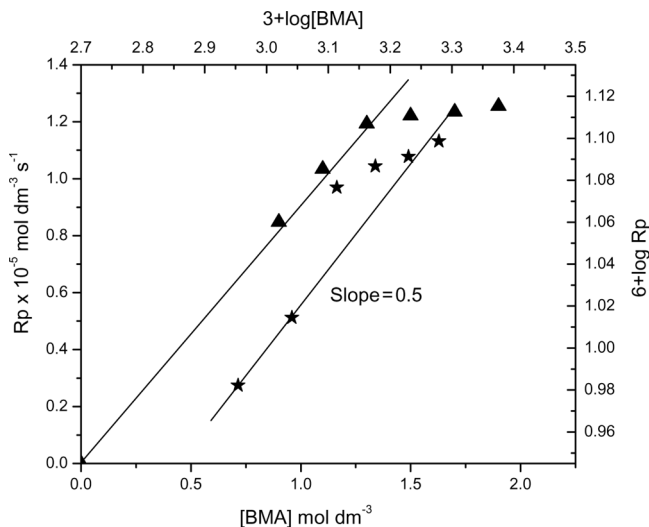


FIGURE 1 Steady state rate of polymerization.



**FIGURE 2** Effect of monomer concentration on  $R_p$ .

### Initiator Concentrations

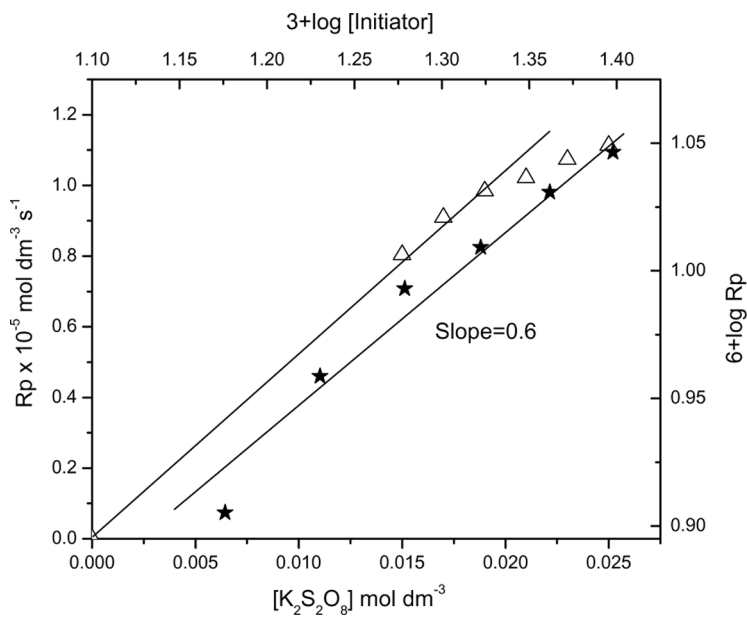
The effect of initiator concentration on  $R_p$  was studied by varying the concentration range ( $0.015\text{--}0.025\text{ mol dm}^{-3}$ ) at fixed monomer concentrations of *n*-BMA, PTC and ionic strength. With an increase in the concentration of  $\text{K}_2\text{S}_2\text{O}_8$ ,  $R_p$  showed an increase. In Figure 3, the plot of  $R_p$  vs.  $\log [\text{PDS}]$  was found to be linear with a slope equal to 0.6 indicating nearly a half order dependence of  $R_p$  on  $[\text{K}_2\text{S}_2\text{O}_8]$ . A plot of  $R_p$  vs.  $[\text{PDS}]^{0.5}$  was found to be linear and passing through the origin. Thus,  $R_p$  is found to be directly proportional to the square root of initiator concentration.

