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Radical Polymerization Kinetics of Hexyl Methacrylate in Dimethylsulfoxide Solution

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Abstract:

In this study, we conducted a series of polymerization studies of hexyl methacrylate in dimethyl sulfoxide with (0.1 - 0.4) mol dm^{-3} of monomer and ($1\times10^{-3} – 4\times10^{-3}$) mol dm^{-3} of benzoyl peroxide as initiators at 70 °C. Using the well-known conversion vs. time technique, the effects of initiator and monomer concentration on the rate of polymerization (R_p) were studied. An initiator of order 0.35 was obtained in accordance with theory and a divergence from normal kinetics was detected with an order of 1.53 with respect to monomer concentration. The activation energy was determined to be (72.90) kJ mol^{-1}, which does not correspond to the value of most thermally initiated monomers. The observed value of activation energy suggests that propagation and termination reactions have equal activation energy and the difference between them is nearly zero. The average degree of polymerization (DP_n) decreased as benzoyl peroxide concentration increase whereas an increase in solvent polarity has slightly increased rate of polymerization value.

Keywords: Hexyl methacrylate, rate of polymerization, activation energy, degree of polymerization.

1. Introduction

The term rate of polymerization is given by the rate at which the monomer disappears [1]. It can be expressed by:

$$R_p = -\frac{d\,[M]}{dt} = Ri + Rprop \qquad (1)$$

Rprop and Ri are the rates of propagation and initiation respectively. After making some simplifying assumption: Finally, the Rp becomes:

$R_p = \{\ k_p\ [\frac{f\ kd}{kt}]^{½}\ \}\{\ [I]_0^{1/2}[M]\}_e\text{-}k_d t/2$ (2)

This equation shows a square-root dependency on the initial initiator concentration and a first-order dependence on the rate of polymerization in relation to the monomer concentration [2]. This reliance has been demonstrated by numerous polymerization systems. For example, 7-(methacroyloxy)-2-oxo-heptylphosphonic acid follows this equation when it was polymerized for kinetic study [1]. It's also noteworthy to observe that the rate of polymerization doubles when the monomer concentration is doubled [3].

When choosing how to carry out a polymerization, the impact of temperature on the degree and Rp is crucial. Increasing the reaction temperature often causes the polymerization rate to increase while the molecular weight of the polymer drops [4, 5]. The quantitative impact of temperature is nevertheless complicated because Rp depends on the interaction of the ki, kp and kt. An Arrhenius type relationship can be used to express the rate constants for termination, propagation and initiation:

$k=Ae^{\ -E/RT}$ or $Ink = In\ A\ - E_a/\ RT$ (3)

Where Ea is the Arrhenius activation energy, A is the collision frequency factor, and T is the Kelvin temperature. Numerous researchers [6–10] have looked into how the polymerization energy deviates from the fundamental set of rules for free radical polymerization. They found that the free radical polymerization end rate constant, kt, is a diminishing capacity of the responding radical's span and that the end rate between polymer radicals isn't always independent of their chain length. Unless the effects of the chain length dependence on end rate constants are taken into account, regular tactics for the dynamic study of radical polymerization appear to result in incorrect ends. In addition, there are many studies discussed kinetic investigation of different monomers. For example, Kumar *et al*. studied the kinetic of free radical polymerization of methyl methacrylate using cyclohexanone/water mixture as a solvent and persulfate potassium as an initiator. The order (0.5) was found with respect to phase transfer catalyst, (1) with respect to monomer concentration and (0.5) with respect to initiator concentration [11]. Victoria-Valenzuela and coworkers [12] 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. The aim of this study is to study the kinetic of polymerization of hexyl methacrylate include the influence of the monomer and initiator concentrations, polarity of solvent and average degree of polymerization on Rp. The overall activation energy was also determined.

2. Experimental Section

Materials

Commercial hexyl methacrylate monomer was shaken 2-3 times with 10% NaOH to eliminate hydroquinone inhibitor and then dried over anhydrous $CaCl_2$ for 5 h. After that, the monomer was passed through a 2.5x15 cm aluminum oxide (Al_2O_3) column until colorless products were obtained. Potassium persulfate and benzoyl peroxide were recrystallized twice from methanol prior to use. The monomers and initiators were filtered and refrigerated prior to use to prevent degradation or polymerization of the monomers. The filtered monomers must be kept in a dark, tight as well closed container. All solvents of 98% purity grade were used as received.

