Kinetic Study of Polymerization Isopropylacrylamide in Aqueous Solution

Hala Rahman Noormohamad [1]   *Ameen Hadi Mohammed* [1] *   *Mansor Bin Ahmad* [2]

[1]Department of Chemistry, College of Science for Women, University of Baghdad, Baghdad, Iraq.
[2]Department of Chemistry, Faculty of Science, University Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
*Corresponding author: ameenhadi80@yahoo.com
E-mail address: hala.rahman1205a@csw.uobaghdad.edu.iq , mansorahmed@gmail.com

Abstract:

An experimental of kinetics investigation of the solution free radical polymerization of isopropylacrylamide (IPAM) initiated with potassium persulfate (PPS) was conducted. The reactions were carried out at constant temperature of 60 °C in distilled water under unstirred and inert conditions. Using the well-known conversion vs. time technique, the effects of initiator and monomer concentration on the rate of polymerization (R_p) were investigated over a wide range. Under the conditions of our work, the orders 0.38 and 1.68 were found with respect to initiator and monomer, respectively. However, the rate of polymerization (R_p) is not straight forwardly corresponding monomer concentration. The value 46.11 kJ mol^{-1} was determined as the overall activation energy of polymerization, which is not satisfactory with the value of most thermal initiated monomers. R_p for IPAM in dimethyl formamide, dimethyl sulfoxide, and distilled water using PPS as initiator at 60 °C, was checked. An increase in solvent polarity has slightly increased (R_p) value. The effect of using different concentrations of PPS 0.001, 0.002, 0.003 and 0.004 mol dm^{-3}, on the average degree of polymerization (DP_n), was also studied, based on viscosity results obtained using distilled water at 20 °C. The results revealed that an increase in the initiator concentration has an effect in lowering (DP) values.

Key words: Activation energy, Isopropylacrylamide, Kinetic of polymerization, Polymerization degree, Radical polymerization.

Introduction:

The interests in study the kinetic of acrylate monomers group have been expanding because of their highly importance in different fields [1, 2]. For the creation of linear and crosslinked polymers, free radical polymerization is a preferred approach. This technique of polymerization has various advantages, including the quick synthesis of high molecular weight polymers, easier manufacturing techniques and faster reaction times [3, 4]. It involves four main reaction steps: initiation, propagation, termination and chain transfer. The mechanism of these reactions and the corresponding rate of polymerization (R_p) can be derived and given in Eqs. 1 and 2, respectively.

$$2f\,k_d\,[I] = 2k_t\,[M]^2 \qquad\qquad 1$$
$$R_p = \frac{K_P}{K_t^{0.5}}\,(f\,K_d)^{0.5}[I]^{0.5}[M] \qquad 2$$

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 [5]. This is known as the "classical" or "ideal" polymerization rate law and it is used to calculate the lumped parameter, kp/kt$^{1/2}$, using simple techniques like dilatometry and gravimetry. The divergence of polymerization energy from the basic set of guidelines for free radical polymerization has been studied by many researchers [6-10]. They discovered that the end rate constant in free radical polymerization, kt, is a declining capacity of the responding radical's span; they also revealed that the rate of end between polymer radicals is not always independent on their chain length. If the impact of the chain length reliance on end rate constants is not recognized,

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 orders 0.5, 1 and 0.5 were found with respect to phase transfer catalyst, monomer and initiator, respectively [11]. Victoria-Valenzuela and coworkers [12] 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. In addition, there are many studies which investigated the polymerization kinetics of acrylamide derivatives monomers. Hong studied the kinetics of radical polymerization of acryl amide, the orders with respect to initiator and monomer were 0.5 and 1.26, respectively [13]. Jens and his coworkers determined the activation energies for some poly acrylamide derivatieves such as N,N-dimethylacrylamide (N,N-dimethylprop-2-enamide), N-methylmethacrylamide (N,2-dimethylprop-2-enamide), and methacrylamide (2-methylprop-2-enamide). However, the activation energy of polymerization methacrylamide was found higher and larger volume as compared with N,N-dimethylacrylamide, and almost identical for N-methylmethacrylamide and for N,N-dimethylacrylamide [14]. The aim of this study is to study the kinetic of polymerization of IPAM including the influence of the monomer and initiator concentrations, polarity of solvent and average degree of polymerization on the rate of polymerization. This study also determines the overall activation energy of this polymerization.