### PTC Concentrations

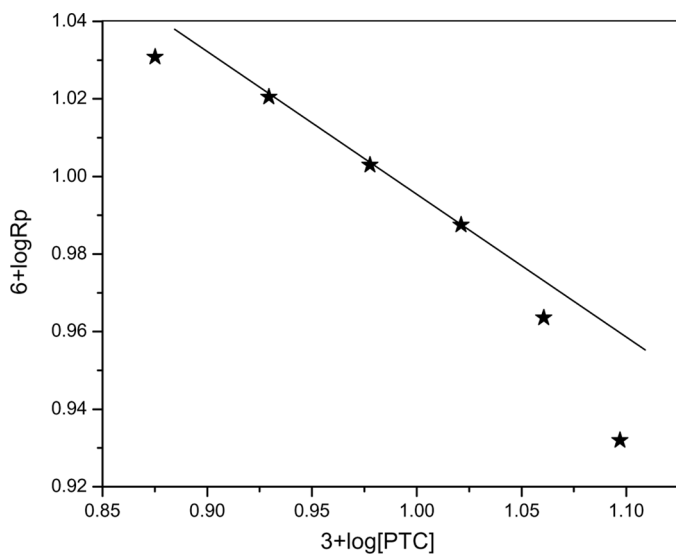
$R_p$  was found to be inversely proportional to catalyst concentration (Figure 4). Researchers have shown a decrease in the rate of polymerization with the increase in the catalyst concentration [20,21]. Polymerization was conducted in the range of  $60 \pm 1^\circ\text{C}$ . Radicals with  $\alpha$ -carbonyl ( $\text{C}=\text{O}$ ) group are greatly destabilized due to the presence of partial positive charge on the adjacent carbon and also interact there. Hence there is a decrease in the rate of polymerization with increase in [PTC] as shown in Scheme 1.

### Effect of Temperature on $R_p$

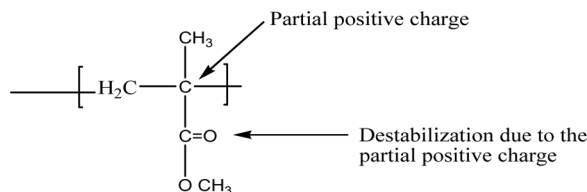
The effect of temperature on the rate of polymerization was studied from  $50$  to  $65^\circ\text{C}$ . With an increase in temperature, the  $R_p$  intensified.



**FIGURE 3** Effect of initiator concentration on  $R_p$ .



**FIGURE 4** Effect of PTC concentration on  $R_p$ .

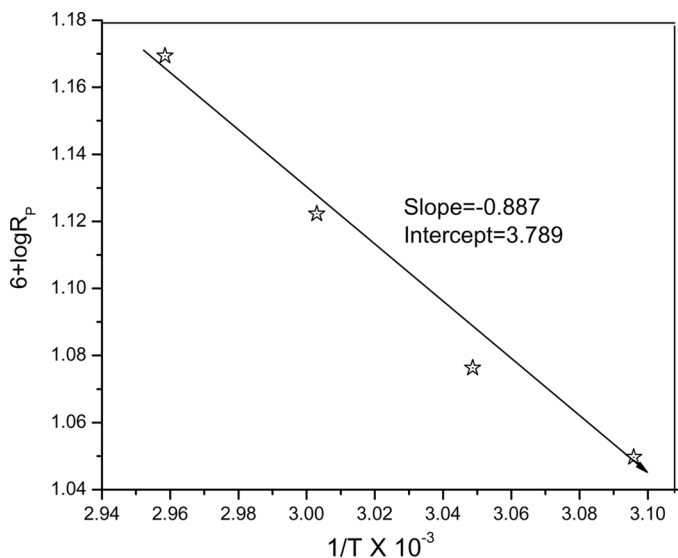


**SCHEME 1** Charge distribution in methacrylate.

The activation energy for the overall  $R_p$  was calculated from the arrhenius plot of  $\log R_p$  vs.  $1/T$  in Figure 5. The 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 evaluated ( $E_a = 16.66 \text{ kJ mol}^{-1}$ ;  $\Delta H^\ddagger = 13.89 \text{ kJ mol}^{-1}$ ;  $\Delta S^\ddagger = -150.99 \text{ J k}^{-1} \text{ mol}^{-1}$ ;  $\Delta G^\ddagger = 64.17 \text{ kJ mol}^{-1}$ ).

