

Polymerization of Acrylamide in Water

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Abstract:

An experimental investigation of kinetics of the solution free radical homopolymerization of acrylamide initiated with potassium per sulfate (PS) was conducted at 70°C. The overall activation energy of homopolymerization was determined to be (24.65) 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 in dilute solution. Under the condition of our work the overall rate of polymerization was proportional to (initiator concentration)^{1/2} however, in contrast to the classical kinetic picture, it is not directly proportional to the monomer concentration .

Key words: Acrylamide, radical polymerization, kinetic aspects.

Introduction:

Polyacrylamide (IUPAC Poly (2-propenamide) or poly (1-Carbamoylethylene)) is apolymer (-CH₂CHCONH₂-) formed from acrylamide subunits that can also be readily cross-linked [1] .In cross-linked from it is highly water-absorbent ,forming a soft gel used in such application as PAM gel electrophoresis and in manufacturing soft contact lenses. Neamtu and Nita prepared gels by polymerization of AM cross-linked with N,N-methylene- Bis-acrylamide using aredox initiation (potassium per sulfate / ascorbic acid) system [2]. In the straight-chain form, it is used as a thickener , it has used as a subdermal for aesthetic surgery [3] .It has used also as flocculants in waste water treatment application [4] as drug reduction agent and drilling fluid in enhanced oil recovery [5,6] as additives in papermaking [7] and as a drug-delivery agent [8-10]. PAM is a synthetic water-soluble polymer made from monomers of AM ,It binds soil particles together once soil particles suspended in water are bound together by PAM [11]. PAM was used as a polymer additive to reinforce the gel electrolyte . Effects of this additive have been investigated in terms

of conductivity gelling time, gel strength and pattery capacity [12]. The polymerization of AM was carried out using t- Butyl peroxide as an initiator in –DMF under microwave irradiation [13].

Free radical polymerizations comprise a number of fundamental reaction steps. In their most simple and Common form, for types of reactions can be distinguished: initiation, propagation, chain transfer and termination. The reaction mechanism and the corresponding rate equations are given in (1). The polymerization rate can be derived quasi steady state assumption [4]:

$$2 f k_d [I] = 2 k_t [M]^2 \quad (1)$$

$$R_p = (k_p / k_t^{0.5}) (f k_d)^{0.5} [I]^{0.5} [M] \quad (2)$$

Where [M] and [I] are the concentration of monomer and initiator respectively, thus the overall rate of Polymerization should, in the early stages of the reaction, be proportional to the square root of the initiator concentration and, if f is independent of [M], the first power of the monomer 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 kinetics from simple system of rules of free radical polymerization have mostly been discussed by several workers [15-16] , they marked that the rate of termination between polymer radicals is not always independent of their chain length; it has been pointed out that the termination rate constant in free radical polymerization , k_t , is a decreasing function of the size of reacting radical . Conventional methods for the kinetic study of radical polymerization are shown to lead to erroneous conclusions if the effect of the chain length dependence of termination rate constants is not taken into account.

Experimental

Materials:

All, monomer, initiator , and solvent were obtained from Aldrich-Oma chemical Co. Acrylamide was recrystillized from chloroform several time and dried under vacuum until all the chloroform are removed. Initiator (Potassium per sulphate) was purified by twice recrystallizations from chloroform and refrigerated prior to use.

Homopolymerization

Homopolymerization kinetic experiments were carried out for acrylamide as follows:

The prescribed amount of monomer AM (1 , 1.5 , 2)mol dm⁻³, PS (1.8×10⁻² , 3×10⁻² , 5×10⁻²) mol dm⁻³, and water were charged in the test

tubes. Nitrogen gas was bubbled through the mixture for 5 minutes, and closed firmly. The polymerization reaction was initiated by placing the tubes in a thermo stated water path at a definite temperature $70 \pm 0.1^\circ\text{C}$. After recorded time, the polymerization was stopped by pouring the reaction mixture in to the a large excess of precipitant absolute ethanol. The resulting polymers were filtered off, dried under reduced pressure 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.

The residual monomer concentration $[M]$ at a given time was calculated from relation:

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

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

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.