Materials and Methods:
Materials and Instruments

The monomer isopropylacrylamide (IPAM) and the initiator potassium persulfate (PPS) from Aldrich chemical were obtained. They were purified before polymerization by recrystallization using ethanol then dried in a vacuum. Ethanol, tetrahydrofuran and chloroform of 98% purity grade were used as received. Perken Elmer-1650 spectrophotometer was used to determine the functional groups in the poly IPAM using a KBr disk method at wavenumber range of 400 to 4000 cm^{-1}. Ubbelohde viscometer was used to measure viscosity of prepared polymers solution.

Homopolymerization of IPAM

The following kinetic experiments were carried out for polymerization IPAM,: The test tubes were charged with the specified amounts of monomer IPAM 0.1, 0.2, 0.3, and 0.4 mol dm^{-3}, PPS 1×10^{-3}, 2×10^{-3}, 3×10^{-3}, and 4×10^{-3} mol dm^{-3}, and distilled water (Table. 1, Exp. 1-96). In order to remove all oxygen in the mixture, nitrogen gas was bubbled for 15 minutes prior to the polymerization, then the tubes were closed firmly. The polymerization reaction was performed by placing the tubes in a thermostated water bath at a definite temperature 60 ± 0.1 °C. For calculation the activation energy, the polymerization was carried out using initial PPS concentration 1×10^{-3} mol dm^{-3} at the initial monomer concentration of 0.1 mol dm^{-3} at four different temperatures 60, 70, 75 and 80 °C (Table 1. Exp. 97-120). The polymerization was halted after recording time by dumping the reaction mixture into a considerable excess of precipitant 100% ethanol. The resultant polymers were filtered out and dried to a consistent weight at 40 °C [15].

Table 1. Experimental data of isopropylacrylamide (IPAM) polymerization

Exp. No.	IPAM mol dm^{-3}	PPS $\times 10^{-3}$ mol dm^{-3}	Water Vol ml	Temperature °C	Time min.
1-24	0.1	1,2,3,4	10	60	0-30
25-48	0.2	1,2,3,4	10	60	0-30
49-72	0.3	1,2,3,4	10	60	0-30
73-96	0.4	1,2,3,4	10	60	0-30
97-120	0.1	1	10	60-75	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] was calculated from the relation:

$$[M]_0 = [M]_0\,(1-C) \qquad 4$$

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, the initial rate of polymerization could be determined. Because 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

The viscosity of poly IPAM solutions was calculated by using ubbelohde viscometer; it was calibrated according to ASTM D446 and ISO 3105 standard method. The measurements were carried out at 20 °C using distilled water as standard solvent. Intrinsic viscosity was determined by plotting C versus Ɲsp/c [11, 12]. Mark-Houwink equation was employed to calculate the average molecular weight of polymers using the obtained intrinsic viscosity data.

$$\eta = K\, M_v^{\alpha} \qquad\qquad 5$$

Where η is intrinsic viscosity, Mv is average molecular weight, $K = 14.5 \times 10^{-2}$ and $\alpha = 0.5$ are poly IPAM constants [16].