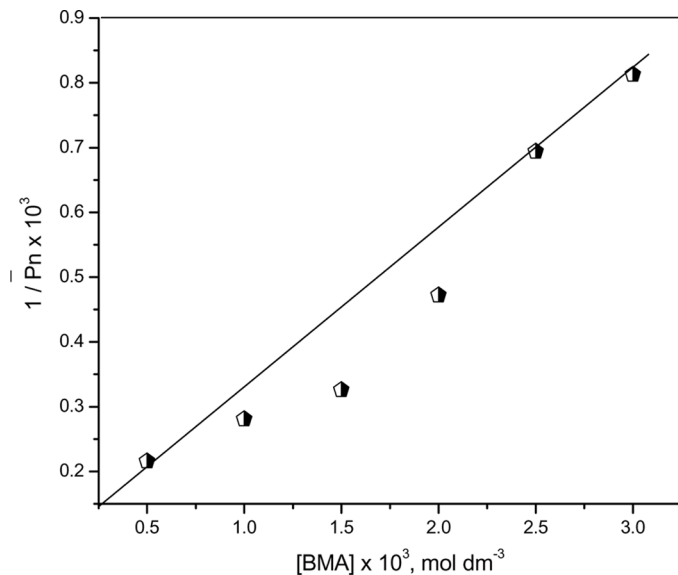
### Degree of Polymerization ( $\bar{P}_n$ )

From the intrinsic viscosity data, the degree of polymerization of the polymers was calculated and an inverse square root relationship was found to exist between the degree of polymerization ( $\bar{P}_n$ ) and monomer concentration. In Figure 6, a plot of  $1/\bar{P}_n$  vs. [monomer], a straight line



**FIGURE 5** Effect of temperature variation on  $R_p$ .





**FIGURE 6** Effect of  $\bar{P}_n$  on n-BMA.

passing through the origin, is obtained. In the following equations, the degree of polymerization and monomer concentration are related to the rate of polymerization.

The degree of polymerization is given by,

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

$$\bar{P}_n = \left[ \frac{k_p[M]}{2(K_3k_tk_d)^{1/2}[Q^+]_wf[S_2O_8]_w^{1/2}} \right]$$

$$\frac{1}{\bar{P}_n} = \left[ \frac{2(K_3k_tk_d)^{1/2}[Q^+]_wf[S_2O_8^2-]_w^{1/2}}{k_p[M]} \right]$$

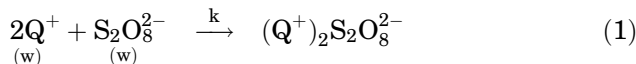
Thus the degree of polymerization  $\bar{P}_n$  was found to be directly proportional to [monomer] and from the plot of  $1/\bar{P}_n$  vs. [n-BMA], a straight line passing through origin was obtained, which supports the rate law derived for the proposed mechanism.

### Kinetic Scheme and Mechanism

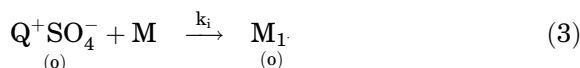
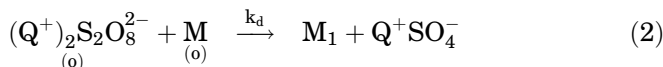
A suitable mechanism has been proposed based upon the reactions carried out. PTC transfers the reactive species, divalent PDS, from

the aqueous to the organic phase containing the monomer and initiates the reaction. Initiation is followed by the propagation step and then by the termination step. Based on these conclusions, the mechanism is given as follows:

### Steps during Polymerization



Initiation



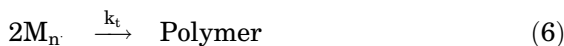
Propagation



:  
:



Termination



The subscripts (o) and (w) in Eqs. (1–6) refer to the organic and aqueous phase,  $k_i$ ,  $k_p$  and  $k_t$  all refer to rate of initiation, propagation and termination, respectively, and  $Q$  refers to the phase transfer catalyst. By applying the general principles of free radical polymerization and steady state hypothesis to the radical species, the rate law for this mechanism, which satisfactorily explains the above experimental observations, was derived as follows:

$$R_P = k_p \left( \frac{k_d k}{k_t} \right)^{0.5} \left( \frac{[\dot{M}]^{0.5} [S_2O_8^{2-}]^{0.5} [Q^+]_{\text{Total}}^{-1}}{1 + k[Q^+]_w [S_2O_8^{2-}]_w} \right) \quad (7)$$

## Spectral Studies of PBMA

### FTIR Spectrum of PBMA

The FTIR spectrum of PBMA in Figure 7 confirms an acrylate stretching band at  $1740\text{ cm}^{-1}$ . The following bands were observed [22]:  $1263\text{--}1045\text{ cm}^{-1}$  (C-O-C stretching band),  $1470\text{ cm}^{-1}$  (C-H deformation) and  $3041\text{ cm}^{-1}$  (C-H stretching band).

### $^1\text{H}$ NMR Spectrum of PBMA

In Figure 8, the  $^1\text{H}$ -NMR spectrum was recorded with a Varian 100HA JEOL 400 MHz spectrometer by using  $\text{C}_6\text{D}_6$  as a solvent and tetramethylsilane as an internal reference. The  $^1\text{H}$ -NMR spectrum of the polymer [22] showed a peak of methyl and methylene group at  $0.9\delta$  ppm and  $2.1\delta$  ppm, respectively. The acrylate protons appear as triplet at  $3.2\delta$  ppm.

### XRD Analysis of PBMA

Wide-angle X-ray diffraction patterns were recorded on a PAN Analytical Xpert PRO instrument operated at the Cu  $K\alpha$  radiation wavelength of  $1.54\text{ \AA}$  at 45 mA and 40 kV. Measurement of diffracted intensities was made over the angular range of  $5$  to  $80^\circ$  at ambient temperature. In Figure 9, the XRD pattern shows a crystalline nature of poly(n-butyl methacrylate).