Experimental result and their evaluation:

Determination of the rate equation system of (AM-PS-Wt)

The rate of polymerization R_p for a series of monomer and initiator concentration were calculated from the slope of typical time-conversion curves .Figure (1-a) show typical time-conversion curves at (fixed initiator and variable monomer concentration), while figure (1-b) shows typical time-conversion curves at (fixed monomer and variable initiator concentration).

$$R_p = [M]_0 / 100 \times \text{slope} \quad (4)$$

$[M]_0$: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 monomer and initiator concentration can be written as :

$$\text{Rate} \propto [M]^\alpha [I]^\beta$$

$$R_p = k [\text{monomer}]^\alpha [\text{initiator}]^\beta \quad (5)$$

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

$$R_p = k [I]^{0.5} [M] \quad (6)$$

$$K = k_p / k_t^{1/2} (f k_d)^{1/2} \quad (7)$$

Where $[I]$ and $[M]$ are the initiator and monomer concentration

respectively, K is the so called overall rate constant of homopolymerization which, in terms of Eq.(7), contain the rate constant of elementary reactions,i.e., those of chain propagation (k_p), chain termination (k_t) and initiation (k_d).

The effect of monomer on the overall rate of polymerization was studied at several fixed initiator concentration, likewise the effect of initiator on the overall rate of polymerization was studied at several fixed monomer concentration.

Figures (2-a) and (2-b) show the dependence of the polymerization rate on monomer and initiator concentration, respectively. The following rate equation was obtained from the slope of the straight lines.

$$R_p = K[AM]^{0.93} [PS]^{0.5} \quad (8)$$

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:

$$R_p \propto [\text{initiator}]^{0.5} \quad (9)$$

On the other hand Eq. (6) does not describe correctly the experiments in respect to the order of monomer concentration, thus the observed order (0.93) 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.

overall activation energy of homopolymerization

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:

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

or

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

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 eqn.(2). The temperature dependence of this ratio, obtained by combining three separate Arrhenius-type equations, is given by:

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

The composite or overall activation energy for the rate of

polymerization

E_R is $[E_p + (E_d/2) - (E_t/2)]$. Since R_p is given by eqn.(2), one can write eqn.(12) as:

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

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

The kinetic investigation of AM was carried out using initial monomer concentration of 1 mol dm^{-3} at the initial PS concentration of $1.8 \times 10^{-2} \text{ mol dm}^{-3}$ at three different temperatures ($56-64^\circ \text{C}$).

R_p were calculated from the slope of typical time-conversion curves, Fig (3-a) show typical time-conversion.

An Arrhenius plot of the overall rates of polymerization (R_p) is shown in Fig.(3-b). The value of $(24.65) \text{ kJ mol}^{-1}$ was calculated for the overall activation energy of polymerization of AM, is considerably lower compared with those of common vinyl monomer [17]. E_d , the activation energy for thermal initiator decomposition, is in range $120-150 \text{ kJ mol}^{-1}$ for most of the commonly used initiator. The, E_p and E_t values for most monomers are in the range $20-40$ and $8-20 \text{ kJ mol}^{-1}$, respectively [18]. The overall activation energy E_R for most polymerizations initiated by thermal initiators decomposition is about $80-90 \text{ kJ mol}^{-1}$, therefore, the value of $(24.65) \text{ kJ mol}^{-1}$ 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 [19].

Conclusions

In the present work, we carried out a set of experiments on the homopolymerization of acrylamide in water with $(1-2) \text{ mol dm}^{-3}$ of monomer and $(1.8 \times 10^{-2} - 5 \times 10^{-2}) \text{ mol dm}^{-3}$ of Potassium per sulfate 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 0.93 with respect to the monomer concentration.

The activation energy was determined to be $(24.65) \text{ kJ mol}^{-1}$, which is not in satisfactory with the value of most monomer that are thermally initiated. The observed value of activation energy of (AM- PS- Wt) system suggests that the difference between the activation energies of propagation and termination reactions is nearly zero.

