

## A KINETIC STUDY ON THE FREE RADICAL POLYMERIZATION OF METHYL METHACRYLATE BY 1,1,4,4-TETRAMETHYL-1,4-DIBENZYLETHYLENEDIAMMONIUM CHLORIDE (TMDBEDAC) AS DI-SITE PHASE TRANSFER CATALYST

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### ABSTRACT

Free radical polymerization of alkyl monomers using water soluble initiator was impractical due to phase separation, it can be overcome by introduction of phase transfer catalyst (PTC). Polymerization using this technique results in polymers of high molecular weight and good mechanical properties. The catalytic activity seems to increase by the aromatic substitution in the alkyl chain of PTC. In the present study kinetics of polymerization of methyl methacrylate in ethyl acetate/water biphasic media using potassium peroxomonosulfate (PMS) as water soluble initiator and aromatic substituted PTC was investigated. The order of the reaction was found to be unity with respect to monomer concentration and 0.5-1.0 for PMS and catalyst concentration. The poly methyl methacrylate formed shows high molecular weight measured from the viscosity. The product formed was endorsed by IR, thermal analysis and the crystallinity was studied from X-ray diffraction.

**Keywords:** Free radical polymerization, PTC, Methyl methacrylate, Peroxomonosulfate, Initiator.

### INTRODUCTION

Phase transfer catalysis made easy accessibility of the reaction involves two or more immiscible reactant. It forms a barrier between two reactants, hence reaction will occur either at prolonged time or no reaction even after long time. Many organic and polymer reaction deals with compounds having different solubilities in such cases PTC forms a complex by exchanging its ion with that of reactant made it to cross the barrier and the reaction will take place at the interface. The advantages of this method are simple experimental procedure, mild reaction conditions and inexpensive<sup>1</sup>. Hence it is noteworthy to study the usage of PTC in reactions. They are mainly alkyl ammonium or phosphonium salts and macrocyclic ethers<sup>2</sup>. The usage of which is not limited only to organic reactions, it has widespread industrial applications<sup>3,4</sup> and also in polymerization reactions especially in free radical polymerization to overcome the phase difference between water soluble initiators and monomers soluble in organic solvents<sup>5</sup>. The insolubility of water soluble initiators in organic solvents and monomers reduce their usage in polymerization reaction. It can be achieved by phase transfer catalyst such as quaternary ammonium salts or macrocyclic polyethers. In phase transfer catalysis monomer in the organic phase made to react with reagent in the aqueous or solid. The reaction is achieved by means of a phase transfer catalyst, it solubilizes and complex the inorganic salts like water soluble initiators into the organic media reaction carried out in the interface of two medium. In the present work the rate of polymerization of methyl methacrylate and PMS using 1,1,4,4-tetramethyl-1,4-dibenzylethylenediammonium chloride (TMDBEDAC) as PTC was studied by changing different parameters like time, concentration of monomer, PMS and PTC, temperature, volume fraction of aqueous phase and ionic strength. The rate law and mechanism was proposed for the above reaction and it shows that the order of the reaction with respect to monomer concentration is unity whereas it falls between 0.5 -1.0 with respect to the concentration of PMS and TMDBEDAC. The rate of polymerization was not influenced by ionic strength ( $\mu$ ) and  $[H^+]$ , it increases with increase in volume fraction of aqueous phase. The polymer was characterised by FT-IR, thermal analysis and amorphous nature of the polymer was revealed by X-ray diffraction.

### MATERIALS AND METHODS

#### Materials

Monomer was obtained from Lancaster, PMS, ethyl acetate, benzene were obtained from Merck. All the other reagents used were of analytical grade.

#### Synthesis of 1,1,4,4-tetramethyl-1,4-dibenzylethylenediammonium chloride (TMDBEDAC)

Catalyst TMDBEDAC was synthesized according to the procedure reported earlier<sup>6</sup>.

#### Kinetics of polymerization using TMDBEDAC as catalyst

##### Steady state approximation

The steady state rate of polymerization was studied by determining the rate of polymerization by varying time at fixed concentration of monomer, initiator, catalyst, and volume fraction of the aqueous phase, ionic and acid strength. The polymerization reactions were performed at  $60 \pm 1^\circ\text{C}$ .

