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Kinetic Investigation of Polymerization Methyl Methacrylate in Benzene.

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ABSTRACT

An experimental investigation of kinetics of the solution free radical homopolymerization of methyl methacrylate (MMA) initiated with benzoyl peroxide (BPO) was conducted. The reactions were carried out at constant temperature of 70 °C in benzene under unstirred and inert conditions. The overall activation energy of homopolymerization was determined to be (68.65) kJ mol^{-1}. The effects of initiator and monomer concentration on the rate of homopolymerization were studied over a wide range using the well-known conversion vs. time approach. Under the conditions of our work, the orders (0.5 and 1.38) were found with respect to initiator and monomer, respectively. However, the rate of polymerization (R_p) is not straight forwardly corresponding monomer concentration. An increase in the polarity of solvent has slightly increased (R_p) value whereas the average degree of polymerization (DP_n) decreased as BPO concentration increase.
Keywords: Methyl methacrylate, radical polymerization, kinetic aspects.

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INTRODUCTION

In the last five decades, the course study of solution free radical polymerization of some acrylate monomers has been important matter. It is well known that at higher conversions, the molecular weight of the polymer produced is very high. In addition, a large auto acceleration of the rate of polymerization (R_P) occurs even under isothermal conditions. Thus, the classical low-conversion free radical kinetics does not apply at these conditions [1].

Free radical polymerizations involve a number of fundamental reaction steps: initiation, propagation, termination and chain transfer. The reaction mechanism and the corresponding rate equations are given in Equation (1). The rate of polymerization can be derived quasi steady state assumption [2]:

$$2f\, k_d\, [I] = 2k_t\, [M]^2 \tag{1}$$

$$R_p = \frac{K_p}{K_t^{0.5}} (f\, K_d)^{0.5} [I]^{0.5} [M] \tag{2}$$

In these equations, [I] and [M] represent the concentration of initiator and monomer respectively; f is the effective free radicals. Thus in the early stages of the reaction and if (f) is independent of [M], the overall rate of polymerization should be proportional to the first power of the monomer concentration and square root of the initiator concentration.

This is the so-called classical or ideal polymerization rate law and serves as the basis to obtain the lumped parameter, $k_p/ k_t^{1/2}$, using simple techniques such as gravimetric and dilatometry.

Deviation of polymerization energy from basic system of guidelines of free radical polymerization have generally been studied by many workers [3, 4], they denoted that the rate of end between polymer radicals isn't constantly autonomous of their chain length; it has been brought up that the end rate consistent in free radical polymerization, kt, is a diminishing capacity of the span of responding radical. Regular strategies for the dynamic investigation of radical polymerization are appeared to prompt mistaken ends if the impact of the chain length reliance of end rate constants isn't considered.

The interests in study the kinetic of acrylate monomers group have been expanding because of their highly importance in different fields [5-8]. Dharmendira and Konguvel studied the kinetic of free radical polymerization of (MMA) monomer using cyclohexanone/water mixture as a solvent and persulfate potassium as an initiator on various experimental conditions, such as different temperature, ionic strength and volume fraction of aqueous phase, and different concentrations of initiator, phase transfer catalyst (PTC), and monomer. The orders (0.5, 1 and 0.5) were found with respect to phase transfer catalyst, monomer and initiator, respectively [9,10]. David Victoria and coworkers have reported the comparison between the kinetic behavior of free radical polymerization of vinyl acetate and methyl methacrylate monomers. Based on the results of this study, the R_p of methyl methacrylate monomer is higher than R_p of vinyl acetate monomer [11].

The main aim of this study is to study the kinetic of homopolymerization of MMA include the effects of initiator and monomer concentration, polarity of solvent and average degree of polymerization on the rate of homopolymerization. This study also determines the overall activation energy of this homopolymerization.

EXPERIMENTAL SECTION

Materials

Commercial samples of MMA from Aldrich chemical were obtained. MMA monomer was purified before polymerization by passing it through an aluminum oxide many times until colorless product was obtained. Benzene and methanol of 98% purity grade were used as received. The initiator benzoyl peroxide was purified by recrystalization using ethanol then dried in a vacuum.