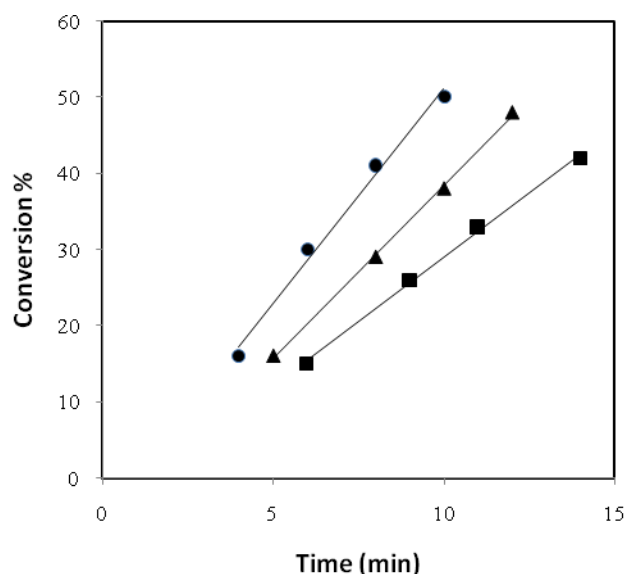


Figure (1-a):- Time – conversion curves for radical polymerization of (AM – PS – Wt) system at 70 C° as a function of monomer concentration; $[AM]_0=(1, 1.5, 2) \text{ mol dm}^{-3}$; $[PS]_0=1.8 \times 10^{-2} \text{ mol dm}^{-3}$.

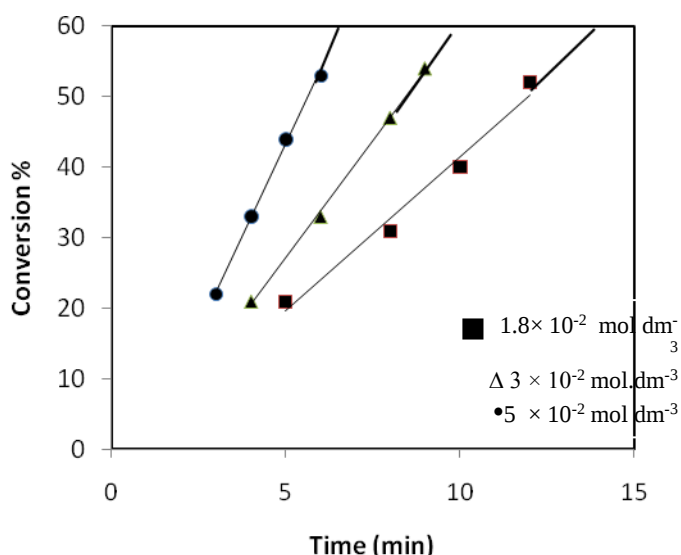


Figure (1-b):- Time – conversion curves for radical polymerization of (AM – PS – Wt) system at 70 C° as a function of Initiator concentration; $[PS]_0=(1.8 \times 10^{-2}, 3 \times 10^{-2}, 5 \times 10^{-2}) \text{ mol dm}^{-3}$; $[AM]_0 = 2 \text{ mol dm}^{-3}$.

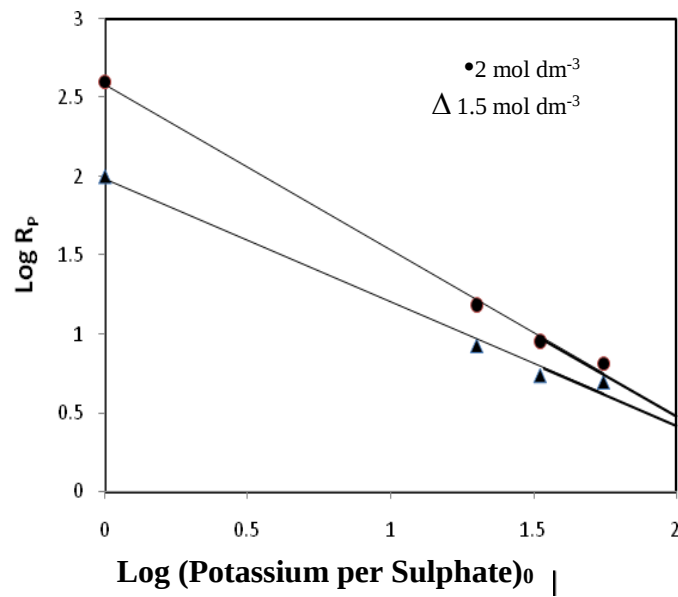


Figure (2-a):- Dependence of overall initial rate of polymerization on the monomer concentration at a fixed initiator concentration