##### Effect of concentration of monomer, initiator and catalyst on rate of polymerization ( $R_p$ )

###### [Monomer]

The rate of polymerization with respect to monomer concentration was studied by varying [monomer] ranging from 0.9 to 1.9 mol  $\text{dm}^{-3}$ , at fixed concentrations of PMS, PTC, ionic strength and pH.

###### [PMS]

The rate of polymerization of methyl methacrylate was studied by varying the PMS concentration in the range 0.015 to 0.025 mole  $\text{dm}^{-3}$ , others remain constant.

###### [PTC]

The dependence of  $R_p$  on the concentration of PTC was examined by varying [PTC] in the range of 0.015 to 0.025, keeping other parameters constant.

##### Effect of Variation of Volume Fraction of Aqueous Phase on the Rate of Polymerization ( $R_p$ )

To study the effect of variation in the volume fraction of aqueous phase on  $R_p$  the reaction have been conducted with varying volumes of aqueous phase with a constant volume of organic phase at fixed concentration of monomer, PMS, PTC and at constant acid and ionic strengths. The ratio of volumes of aqueous phase to that of organic phase  $V_w/V_o$  was varied in the range 0.3 to 0.9

##### Effect of Variation of Temperature on the Rate of Polymerization ( $R_p$ )

The effect of variation of temperature from  $50^\circ\text{C}$  to  $65^\circ\text{C}$  on the rate of polymerization was studied by keeping the variables [monomer], [PDS], [TMDEEDAB], ionic strength and pH constant.

### Effect of ionic strength ( $\mu$ )

The effect of ionic strength was observed by varying the ionic strength in the range, 0.4 to 0.6 mol dm<sup>-3</sup>.

### Effect of [H<sup>+</sup>] Variation

The effect of [H<sup>+</sup>] variation was observed by varying the [H<sup>+</sup>] concentration in the range, 0.1 to 0.3 mol dm<sup>-3</sup>.

### Characterisation of methyl methacrylate

The synthesised polymer from the above reaction was characterised by FTIR, thermal analysis and X-ray diffraction pattern.

### Fourier Transform Infra Red Spectroscopy (FTIR)

Nicolet Impact 400 Fourier Transform Infrared (FT-IR) spectrometer was used to examine the structure of polymer. The solid samples were recorded by making pellets with potassium bromide (E-Merck, IR Grade).

### Thermal Analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was performed to assess thermal stability of synthesised polymer.

### TGA

Thermo grams were obtained using TA instruments Q100 series Thermo gravimetric analyzer. The sample weight was approximately 10mg. All the runs were carried out under nitrogen atmosphere with a heating rate of 20° C/min.

### DSC

Differential scanning calorimetry was performed on TA instruments Q10 series equipment. The experiments were carried out in nitrogen atmosphere at a heating rate of 10C/min from ambient to 300 °C with a nitrogen flow of 60ml/min.

### X-ray diffraction (XRD) study

Wide angle X-ray diffraction measurements were performed at room temperature (about 25°C) on a X -pert PAN analytical X-ray diffractometer using Cu K $\alpha$  radiation.

## RESULTS AND DISCUSSIONS

### Steady state approximation

The rate of polymerization at regular interval of time was shown in figure 1, initially it shows increase in R<sub>p</sub>, then slightly decreased and remains constant. It seems to reach steady state rate within 30-60 minutes and can be explained from the figure 1, plot of R<sub>p</sub> versus time.