Homopolymerization of MMA

Kinetic experiments were carried out for MMA as follows: The prescribed amount of monomer MMA (1, 2, 3, 4) mol dm^{-3}, BPO (1x10^{-3}, 2x10^{-3}, 3x10^{-3}, 4x10^{-3}) mol dm^{-3}, and benzene were charged in the test tubes. In order to remove all oxygen in the mixture, Nitrogen gas was bubbled for 15 minutes prior to the polymerization, then the tubes are closed firmally. The polymerization reaction was carried out by placing the tubes in a thermostated water bath at a definite temperature 70 ± 0.1 °C. For calculation the activation energy, the polymerization was carried out using initial BPO concentration (1x10^{-3} mol dm^{-3}) at the initial monomer concentration of 1 mol dm^{-3} at four different temperatures (70, 75, 80 and 85 °C). After recording time, the polymerization was stopped by pouring the reaction mixture into a large excess of precipitant absolute methanol. The resulting polymers were filtered off, dried at 40 °C to a constant weight. Conversion was estimated using the well- known gravimetric technique. The reproducibility of the experiments was ensuring by the replication of runs. At a given time, the residual monomer concentration [M] was calculated from the relation:

$$[M]_0 = [M]_0 (1-C) \qquad (3)$$

Where, C is the fraction conversion and [M]$_0$ is the initial concentration of the monomer. Thus, from the slope of the time–conversion curve, the initial rate of polymerization could be determined.

Free-radical initiator in kinetic studies is normally present in low concentrations, so that their concentrations and thermodynamic activities are likely to be effectively equal.

Ubbelohde viscometer was used for viscosity of the poly MMA solutions. The measurements were carried out at 30 °C using benzene as standard solvent. Intrinsic viscosity was determined by plotting C versus Ɲsp/c [12]. Mark-Houwink equation was employed to calculate the average degree of polymerization using the obtained intrinsic viscosity data [13].

RESULTS AND DISCUSSION

Determination of the rate equation

From the lines slope of typical time-conversion curves, the rate of polymerization R$_P$ for a series of initiator and monomer concentration could be estimated. Figure (1-a) show typical time-conversion curves at (variable initiator concentration and fixed monomer), while Figure (1-b) shows typical time-conversion curves at (variable monomer concentration and fixed initiator).

$$R_p = [M]_0 /100 \times slope \qquad (4)$$

[M]$_0$:Initial concentration of monomer.
Slope: of the initial points of % conversion vs time.

In such a system, the relation between the rate of polymerization and the initiator and monomer concentrations can be written as:

Rate α [M]^α [I]^ß

$$R_p = k [monomer]^α [initiator]^ß \qquad (5)$$

Here β and α the order of the reaction with respect to initiator and monomer concentrations respectively. The steady rate in homopolymerization can be described using the classical rate equation:

$$R_p = k [I]^{0.5} [M] \qquad (6)$$
$$K = k_p / k_t^{1/2} (f k_d)^{1/2} \qquad (7)$$

Where [M] and [I] are the monomer and initiator concentration respectively, K is the so called overall rate constant of homopolymerization which, in terms of Equation (7), contain the rate constant of elementary reactions, i.e., those of chain initiation (k_d), chain termination (k_t) and chain propagation (k_p),.

The effect of initiator on the overall R_P was studied at several fixed initiator concentration, likewise the effect of monomer on the overall R_P was studied at several fixed monomer concentration. Figures (2-a) and (2-b) show the dependence of R_P on initiator and monomer concentration, respectively. From the slope of the straight lines, the following rate equation was obtained

$$R_p = K[BA]^{1.38}[BPO]^{0.5} \qquad (8)$$

According to the classical kinetic treatments of the free radical polymerization, the relation between the rate of polymerization and the initiator concentration can be expressed as:

$$R_p \ \alpha \ [initiator]^{0.5} \qquad (9)$$

On the other hand Equation (6) does not describe correctly the experiments in respect to the order of monomer concentration, thus the observed order (1.38) is in contradiction with the classical kinetic description. In general classical kinetic description would be expected to follow the monomer-solvent mixtures which are ideal.
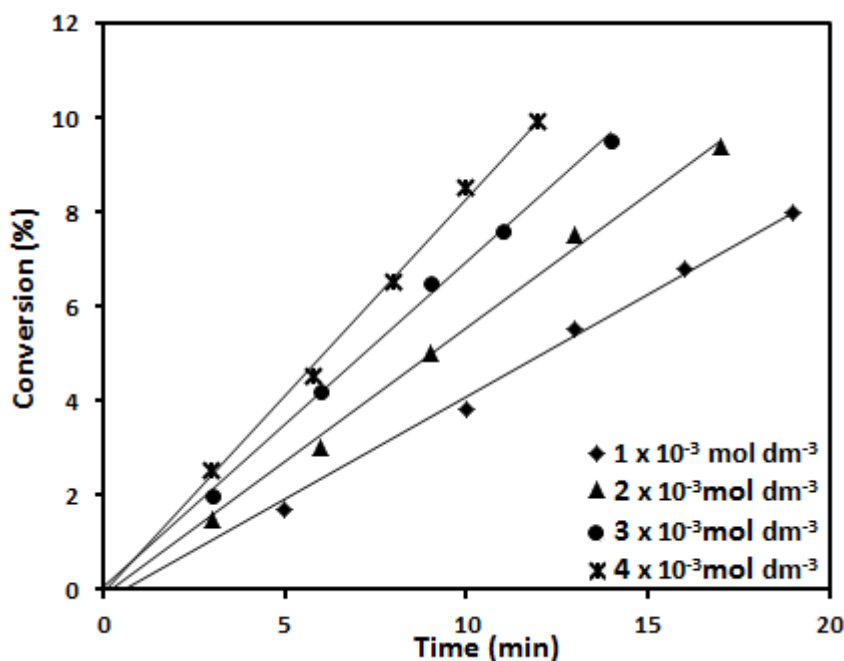

Figure (1-a): Time-conversion curves for polymerization of MMA. [BPO]$_0$= (1, 2, 3, 4) x 10^{-3} mol dm^{-3}, [MMA]$_0$ = 4x10^{-3} mol dm^{-3}.

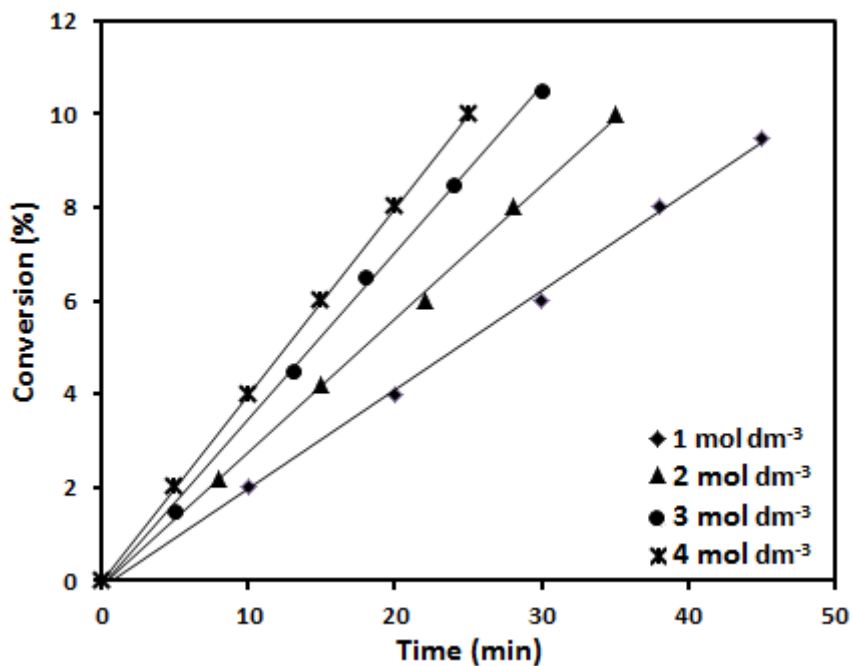**Figure (1-b): Time-conversion curves for polymerization of MMA. $[MMA]_0 = (1, 2, 3, 4)$ mol dm^{-3}, $[BPO]_0 = 1 \times 10^{-3}$ mol dm^{-3}.**
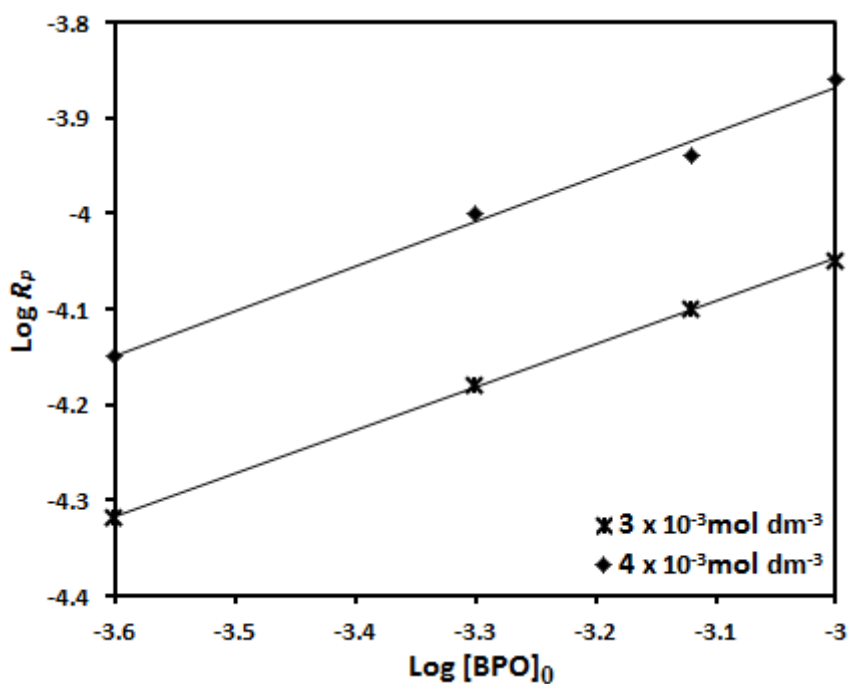