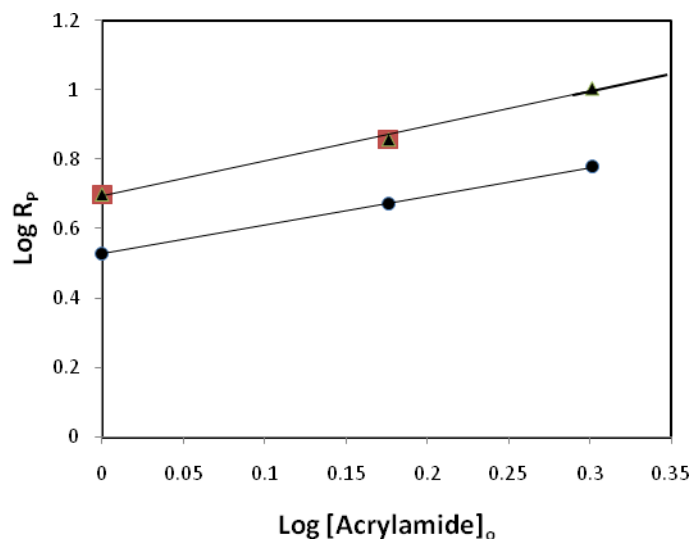


Figure (2-b):- Dependence of overall initial rate of polymerization on the initiator concentration at a fixed monomer concentration.

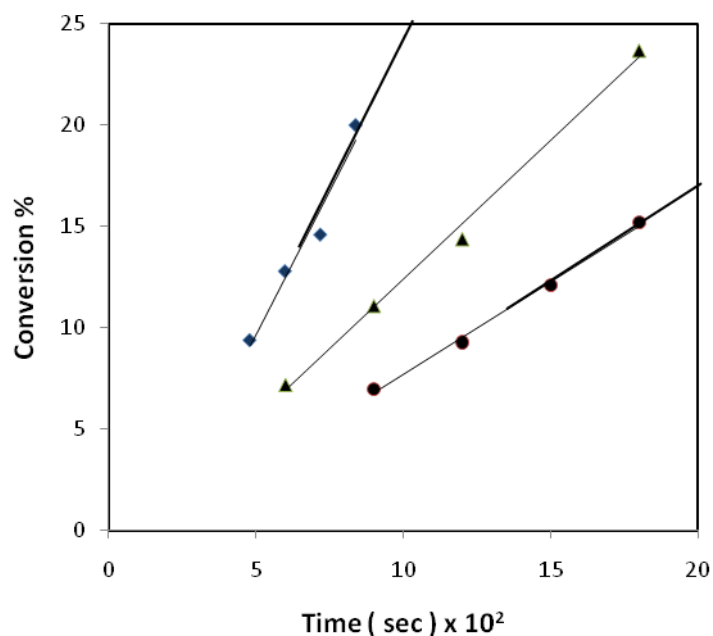


Figure (3-a):- Time – conversion curves for radical polymerization of (AM – PS – Wt) system at various temperatures; $[AM]_0 = 1 \text{ mol.dm}^{-3}$; $[PS]_0 = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$.

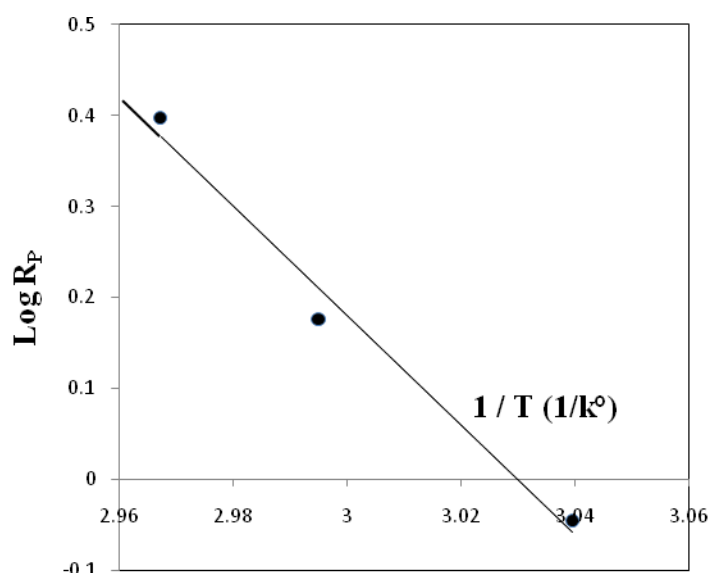


Figure (3-b):- Arrhenius plot of overall rate of polymerization R_P for the (AM – PS – Wt) System.