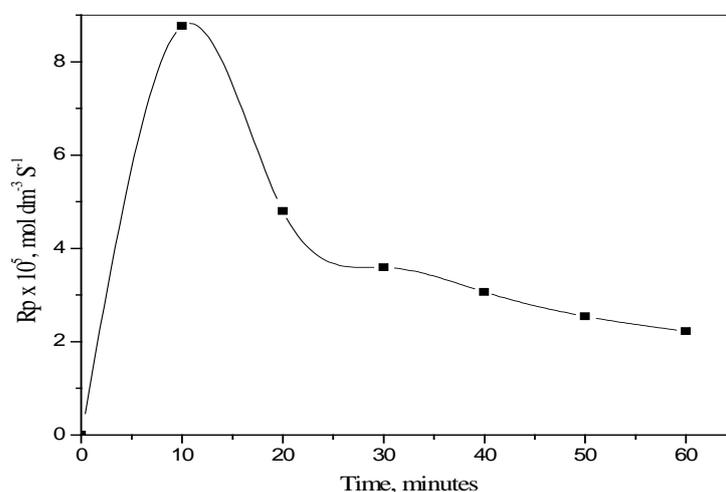
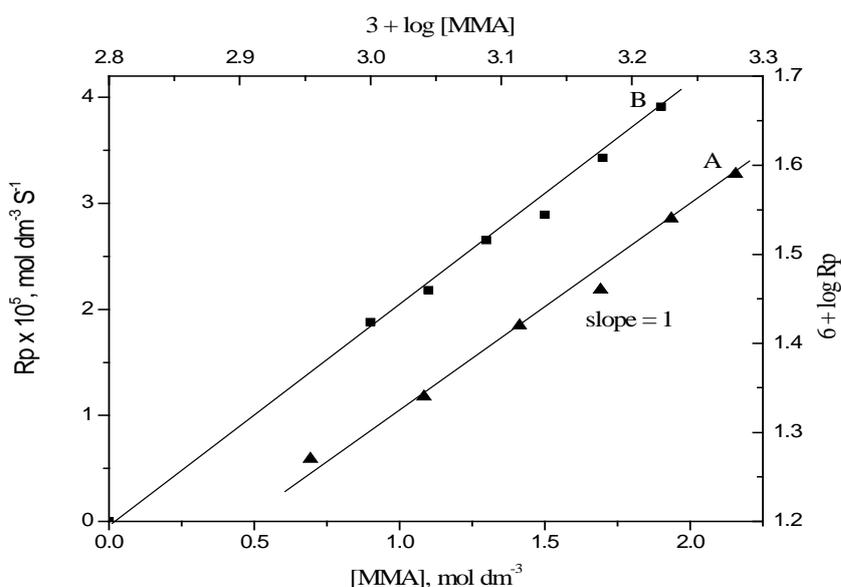


Fig. 1: Steady State Rate of Polymerization



A: 6 + log Rp Vs 3 + log [MMA]; B: R<sub>p</sub> × 10<sup>5</sup>, mol dm<sup>-3</sup> S<sup>-1</sup> Vs [MMA], mol dm<sup>-3</sup>

Fig. 2: Variation of [MMA]

**Effect of concentration of monomer, initiator and catalyst on rate of polymerization (Rp)**

**[Monomer]**

Influence of monomer concentration on rate of polymerization was shown in figure 2, it indicates that Rp increases with increase in monomer concentration. The order of reaction was found to be unity with respect to monomer concentration. The results show the similar trend reported for MMA<sup>7,8,9</sup>.

**[PMS]**

The significant increase in concentration of PMS increases Rp for the polymerization of MMA was clearly seen in figure 3, a plot of Rp versus [PMS]. The reaction order with respect to initiator concentration was 0.5. It gives straight line passing through the origin supporting the above deduction.

**[PTC]**

A plot of Rp versus [PTC] was shown in figure 4, Rp was found to increase with increase in concentration of catalyst and the order was

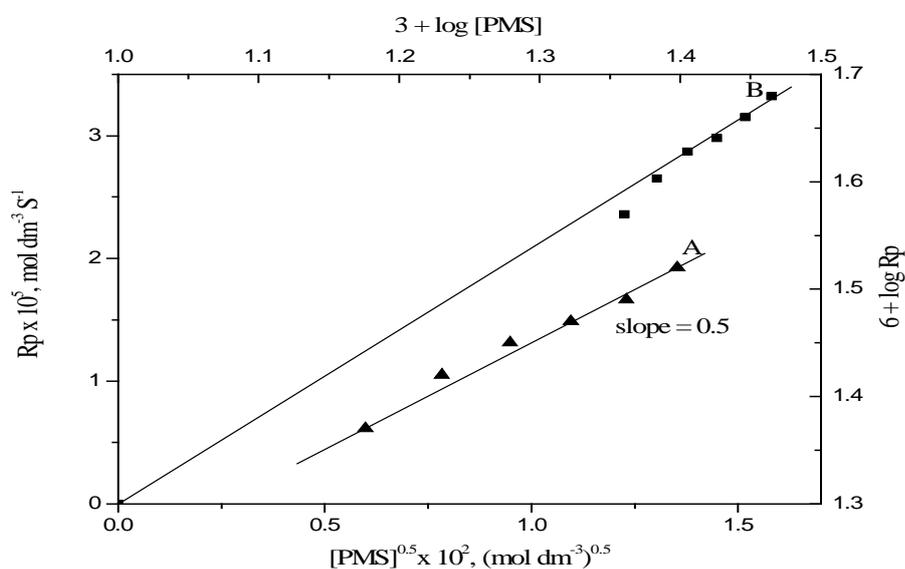
deduced as 1. The linearity of graph and passes through the origin confirms the above results.