Figure (2-a): Dependence of overall initial rate of polymerization on the initiator concentration at a fixed monomer concentration.
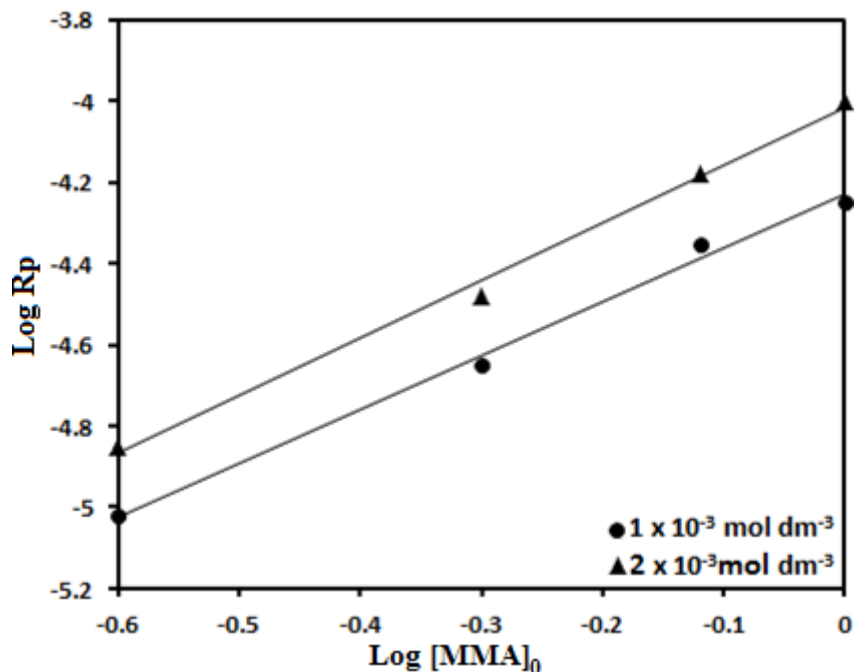
Figure (2-b): Dependence of overall initial rate of polymerization on the monomer concentration at a fixed initiator concentration.

Overall activation energy of homoploymerization

The quantitative effect of temperature is complex since R_p depend on a combination of three rate constants– k_d, k_p and k_t. Each of the rate constants for initiation, propagation, and termination can be expressed by an Arrhenius-type relationship [14]:

$$k = Ae^{-E/RT} \qquad (10)$$

$$or$$

$$\ln k = \ln A - E/RT \qquad (11)$$

Where A is the collision frequency factor, E the arrhenius activation energy, and T the Kelvin temperature. A plot of ln k verses 1/T allows the determination of both E and A from the slope and intercept, respectively.