Homo polymerization of Hexyl Methacrylate

For homo polymerization of hexyl methacrylate, the following kinetic experiments were carried out: The test tubes were charged with the specified amounts of monomer HMA (0.1, 0.2, 0.3 and 0.4) mol dm^{-3}, benzoyl peroxide ($1x10^{-3}$, $2x10^{-3}$, $3x10^{-3}$, and $4x10^{-3}$) mol dm^{-3} and dimethyl sulfoxide. (Table 1, Exp. 1-96). In order to remove all oxygen in the mixture, 15 minutes of nitrogen gas bubbling preceded the polymerization and then the tubes were closed firmly. By putting the tubes in a thermostated water bath set at a certain temperature of 70 0.1 °C, the polymerization reaction was carried out. For calculation the activation energy, the polymerization was carried out using initial benzoyl peroxide (BPO) concentration ($1x10^{-3}$ mol dm^{-3}) at the initial monomer concentration of 0.1 mol dm^{-3} at four different temperatures (70, 75, 80 and 85 °C) (Table 1, Exp. 97-120). The polymerization was stopped after recording time by dumping the reaction mixture into a considerable excess of precipitant 100% methanol. The resultant polymers were filtered out and dried to a consistent weight at 40 °C.

Table 1: Experimental data of hexyl methacrylate (HMA) polymerization

Exp. No.	HMA mol dm^{-3}	BPO x 10^{-3} mol dm^{-3}	DMSO Vol ml	Temperature °C	Time min.
1-24	0.1	1,2,3,4	10	70	0-30
25-48	0.2	1,2,3,4	10	70	0-30
49-72	0.3	1,2,3,4	10	70	0-30
73-96	0.4	1,2,3,4	10	70	0-30
97-120	0.1	1	10	70-85	0-30

The well-known gravimetric approach was used to quantify monomer to polymer conversion.

$$wt\ \%\ of\ Conversion = \frac{weight\ of\ polymer}{weight\ of\ monomer\ feed} \times 100 \qquad (3)$$

The replication of runs ensured that the experiments were repeatable. At a given time, the residual monomer concentration [M] can be calculated using the following equation:

$[M]_0 = [M]_0 (1\text{-}C)$ (4)

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, Rp could be determined. Since the free-radical initiator is frequently present in low quantities in kinetic investigations, its concentrations and thermodynamic activity are likely to be similar.

Viscosity Measurement

Ubbelohde viscometer was calibrated according to ASTM D446 and ISO 3105 standard method. It was used to calculate the viscosity of the Poly HMA solutions. The measurements were carried out at 30 °C using DMSO as standard solvent. Intrinsic viscosity was determined by plotting C versus Ƞsp/c [11, 12]. By using the obtained intrinsic viscosity results, Mark-Houwink equation was employed to calculate the average degree of polymerization [13].

3. Results and Discussion

Determination of the Rate Equation

R_P for a variety of initiator and monomer concentrations might be determined from the lineslope of typical time-conversion curves. Typical time-conversion curves are shown in Figurs (1 and 2) for (variable initiator concentration and fixed monomer) and Figurs (4 and 5) for (variable monomer concentration and fixed initiator).

$R_p = [M]_0 /100 \times slope$ (5)

$[M]_0$:Feed monomer concentration, slope should be calculated from the initial lines of % conversion vs time.