Results and Discussion:

The prepared polymer was characterized by using Fourier Transform Infrared (FTIR). The structure of poly IPAM is shown in Fig1. The absorption bands are as follows: The carbonyl absorption was observed at1651 (amide C=O). The bands at 3356 and 3402 cm^{-1} corresponded to the N-H asymmetrical stretching vibration of the amide group. A band at 1396 cm^{-1} corresponded to N-H stretching vibration. A band at 1450 cm^{-1} is attributed to the C-N stretch. A bands at 700 -990 cm^{-1} is ascribed to the mono and di substituted of vinyl group of IPAM.
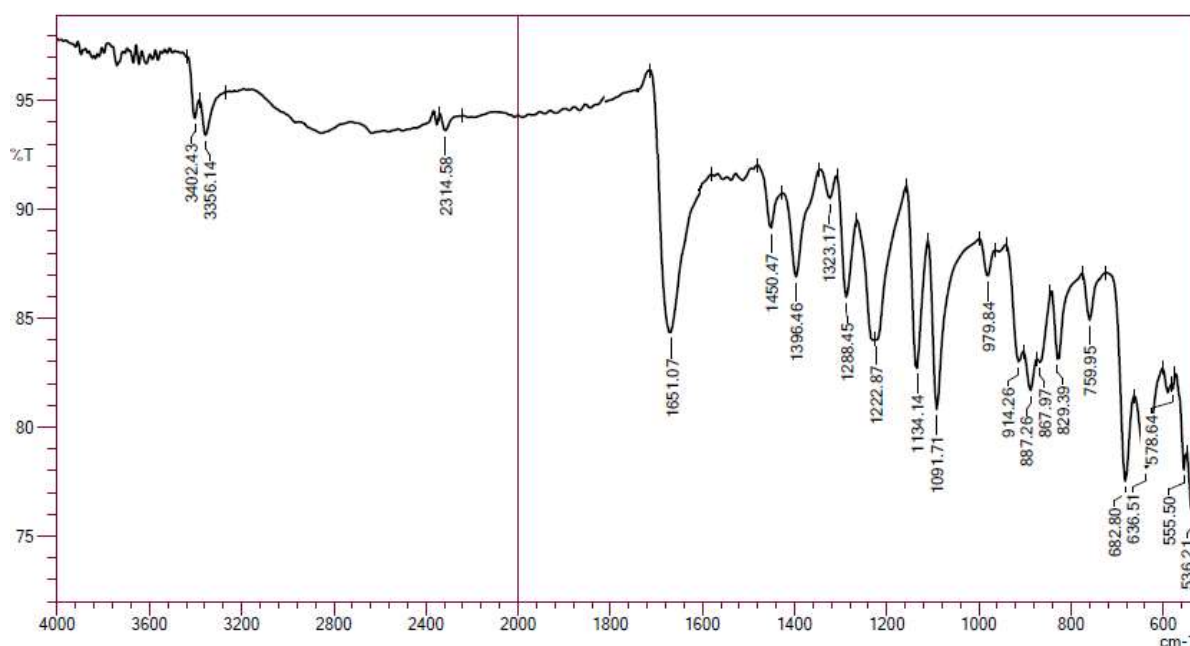

Figure 1. FTIR of poly isopropylacrylamide

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. Figs 2 and 3 show typical time-conversion curves at (variable initiator concentration and fixed monomer), while Figs. 5 and 6 show typical time-conversion curves at (variable monomer concentration and fixed initiator).

$$R_p = [M]_0 / 100 \times slope \qquad\qquad 6$$

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

The relation between polymerization rate and initiator and monomer concentrations in such a system, can be written as:

Rate α $[M]^{\alpha}$ $[I]^{\beta}$

$$R_p = k\,[monomer]^{\alpha}\,[initiator]^{\beta} \qquad\qquad 7$$

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

$$R_p = k\,[I]^{0.5}\,[M] \qquad\qquad 8$$

$$K = k_p / k_t^{1/2}\,(f\,k_d)^{1/2} \qquad\qquad 9$$

Where [M] and [I] are the monomer and initiator concentration respectively, K is the so called overall rate constant of homopolymerization