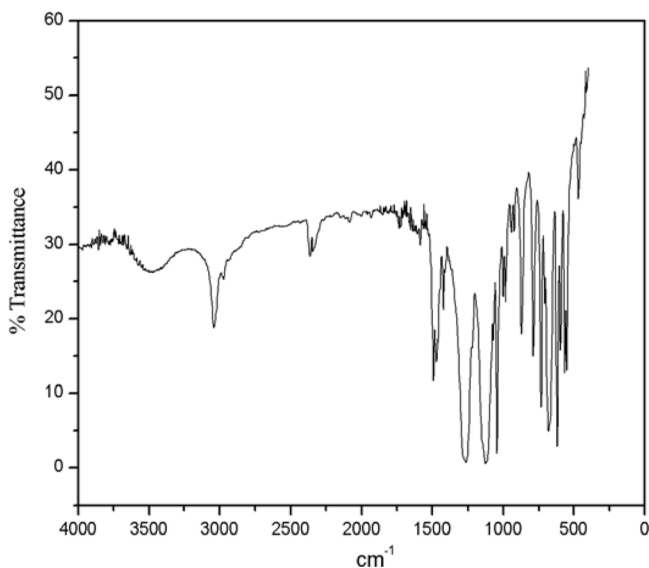
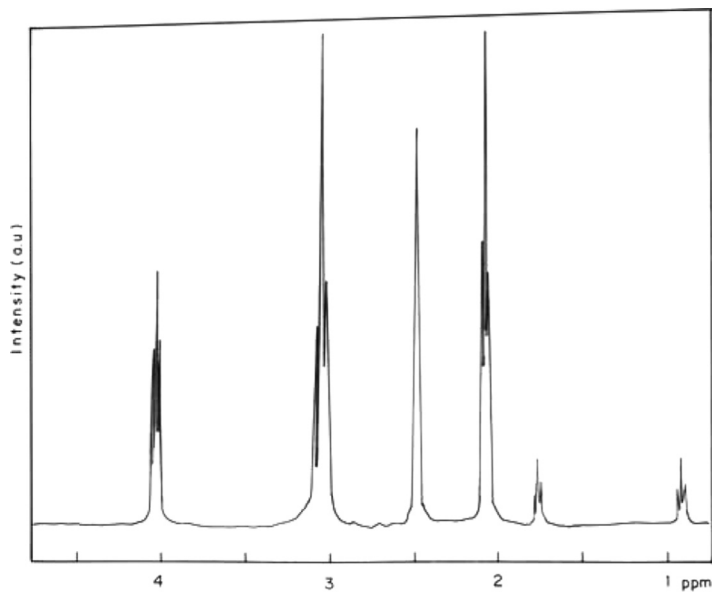
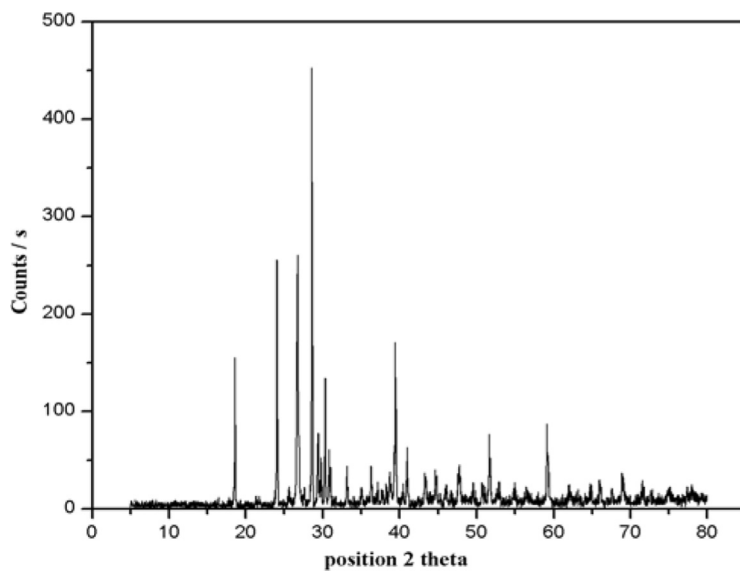


FIGURE 7 FTIR spectrum of PBMA.



**FIGURE 8**  $^1\text{H-NMR}$  spectrum of PBMA.



**FIGURE 9** XRD pattern of PBMA.

## CONCLUSION

The free radical polymerization of n-BMA using PDS initiator in aqueous organic biphasic system was successfully performed with a di-site PTC and studies on  $R_p$  over various concentrations of monomer, initiator and catalyst were performed.  $R_p$  was found to increase with increase in concentrations of monomer and the initiator but was found to decrease with increase in concentration of the catalyst. Hydrogen ion concentration and ionic strength do not show any appreciable effect on  $R_p$ . Molecular weight of the polymers obtained in this work was determined by viscometry to find the dependency of degree of polymerization on the monomer concentration. Based upon the results obtained, a suitable kinetic scheme and mechanism has been proposed.

During the past decade, each successful PTC application stimulated research which in turn led to additional applications and improved processes and, hence, research in PTC have achieved great progress in the development of basic theory and applications. There is every reason to believe that this trend will continue in the near future. It is believed that numerous novel catalysts, methodologies, and applications based on phase transfer catalysis await new discovery and exploration.

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