For polymerization initiated by the thermal decomposition of an initiator, the polymerization rate depends on the ratio of three rate constants $k_p (k_d / k_t)^{1/2}$ in accordance with Equation (2). The temperature dependence of this ratio, obtained by combing three separate Arrhenius-type equations, is given by:

$$\ln \{ k_p [k_d/ k_t]^{1/2} \} = \ln \{ A_p [A_d/ A_t]^{1/2} \} - [E_{Pt} (E_d/2) - (E_t / 2)]/ RT \qquad (12)$$

The composite or overall activation energy for the rate of polymerization E_R is $[E_p+(E_d /2) -(E_t /2)]$. Since Rp is given by Equation (2), one can write Equation (12) as:

$$\ln R_P = \ln \{ A_p [A_d/ A_t]^{1/2} \} + \ln [(f [I]^{1/2} [M])] - (E_R/RT) \qquad (13)$$

E_R and $A_p (A_d /A_t)^{1/2}$ can be obtained from the slope and intercept, respectively, of a plot of ln R_p verses 1/T.

The kinetic investigation of MMA was carried out using initial monomer concentration of 1 mol dm^{-3} at the initial BPO concentration of 1 x10^{-3} mol dm^{-3} at four different temperatures (70, 75, 80 and 85 °C). Rp were calculated from the slope of typical time-conversion curves, Figure (3-a) show typical time-conversion.

An Arrhenius plot of the overall rates of polymerization (R_p) is shown in Figure (3-b). The value of (68.65) kJ mol^{-1} was calculated for the overall activation energy of polymerization of MMA, is considerably higher compared with those of common acrylate monomers [15,16] . E_d, the activation energy for thermal initiator decomposition, is in range 120-150 kJ mol^{-1} for most of the commonly used initiator. The, E_p and E_t values for most monomers are in the range 20-40 and 8-20 kJ mol^{-1}, respectively [17]. The overall activation energy E_R for most polymerizations initiated by thermal initiators decomposition is about 80-90 kJ mol^{-1}, therefore, the value of (68.65) kJ mol $^{-1}$ suggests that the difference between the activation energies of propagation and termination reaction is very small, similar finding have been observed in the polymerization of methyl α - acetylaminoacrylate [18].
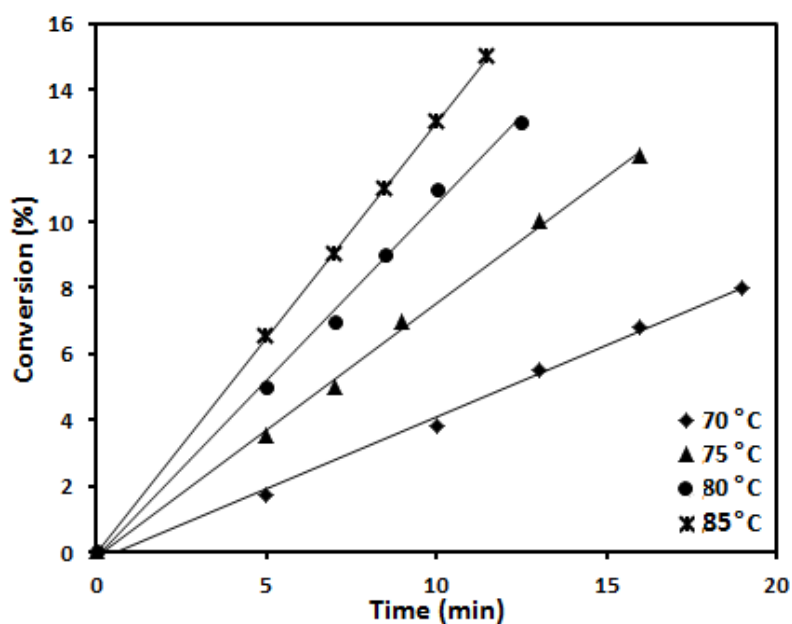