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which, in terms of Eq. 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 influence of the initiator on the total R_P was investigated at a number of different initiator concentrations, while the effect of the monomer on the overall R_P was investigated at a number of different monomer concentrations. The influence of R_P on monomer and initiator concentrations is seen in Figs. 4 and 7, respectively. From the slope of the straight lines, the following rate equation was obtained

$$R_P = K[IPAM]^{1.68}[PPS]^{0.38} \qquad 10$$

The relation between the initiator concentration and the rate of polymerization can be expressed as follow using classical kinetic treatments of the free radical polymerization:

$$R_p \; \alpha \; [initiator]^{0.5} \qquad 11$$

However, Eq. 7 does not accurately characterize the results in terms of monomer concentration order; therefore, the observed order 1.68 contradicts the classical kinetic description. The ideal monomer-solvent mixtures would be anticipated to follow the classical kinetic description in general.
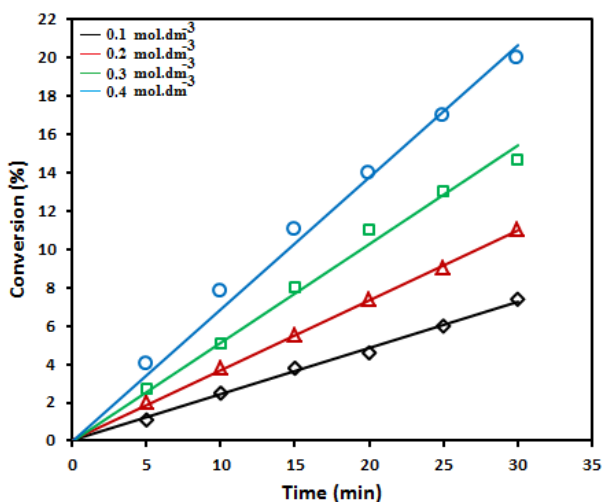

Figure 2. Conversion-time curves for polymerization of IPAM [IPAM]$_0$ =(0.1, 0.2, 0.3, 0.4) mol dm^{-3}, [PPS]$_0$ = 1×10^{-3} mol dm^{-3}
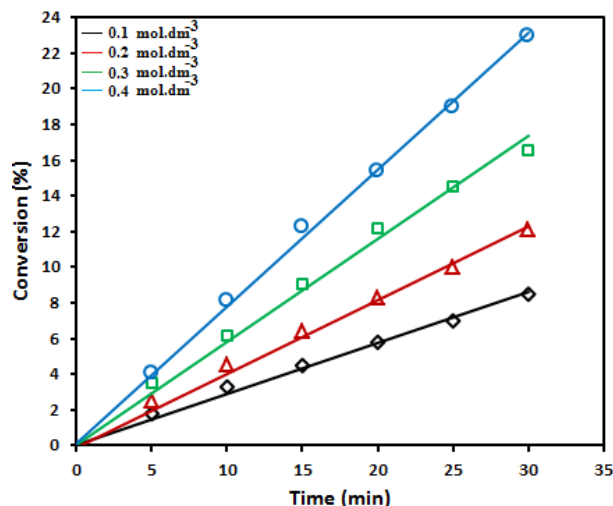

Figure 3. Conversion-time curves for polymerization of IPAM [IPAM]$_0$ =(0.1, 0.2, 0.3, 0.4) mol dm^{-3}, [PPS]$_0$ = 2×10^{-3} mol dm^{-3}
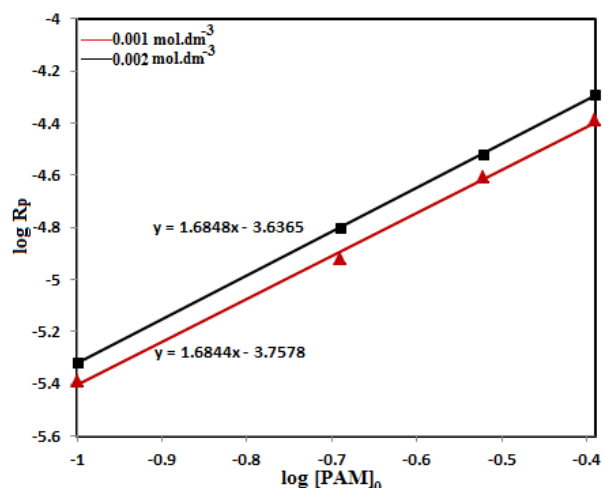