**Effect of Variation of Volume Fraction of Aqueous Phase on the Rate of Polymerization (Rp)**

Influence of volume fraction of aqueous phase was depicted in figure 5, rate of polymerization increases with increase in  $V_w/V_o$  for monomer. The observed order with respect to  $V_w/V_o$  was found to be in the range 0.1-0.2. It indicates that rate of initiation is directly proportional to the volume of aqueous on the rate of polymerization.

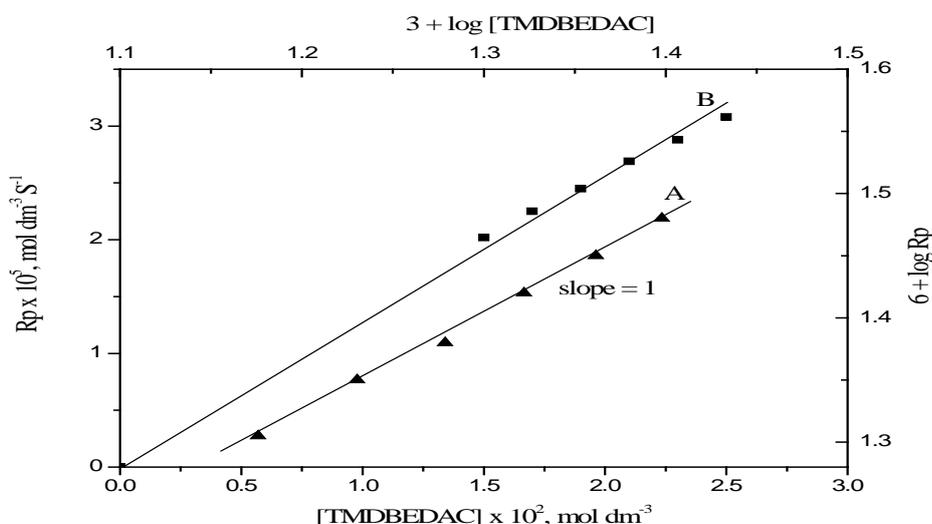
**Effect of Variation of Temperature on the Rate of Polymerization (Rp)**

The Rp increases with increase in temperature. Arrhenius plot of log Rp versus  $1/T$  was shown in figure 6, from the slope activation energy values for polymerization reaction was calculated. The thermodynamic parameters - entropy of activation  $\Delta S^\ddagger$ , enthalpy of activation  $\Delta H^\ddagger$  and energy of activation  $\Delta G^\ddagger$  has been calculated from the values of activation energy was reported in table 1.



A:  $6 + \log Rp$  Vs  $3 + \log [PMS]$ ; B:  $[PMS]^{0.5} \times 10^2, (mol dm^{-3})^{0.5}$  Vs  $Rp \times 10^5, mol dm^{-3} s^{-1}$

**Fig. 3: Variation of [PMS]**



A:  $6 + \log Rp$  Vs  $3 + \log [TMDBEDAC]$ ; B:  $[TMDBEDAC] \times 10^2, mol dm^{-3}$  Vs  $Rp \times 10^5, mol dm^{-3} s^{-1}$