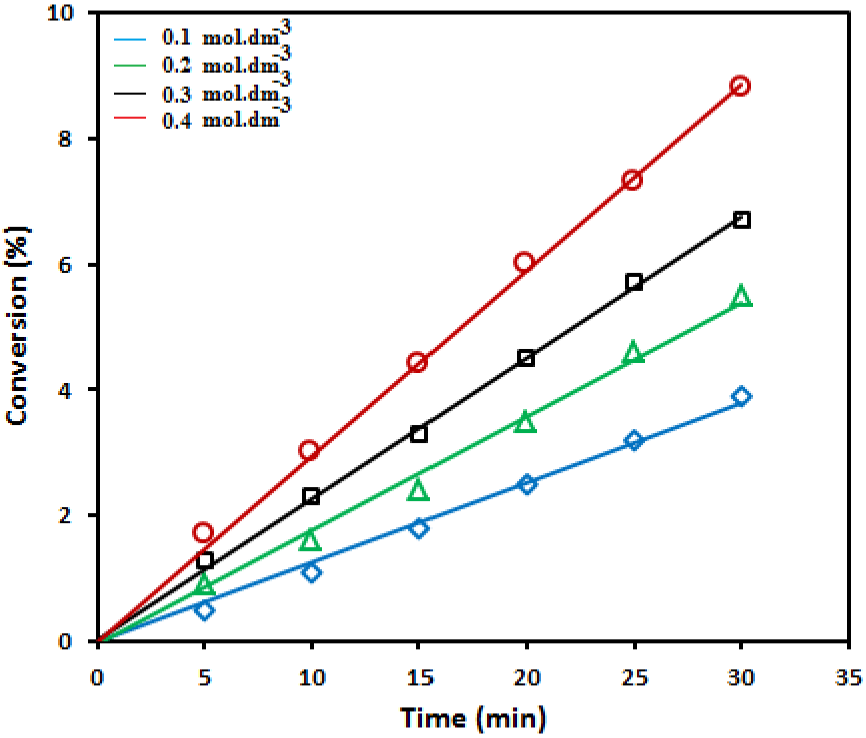

Figure 1: Conversion-time curves for polymerization of HMA $[HMA]_0$ =(0.1, 0.2, 0.3, 0.4) mol dm^{-3}, $[BPO]_0$ = 1×10^{-3} mol dm^{-3}

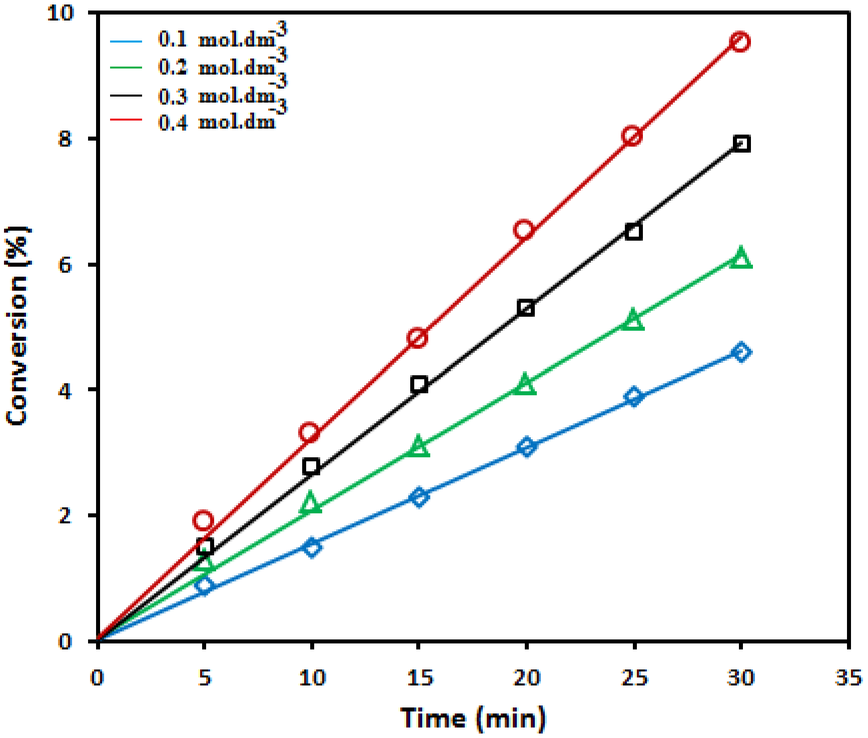

Figure 2: Conversion-time curves for polymerization of HMA $[HMA]_0$ =(0.1, 0.2, 0.3, 0.4) mol dm^{-3}, $[BPO]_0$ = 2×10^{-3} mol dm^{-3}