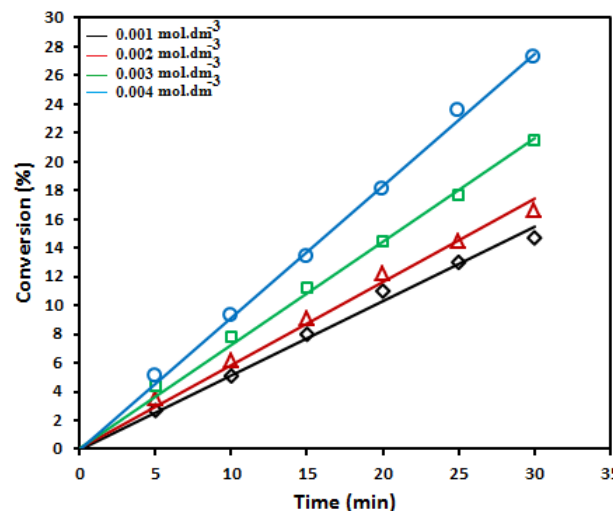**Figure 4. Dependence of Rp on the concentration of IPAM at a fixed PPS concentration**

Figure 5. Conversion-time curves for polymerization of IPAM. [PPS]$_0$ =(1, 2, 3, 4) ×10^{-3} mol dm^{-3}, [IPAM]$_0$ = 0.3 mol dm^{-3}

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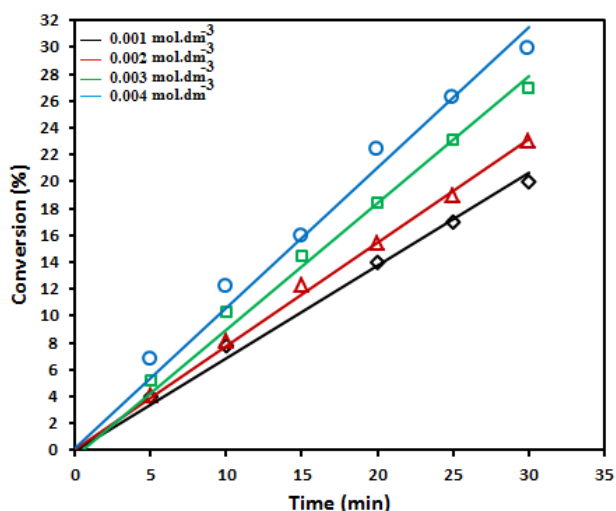2023, 20(5 Suppl.): 1926-1932
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Figure 6. Conversion-time curves for polymerization of IPAM. $[PPS]_0 =(1, 2, 3, 4) \times 10^{-3}$ mol dm^{-3}, $[IPAM]_0 = 0.4$ mol dm^{-3}
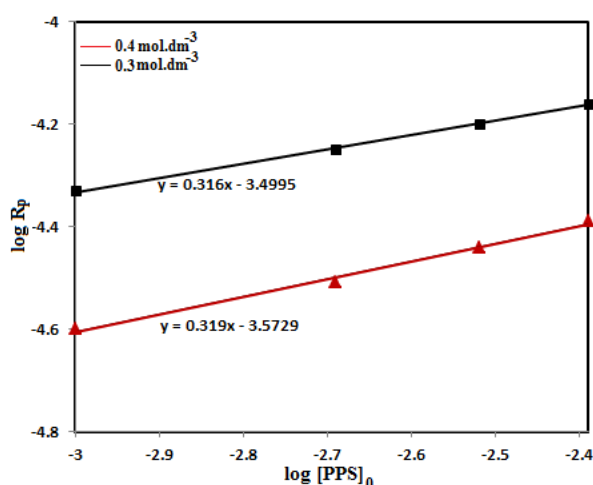