REFERENCES:

1. Wisconsin Dep. of Transportation. Madison, WI."polyacrylamide as a soil stabilizer for Erosion control.Report No. WI 06-98 2001.
2. I. NEAMTU , L. E . NITA , Institute of Macromol. chem.. J. of optoelectronics and advanced Materials 8, 201-204, 2006.
- 3.R.WANG , G.L.Mc Cormick, A.B.Lowe,Macromol,38,9518. 2005.
- 4.T.Wada,H.Sekiya ,S.Machi, J. Appl. Polym. Sci,20,3233 ,1976
- 5.P.S.Virt,J,Fluid Mech.,45,225,1971. 6.D.P.Enright, A.C.Perricone, Pet. Eng. Int,60,55,1988.
- 7.J.L.Date,J.M.Shute, Tappi,42,824,1959.
- 8.S.Buck,P.S.Pennefather, H.Y.Xue,J.Grand,Y,-L Cheng,C.J.Allen,Biomacromol.,5,2230, 2004.
- 9.B.Singh,G.S.Chauhan,S.Kumer,N.Chauhan,Carbohydr.polym,67,190,2007.
- 10.C,-S Chaw ,K- W .Chooi, X.-M.Liu, Tan,L Wang,Y-Y.Yang. Biomaterials, 25,4297,2004.
- 11.A.Nishihara and C.Shock, Melheur Exp. Station, Oregon state Univers,56,429-444,2001.
- 12.W.Siridetpan.program in petrochem. And polym Sci.,45, 10330, 2006.
- 13-T.Iwamura,K.Ashizawa and M.Sakaguchi Institute for Enviromental Sci.,42,5001,5006,2009.
- 14.J.W.Breitenbach and Ch. Srna,Pure Appi, Chem.,4,245,1962.
- 15.S.Tazuke and T.Yamane,J.Polym.Sci,part B,9,331,1971.
- 16.G.E.S cott, and E.Senogles,J,Macromol., Sci.-Chem. 8(4),753-37,1974.
- 17.F.Tudos, T.Kelen, J.Macromol. Sci.,Part A, 16, 1283,1981.
- 18.Principles of polymerization / Fourth Edition / Chapter 3, edited by GEORGD ODIAN. Wiley- Interscience, 2004.
- 19-Seizo. Masuda, Keiji. Minagawa, Hiroyuki. Ogama, Masami. Tanaka. Macromol.Chem. Phys. 201, 1787-1792, 2000.

بلمرة الاكريل امايد في الوسط المائي

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الخلاصة :

تضمن البحث بلمرة مونومر الاكريل امايد بلمرة جذرية متجانسة باستعمال احد انواع البادئات الحرارية للجذور الحرة وهو (بيرسلفات البوتاسيوم) بدرجة حرارة 70° م كما تم ايجاد طاقة التنشيط الكلية لتفاعل البلمرة المتجانسة من خلال دراسة العلاقة بين معدل سرعة البلمرة ودرجة الحرارة عند ثبوت التركيز المولاري للمونومر والبادئ وقد وجد ان طاقة التنشيط تبلغ (24.65) كيلو جول / مول , وتضمنت الدراسة بحث حركية البلمرة المتجانسة من خلال دراسة العلاقة بين معدل سرعة البلمرة والتركيز المولاري للمونومر عند ثبوت التركيز المولاري للبادئ بدرجة حرارة 70° م ودراسة العلاقة بين معدل سرعة البلمرة والتركيز المولاري للبادئ عند ثبوت التركيز المولاري للمونومر بدرجة حرارة 70° م , وقد اوضحت الدراسة ان معدل سرعة تفاعل البلمرة المتجانسة بطريقة الجذور الحرة لمونومر الاكريل امايد يخضع لتفاعلات البلمرة المتسلسلة النموذجية .