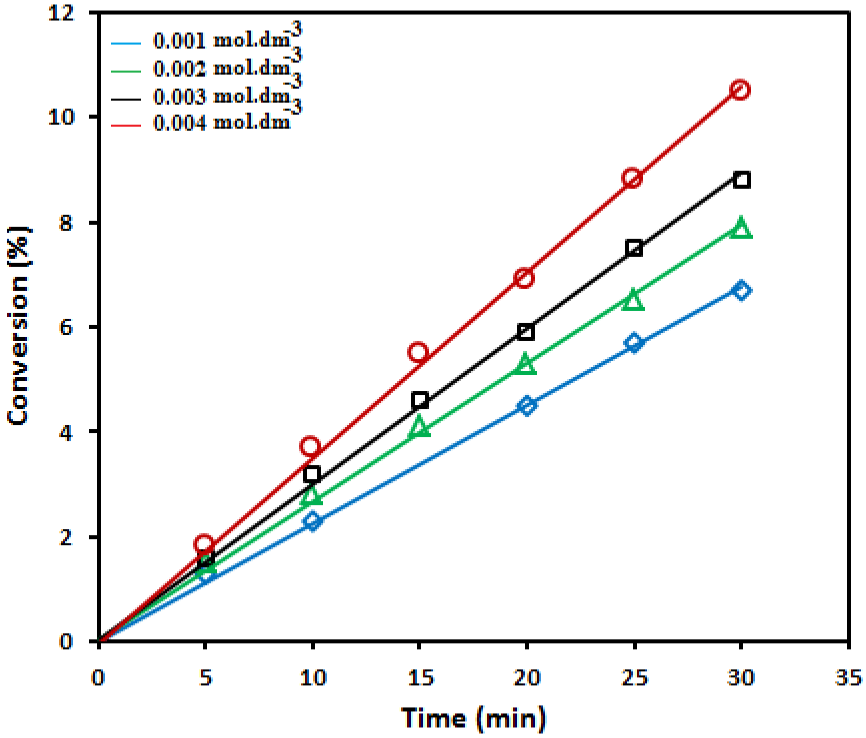

Figure 3: Conversion-time curves for polymerization of HMA. $[BPO]_0$ =(1, 2, 3, 4) ×10^{-3} mol dm^{-3}, $[HMA]_0$ = 0.3 mol dm^{-3}

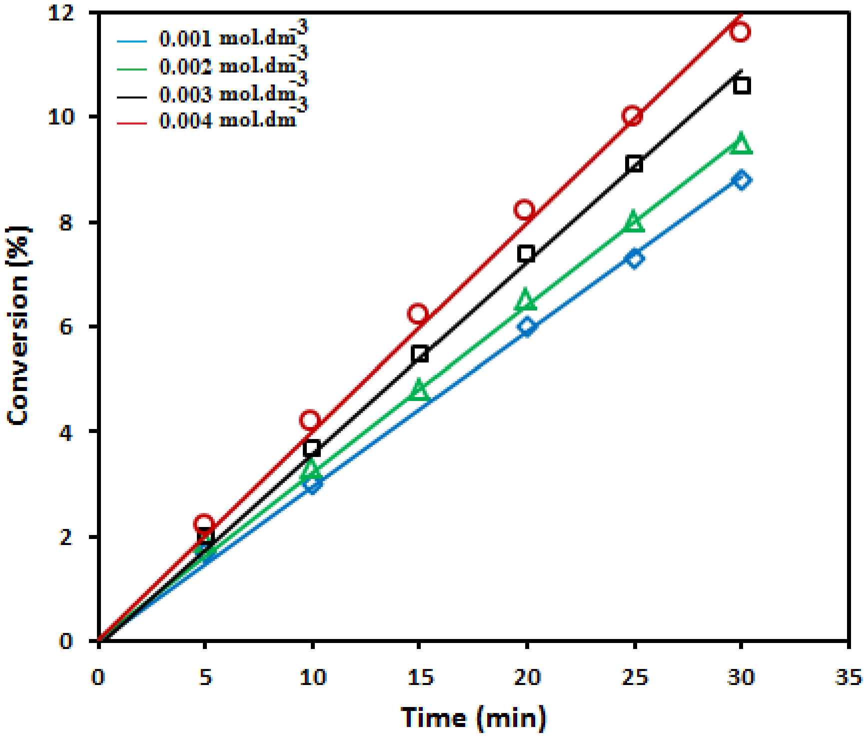

Figure 4: Conversion-time curves for polymerization of HMA. $[BPO]_0$ =(1, 2, 3, 4) ×10^{-3} mol dm^{-3}, $[HMA]_0$ = 0.4 mol dm^{-3}