Figure (3-a): Time – conversion curves for polymerization of MMA at various temperatures. [MMA]$_o$=1 mol.dm^{-3}; [BPO]$_o$ = 1x10^{-3} mol dm^{-3}.
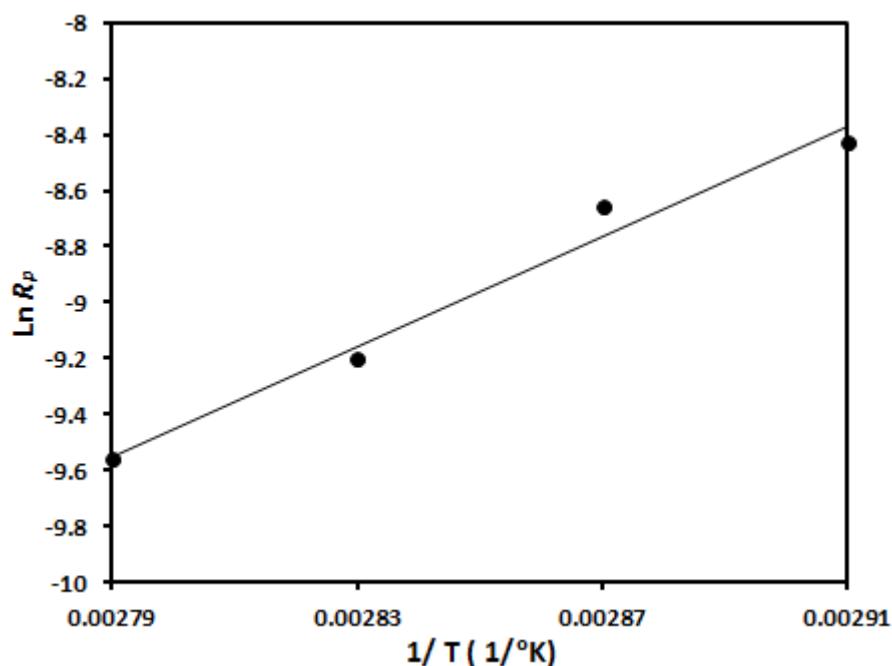

Figure (3-b): Arrhenius plot of overall rate of polymerization R$_P$ for MMA.

Effect of Solvent Polarity on R_P

Three different solvents tetrahydrofuran, chloroform and benzene having the dielectric constants 7.58, 4.81 and 2.27, respectively were used to examine the effect of solvent on R_P. The polymerization reaction for MMA (1 mol.dm^{-3}) was carrying out using 1x10^{-3} mol.dm^{-3} of BPO at 70 °C. However, it was found that the R_P arrange in the following order:

tetrahydrofuran > chloroform > benzene

The decrease in the rate of polymerization could be explained in terms of the increase in the polarity of the organic medium. Thus, greater transfer of benzoyl peroxide radicals to the organic phase may occur.

Average degree of Polymerization (DP$_n$)

From the intrinsic viscosity data which has been obtained using the viscosity measurements of poly MMA, the average degree of polymerization (DP$_n$) of MMA with different concentrations of BPO was determined. The average degree of polymerization decreases with increasing BPO concentration. An increase of benzoyl peroxide radicals decreases the length of the poly MMA chain and this leads to a reduction in the molecular weight of the polymer which is directly proportional to the average degree of polymerization of the polymer according to the following Equation [19]:

M.wt of polymer = DP$_n$ x M.wt of monomer

However, a straight line passing through the origin could be obtained by plotting of $1/DP_n$ versus $[BPO]^{1/2}$ (Table 1).

Table 1: Dependence of DP$_n$ on [BPO]

[BPO] x10^{-3} mol dm^{-3}	[BPO]$^{1/2}$ x10^{-2} (mol dm^{-3})$^{1/2}$	DP$_n$ x10^{-3}	$1/DP_n$ x10^3
1.0	3.16	3.12	0.320
2.0	4.47	2.33	0.429
3.0	5.48	1.98	0.505
4.0	6.32	1.85	0.540

CONCLUSIONS

In the present work, we carried out a set of experiments on the homopolymerization of methyl methacrylate in benzene with (1-4) mol dm^{-3} of monomer and $(1 \times 10^{-3} – 4 \times 10^{-3})$ mol dm^{-3} of benzoyl peroxide as initiator at 70 °C. In accordance with theory, an initiator of order 0.5 was obtained, and deviation from normal kinetic was observed with an order of 1.38 with respect to the monomer concentration. The value (68.65) kJ mol^{-1} was determined to be the activation energy, which is not in satisfactory with the value of most monomer that are thermally initiated. The observed value of activation energy of (MMA-BPO-Bz) system suggests that propagation and termination reactions have equal activation energy and the difference between them is nearly zero.

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