**Fig. 4: Variation of [TMDBEDAC]**

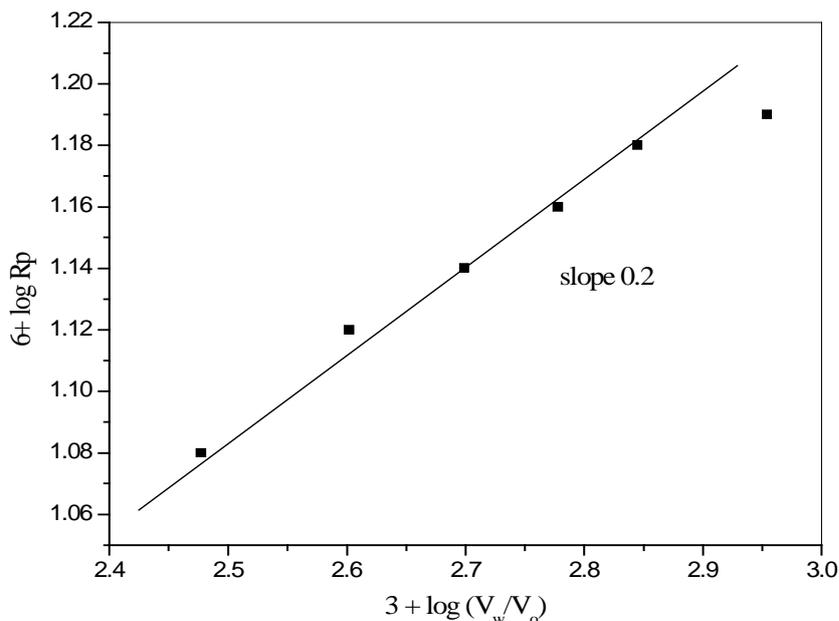


Fig. 5: Variation of Aqueous Phase Volume

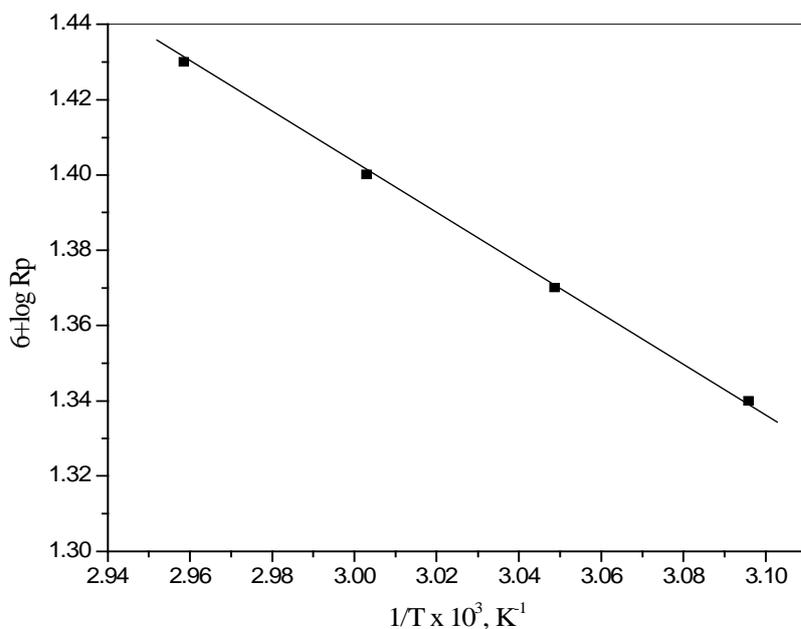


Fig. 6: Arrhenius Plot

Table 1: Thermodynamic Parameters

Monomer	$E_a$ , KJ.mol <sup>-1</sup>	$\Delta S^\ddagger$ , J.mol <sup>-1</sup> K <sup>-1</sup>	$\Delta H^\ddagger$ , KJ.mol <sup>-1</sup>	$\Delta G^\ddagger$ , KJ.mol <sup>-1</sup>
MMA	12.54	-150.09	10.17	60.14

**Effect of ionic strength ( $\mu$ )**

The variation of ionic strength was found to exert no significant change in the rate of polymerization.

**Effect of [H<sup>+</sup>] Variation**

The variation of [H<sup>+</sup>] has no influence on rate of polymerization.

**Mechanism and rate law**

A mechanism has to be proposed to explain the above observation. In general two factors will account in phase transfer catalysis,

transfer of reactive species from aqueous phase to organic phase and reaction of which with monomer in organic phase.

In the present study peroxomonosulfate is used as the initiator, the migration of HSO<sub>5</sub><sup>-</sup> ions from its aqueous phase to the monomer containing organic phase is facilitated by the quaternary ammonium salts, which serve as the phase transfer agent. The decomposition of HSO<sub>5</sub><sup>-</sup> to sulfate ion radicals in the presence of phase transfer catalyst caused the polymerization<sup>10</sup>. Thus the quaternary ammonium salts not only transfer the PMS ion from aqueous to organic phase but also enhance the rate of its decomposition. The rate of decomposition was



### Characterisation of polymer

#### FT-IR Study of poly (methyl methacrylate)

FT-IR spectrum of poly (methyl methacrylate) is shown in the Figure 7. The broad peak around  $2900\text{ cm}^{-1}$  is due to the presence of symmetric and asymmetric stretching vibrations of the methylene group. The peak at  $1119\text{ cm}^{-1}$  is due to C-O stretching vibration. The peak at  $619\text{ cm}^{-1}$  is due to C-H bending vibration.