The relationship between Rp and the concentrations of the initiator and monomer in such a system can be expressed as follows:

$$Rp = K\,[\text{monomer}]^{\alpha}\,[\text{initiator}]^{\beta} \qquad (6)$$

The logarithmic form of the equation presented above can be used to experimentally determine the order of the reaction with regard to the concentrations of initiator and monomer:

$\log Rp = \log K + \alpha \log[\text{monomer}] + \beta \log[\text{initiator}]$ (7)

The following results can be obtained:

From the dependence of Rp, on the monomer concentrations from 0.1 to 0.4 mol dm^{-3}; at a fixed initiator concentration:

Rate $\propto [M]^{\alpha}$

Plot of log Rp, verses log [monomer] has been fitted by linear least-square analysis, allowing both K and α to be calculated from the intercept and slope respectively, as shown in Figure 5 and the rate of polymerization was proportional to the 1.53 power of the monomer concentration.

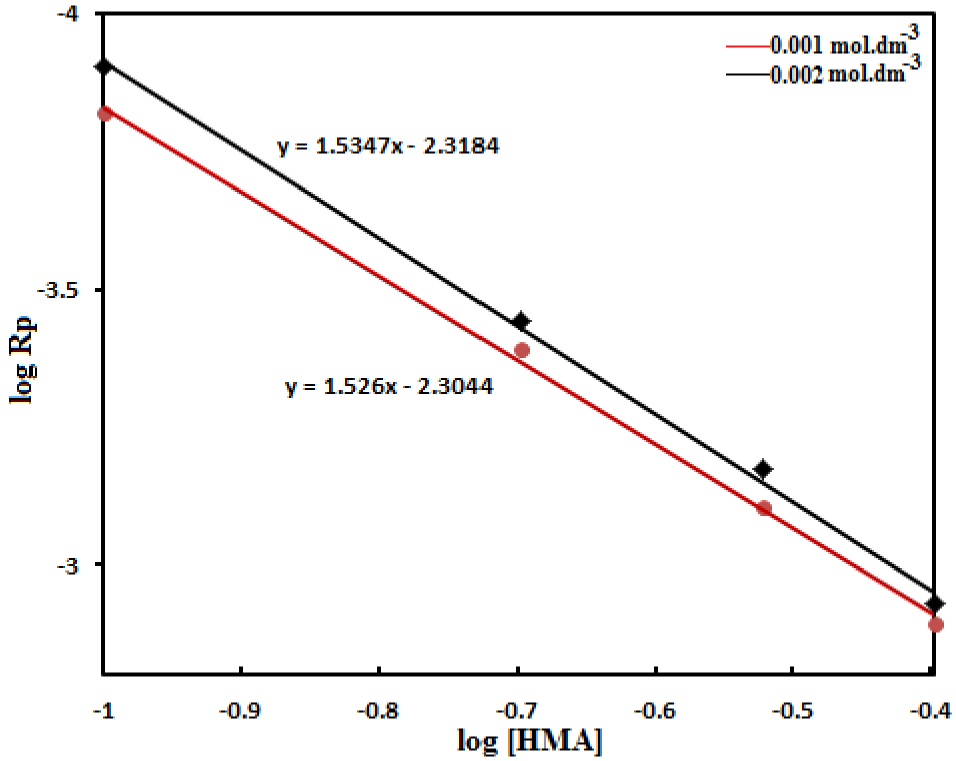

Figure 5: Dependence of Rp on the concentration of HMA at a fixed BPO concentration

Likewise, from the dependence of Rp, on the initiator concentrations from 0.001 to 0.004 mol dm^{-3}; at a fixed monomer concentration:

Rate $\propto [I]^{\beta}$

A plot of log R, verses log [initiator] has been fitted by linear least-square analysis, allowing both K and β to be determined from the intercept and slope, respectively, as shown in Figure 6 and the rate of polymerization correlated with the initiator concentration to the 0.35 power.