Figure 7. Dependence of Rp on the PPS concentration at a fixed IPAM concentration

Overall Activation Energy of Polymerization

The effect of temperature on polymerization rate is critical in determining how to do a polymerization. Increasing the reaction temperature speeds up polymerization and lowers the molecular weight of the polymer. However, an Arrhenius-type relationship can be used to express each of the rate constants for termination, initiation, and propagation [17]:

$$k = Ae^{-E/RT} \qquad\qquad 12$$
or
$$ln\, K = ln\, A - \frac{E}{RT} \qquad\qquad 13$$

Here T represents the Kelvin temperature, E the arrhenius activation energy and A is the collision frequency factor. By plotting 1 /T verses ln k (R_p), both A from the intercept and E from slope can be determined. The activation energy investigation of IPAM was conducted using initial PPS concentration 0.001 mol dm^{-3} and initial IPAM

concentration 0.1 mol dm^{-3} at four different temperatures 60, 65, 70 and 75 °C. Fig. 8, shows typical time-conversion, the slope of each line represents R_p at defined temperature. Figure 9 shows an Arrhenius plot of (R_p). The overall activation energy of polymerization of IPAM was calculated to be 46.11 kJ mol^{-1}, which is significantly lower than that of typical acrylate monomers [18, 19].
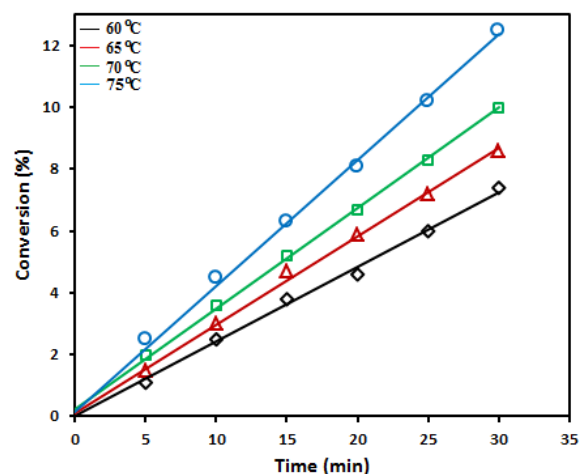

Figure 8. Time – conversion curves for polymerization of IPAM at different temperatures. $[IPAM]_0$=0.1 mol.dm^{-3}; $[PPS]_o$ = 0.001 mol dm^{-3}
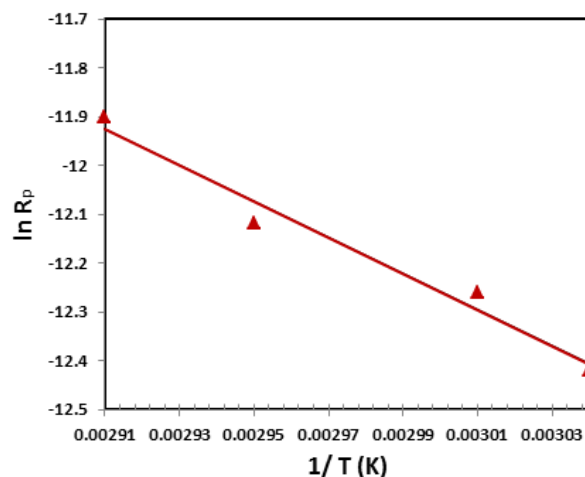

Figure 9. Arrhenius plot of R_P for IPAM

The activation energy for thermal initiators decomposition is in range 120-150 kJ mol^{-1} for most of the commonly used initiator. The, Ep and Et values for most monomers are in the range 20-40 and 8-20 kJ mol^{-1}, respectively [20, 21]. The overall activation energy ER for most polymerizations initiated by thermal initiators decomposition is about 80-90 kJ mol^{-1}, therefore, the value of 46.11 kJ mol^{-1} suggests that the difference between the activation energies of propagation and termination reaction is very small, similar findings have been

observed in the polymerization of methyl - acetylaminoacrylate [22].