#### TGA and DSC Study of poly (methyl methacrylate)

The TGA curve of poly (methyl methacrylate) is shown in the Figure 8. The polymer starts to degrade at  $200^\circ\text{C}$ , followed by a second stage commencing at  $353^\circ\text{C}$ .

The DSC curve of the polymer is shown in the Figure 9. The Tg value obtained is  $108^\circ\text{C}$ .

The endothermic peak at  $275^\circ\text{C}$  is characteristic of high molecular weight poly (methyl methacrylate) and is believed to be due to the disentanglements of the high molecular weight chains. A second endothermic peak at  $385^\circ\text{C}$  may be due to the relaxation phenomena.

#### XRD Study of poly (methyl methacrylate)

The XRD pattern of poly(methyl methacrylate) is shown in the Figure 10. The Figure shows diffuse halos at lower  $2\theta$  values, which is typical of amorphous polymer.

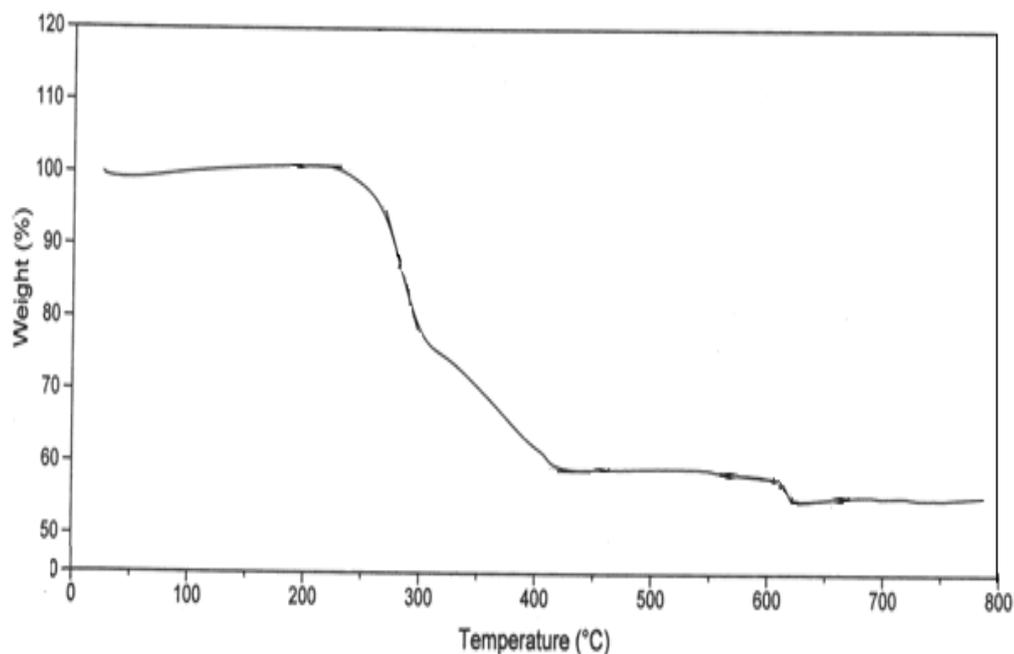


Fig. 8: TGA curve of poly(methyl methacrylate)