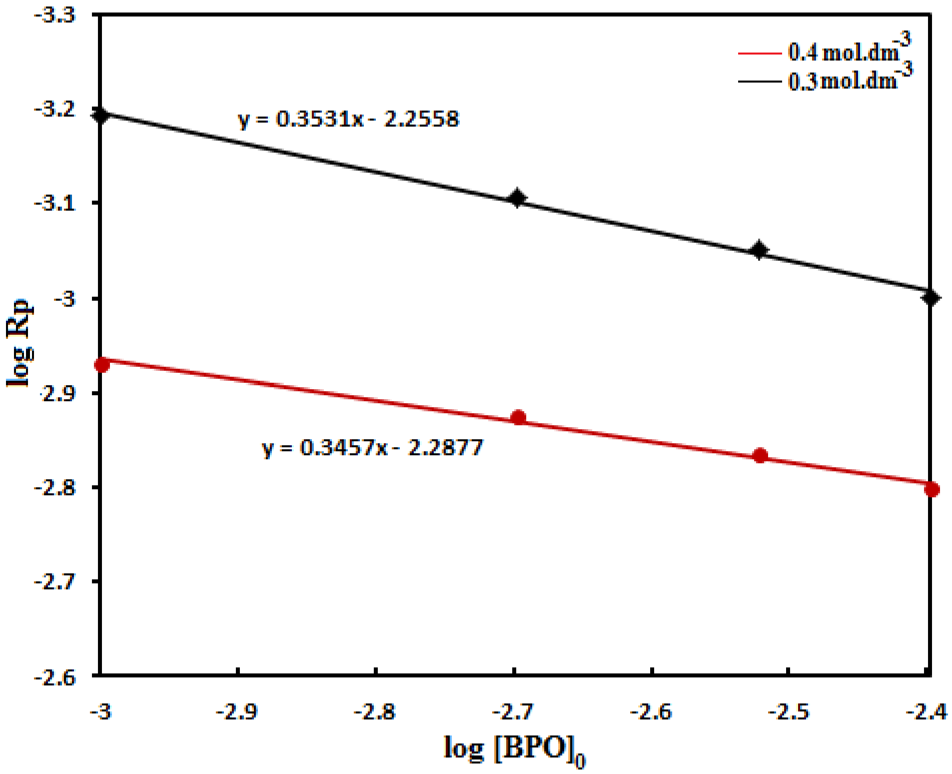

Figure 6: Dependence of Rp on the BPO concentration at a fixed HMA concentration

Using the experimental data and the slopes of the straight lines, the polymerization rate equation of hexyl methacrylate may be expressed as:

$R_P=K[NIPA]^{1.53}\ [PPS]^{0.35}$

K: is the overall rate constant.

The most typical instance of radical chain polymerization is described by equation (2.2). It demonstrates a first order dependence between the monomer concentration and the polymerization rate, which is reliant on the initiator exponent of 0.5. Any mechanism that prevents second-order termination between propagating chains could result in a deviation from the initiator exponent of 0.5. Common examples include primary radical termination and degradative chain transfer (147), which give rise to exponent < 0.5. A situation may also arise when the order of dependence of R, on [1] will be greater than 0.5 [14].

Overall Activation Energy of Polymerization

Rate of polymerization was calculated from the slope of typical time-conversion curves by using equation (4.1). Typical time-conversion curves and plot of the overall rates of polymerization Rp are shown in Figures 7 and 8 respectively. The activation energy of polymerization of HMA is determined to be (72.90) kJ mol^{-1}. However, this value is significantly lower than that of typical acrylate monomers such as methyl methacrylate [15, 16].