Effect of Solvent Polarity on R_P

Three different solvents dimethyl formamide, dimethyl sulfoxide, and distilled water having the dielectric constants 36.71, 46.68 and 80.1, respectively were used to examine the effect of solvent on R_P. The polymerization reaction for IPAM 1 mol.dm^{-3} was carried out using 1×10^{-3} mol.dm^{-3} of PPS at 60 °C. However, it was found that the R_P arrange in the following order:

distilled water > dimethyl sulfoxide > dimethyl formamide

The increase in the rate of polymerization could be explained in terms of the increase in the polarity of the organic medium. Thus, greater transfer of potassium persulfate 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 IPAM, the average degree of polymerization (DP_n) of IPAM with different concentrations of PPS was determined. The average degree of polymerization decreases with increasing PPS concentration. An increase of potassium persulfate radicals decreases the length of the poly IPAM 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 [23]:

$M.wt \ of \ polymer = DP_n \times M.wt \ of \ monomer$

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

Table 2. Dependence of DP_n on [PPS]

PPS mol dm^{-3}	$[PPS]^{0.5}$ mol dm^{-3}	DP_n	$1/DP_n$
0.001	0.031	0.0028	357
0.002	0.044	0.0024	416
0.003	0.054	0.0020	500
0.004	0.063	0.0017	588

Conclusions:

From the above study it is found that 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 activation energy was determined to be 46.11 kJ mol^{-1}, which does not correspond to the value of most thermally, initiated monomers. The observed value of activation energy of (IPAM-PPS-Wt.) system suggests that propagation and termination reactions have equal activation energy and the difference between them is nearly zero.

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad, Iraq.

Authors' contributions statement:

H.R.N. carried out the synthesis and characterization of polymers. She also prepared the manuscript. A.H.M. and M.B.A supervised the study and reviewed the manuscript. All authors read and approved the final manuscript.

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دراسة حركية بلمرة الايزوبروبيل اكريلاfront في المحلول المائي

هالة رحمان نور محمد [1]   أمين هادي محمد [1]*   منصور بن احمد [2]

[1] قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد، بغداد، العراق.

[2] قسم الكيمياء، كلية العلوم، جامعة بوترا الماليزية

الخلاصة:

تم إجراء دراسة تجريبية حول الحركية لبلمرة محاليل الجذور الحرة لأيزوبروبيل أكريلاميد (IPAM) الذي بدأ باستخدام بيرسلفات البوتاسيوم (PPS). تم إجراء التفاعلات عند درجة حرارة ثابتة 60 درجة مئوية في ماء مقطر تحت ظروف خاملة. باستخدام تقنية التحويل المعروفة مقابل الوقت ، تم فحص تأثيرات تركيز البادئ والمونومر على معدل البلمرة (Rp) على مدى واسع. في ظل ظروف عملنا ، تم التوصل الى الرتب (0.38 و 1.68) فيما يتعلق بالبادئ والمونومر ، على التوالي. ومع ذلك ، فإن معدل البلمرة (Rp) لا تتبع او تعتمد تركيز المونومر المقابل مباشرة. تم تحديد القيمة (46.11) $kJ\ mol^{-1}$ على أنها طاقة التنشيط الكلية للبلمرة ، والتي لا تتوافق مع قيم معظم المونومرات الحرارية. أدت الزيادة في قطبية المذيب إلى زيادة طفيفة في قيمة (Rp) بينما انخفض متوسط درجة البلمرة (DPn) مع زيادة تركيز PPS.

الكلمات المفتاحية: طاقة التنشيط، أيزوبروبيل اكريلاميد، حركية البلمرة، درجة البلمرة، البلمرة الجذرية.

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