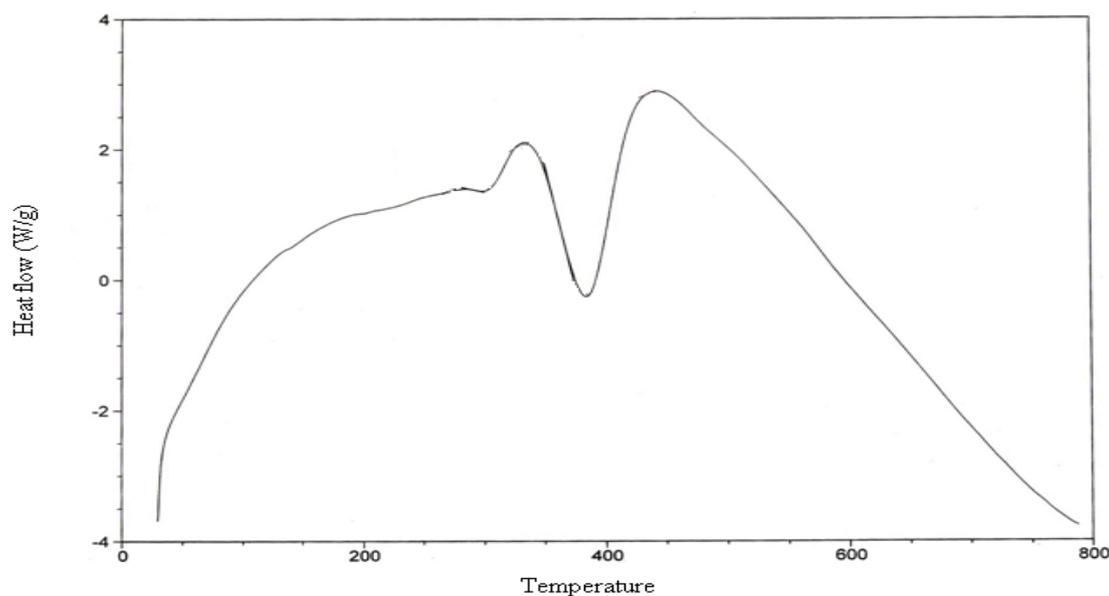


Fig. 9: DSC curve of poly(methyl methacrylate)

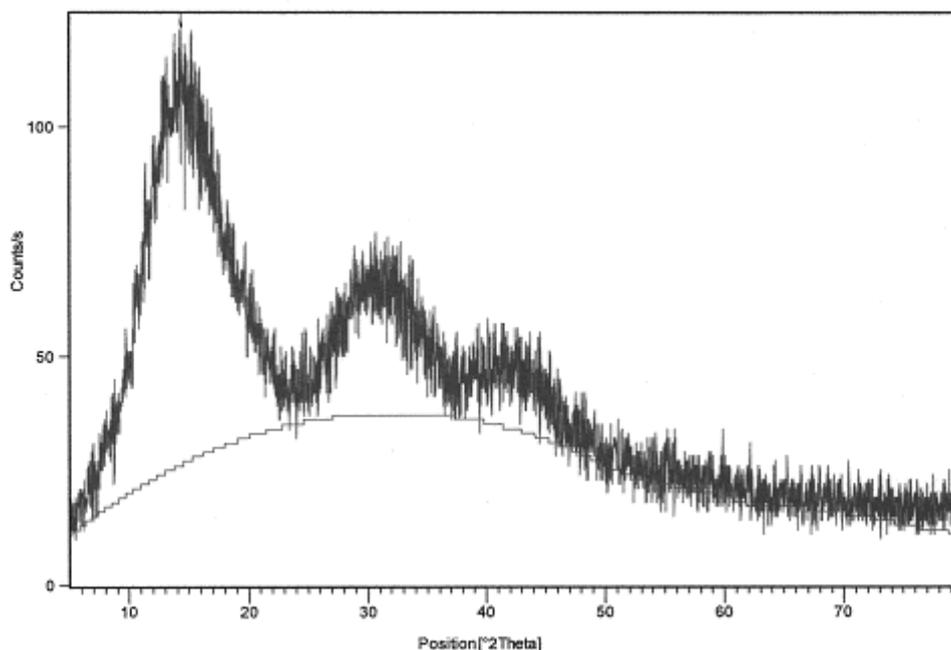


Fig. 10: XRD spectrum of poly(methyl methacrylate)

## CONCLUSIONS

The catalytic efficiency of 1,1,4,4-tetramethyl-1,4 dibenzylethylenedi-ammonium chloride as disited phase transfer catalyst on free radical polymerization methyl methacrylate using PMS as water soluble initiator was investigated in the present study. The results shows that rate of polymerization increases with increase on various experimental parameters such as concentration of monomer, initiator, catalyst and volume fraction of the aqueous phase whereas it is independent of pH and ionic strength. The order with respect to monomer was found to be unity, the higher order was observed with respect to initiator and catalyst concentration. Degree of polymerization supports the proposed mechanism. The spectroscopic results confirm the structure of polymer.

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