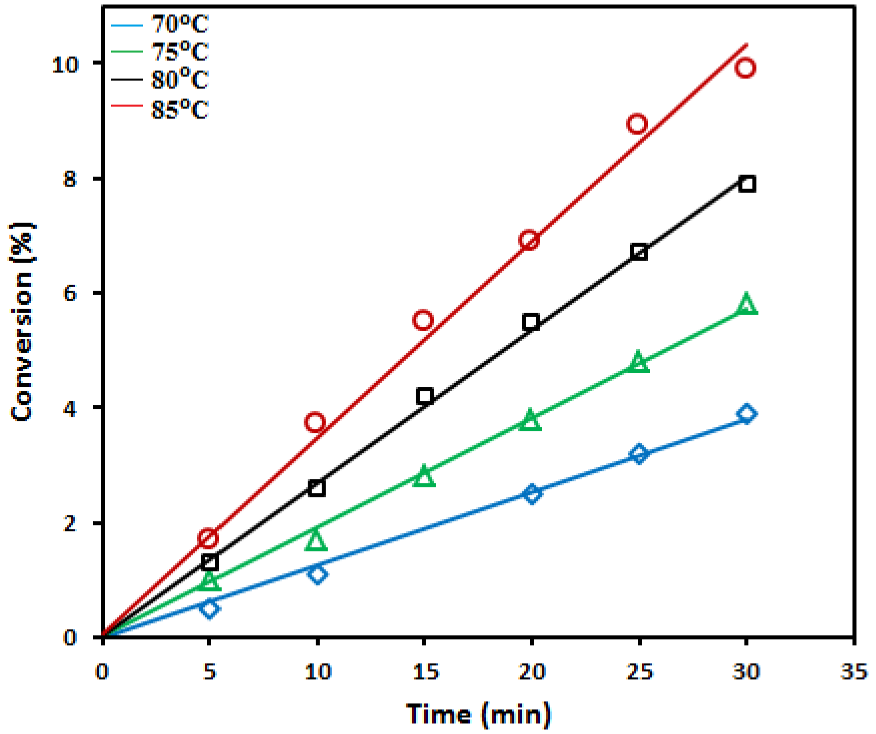

Figure 7: Time – conversion curves for polymerization of HMA at different temperatures. $[HMA]_o$=0.1 mol.dm^{-3}; $[BPO]_o$ = 0.001 mol dm^{-3}

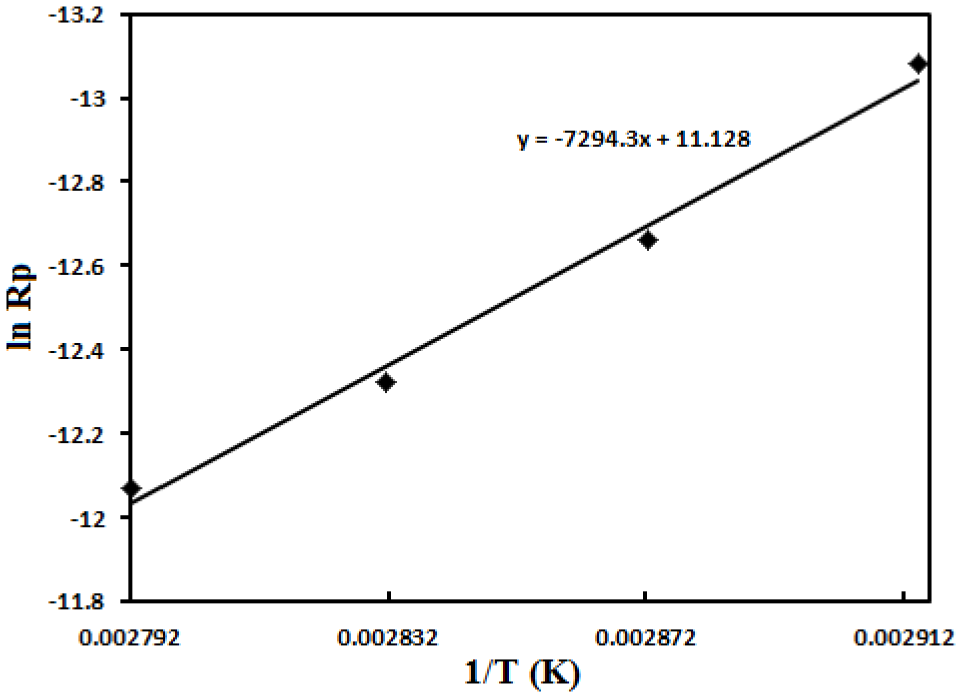

Figure 8: Arrhenius plot of R_P for HMA

For most common used initiators, the activation energy for thermal initiator decomposition, E_d, is in the range of 120-150 kJ mol^{-1}. Most monomers have activation energy for termination and propagation (E_t and E_p) values in the range of 8-20 and 20-40 kJ mol^{-1} respectively [17, 18]. Because most polymerizations initiated by thermal initiators have an overall activation energy ER of around 70-90 kJ mol^{-1}, the value of (72.94) kJ mol^{-1} proposes that the variance between the termination and propagation activation energies is quite modest. For methyl - acetylaminoacrylate polymerization, similar results have been obtained in the literature [19].

Effect of Solvent Polarity on Rate of Polymerization

Figure 9 shows time – conversion curves for polymerization of HMA using three different solvents (benzene, methyl ethyl ketone and dimethyl sulfoxide) having the dielectric constants (2.274, 18.51 and 46.68) respectively, to examine the effect of solvent on R_P. The polymerization reaction for HMA (1 mol.dm^{-3}) was carried out using 1×10^{-3} mol.dm^{-3} of BPO at 70 °C. However, it was observed that the R_P arranges according to the following order:

12.7×10^{-5} mol dm^{-3} min^{-1}, dimethyl sulfoxide > 10.5×10^{-5} mol dm^{-3} min^{-1}, methyl ethyl ketone > 7.7×10^{-5} mol dm^{-3} min^{-1}, benzene

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

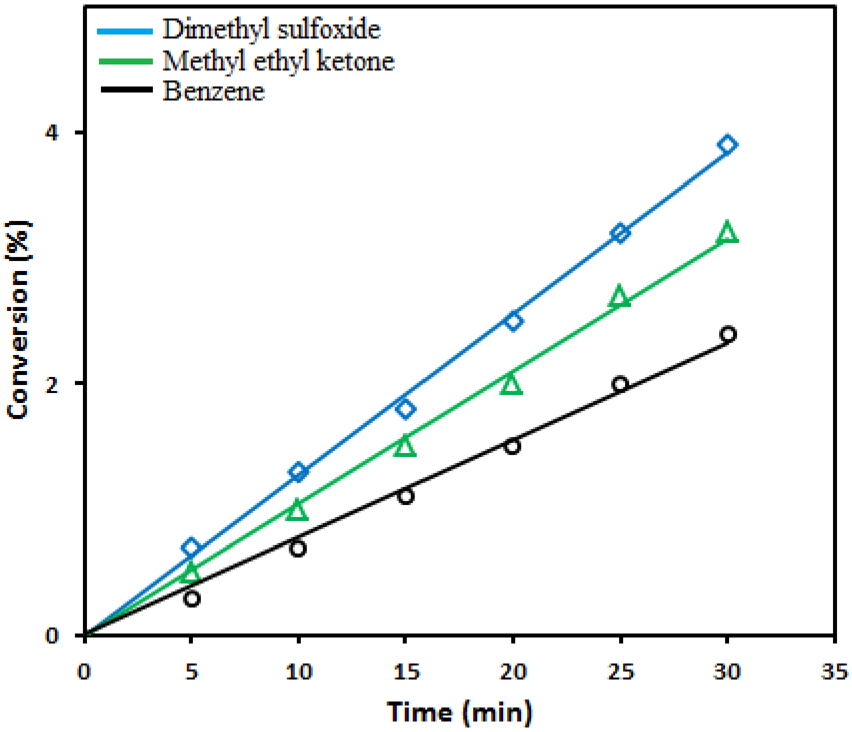

Figure 9: Effect of solvent polarity on time-conversion behavior

Effect of BPO Concentration on Degree of Polymerization

The average degree of polymerization (DPn) of HMA with various concentrations of BPO was calculated using the intrinsic viscosity data that was collected utilizing the viscosity measurements of poly HMA using Mark-Houwink equation. Increasing BPO concentration causes a decrease in the average degree of polymerization. An increase of benzoyl peroxide radicals decreases the length of the poly HMA 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 [20]:

$$M.wt\ of\ polymer = DP_n \times M.wt\ of\ monomer \qquad (7)$$

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

Table 2: Dependence of DP_n on [BPO]

BPO mol dm^{-3}	**$[BPO]^{0.5}$ mol dm^{-3}**	**DP_n**	**$1 / DP_n$**
0.001	0.031	0.0019	526
0.002	0.044	0.0015	666
0.003	0.054	0.0011	909
0.004	0.063	0.0008	1250

4. Conclusions

In this study, we conducted a series of polymerization studies of hexyl methacrylate in distilled water with (0.1 - 0.4) mol dm^{-3} of monomer and ($1\times10^{-3} - 4\times10^{-3}$) mol dm^{-3} of benzoyl peroxide as initiator at 70 °C. An initiator of order 0.38 was obtained in accordance with theory and a divergence from normal kinetics was detected with an order of 1.68 with respect to monomer concentration. The calculated activation energy was (72.94) kJ mol^{-1}, which is lower than the value for the 95% of thermally started monomers. The observed activation energy value indicates that propagation and termination reactions have equal activation energy and the difference between them is nearly zero.

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