

Polymerization of MMA and 2-HPMA, Initiated by the Azobisisobutyronitril and BenzoyelP roxide: a Kinetic Study

Majid Abdoussⁱ, Soheila Farajiⁱⁱ and Mehran Javanbakhtⁱⁱⁱ

ABSTRACT

Kinetic investigations of the radical polymerization of methylmethacrylate (MMA) and 2-hydroxypropyl methacrylate (2-HPMA) as monomers with azobisisobutyronitrile (AIBN) and benzoyel proxide (BPO) as initiators in toluene solvent were carried at 65-75°C and 70-90 °C respectively. Using analytical technique with UV detection, the consumption of both monomer and initiators as well as the formation of reaction products of the latter could be followed. The rate equation is proposed as $R_p \propto [M]^1 [I]^{1/2}$. The effect of temperature and concentration of the monomer were studied on the polymerization of MMA and 2-HPMA. By increasing the temperature and the concentration of the monomer and initiators the percent of conversion is increased. The activation energy of reaction of MMA and 2-HPMA with AIBN and BPO were defined. Rate constant and pre-exponential factor of Arrhenius equation of MMA and 2-HPMA with AIBN and BPO were determined, so standard entropy, enthalpy and Gibbs free energy changes were defined.

KEYWORDS

Kinetics, Polymerization, Methyl Methacrylate, 2-Hydroxypropyl Methacrylate, Azobisisobutyronitrile, Benzoyel proxide, UV Spectrophotometry.

1. INTRODUCTION

Poly(methyl methacrylate) or PMMA is a transparent thermoplastic, which is extensively used in manufacturing industry because of its high resistance to ultraviolet degradation and corrosion. PMMA is generally produced by the free radical polymerization of methyl methacrylate (MMA) in batch reactors, which are easily adaptable to production demands, and are simple to operate. The performance of batch reactors can be enhanced by optimizing various process parameters that are available for manipulation. The polymers and copolymers of MMA and 2-hydroxypropyl methacrylate (2-HPMA) are broadly used as adhesives, coatings, lacquers and for medical applications. In the functional monomers, the hydroxyalkyl methacrylate is an important commercial monomer with a wide range of biomedical applications and soft contact lenses [1-3]. It can be used for several applications, such as paint formation, photoresists, binders for textiles and paper, reactive adhesives and coatings, and radiation curing [4, 5]. From a technical and scientific point of view, polymerization processes are quite

challenging, essentially because they involve complex temperature-dependent chain reactions and heat transfers, described by sets of highly nonlinear algebraic and differential equations. Moreover, the rate of these reactions can modify the final polymeric material properties. A better control of the homogeneity can result from a good knowledge of the kinetic behaviour of these systems. Control design for these processes is difficult task and thus, more attention is focused on modeling and kinetic parameters estimation. Several reports are available in the kinetic studies of the polymerization/copolymerization of MMA or hydroxyalkyl methacrylate. Some of the examples are: kinetic studies of MMA/methyl acrylate (MA) copolymerization system [6], MMA bulk radical polymerization [7], high-conversion copolymerization of butyl acrylate with MMA [8], the homogeneous atom transfer radical polymerization of MMA [9], polymerization of 2-hydroxyethyl methacrylate (2-HEMA) in the presence of initiating systems [10], metal free anionic polymerization of MMA initiated by Ce⁴⁺-poly(ethylene glycol) redox system [11], polymerization of 2-HEMA initiated by the system manganese tris(acetylacetonate)-acetic acid [12] and free-

ⁱ Corresponding Author: Department of Chemistry, Amirkabir University of Technology, Tehran, Iran (e-mail: Majidabdouss@yahoo.com)

ⁱⁱ Corresponding Author: Department of Chemistry, Amirkabir University of Technology, Tehran, Iran

ⁱⁱⁱ Corresponding Author: Department of Chemistry, Amirkabir University of Technology, Tehran, Iran

radical copolymerization of MA and MMA in benzene [13]. The mathematical model for a both MMA and MA copolymerization system was simplified by applying the pseudo kinetics rate constant method and used for the estimation of parameters for various reaction rate constants [14]. The mechanism and kinetics of reversible addition- fragmentation chain transfer (RAFT)-based living radical polymerizations of styrene and MMA were studied by using gel permeation chromatography (GPC) [15]. The thermal decomposition of some homopolymers and copolymers of 2-HEMA/2-HPMA and acrylonitrile cross-linked with ethylene glycol dimethacrylates has been studied using pyrolysis in combination with gas chromatography and thermogravimetry [16]. Thermal degradation of poly(2-HPMA) has been investigated by using FT-IR, NMR and GC-MS [17]. Polymerization of hydroxyalkyl methacrylate was characterized by combination of FT-Raman and step-scan FT-IR photoacoustic spectroscopy [18]. The effects of composition on the glass transition of dry and hydrophasticise copolymers of MMA, butyl methacrylate (BMA) and 2-HPMA were studied by differential scanning calorimetry [19]. In this paper, we present the kinetics results of polymerization of MMA and 2-HPMA at 65-75°C and 70-90 °C, respectively in toluene solvent with AIBN and BPO as initiators by UV spectrophotometry.

2. EXPERIMENTAL

MMA, 2-HPMA, AIBN, BPO, toluene and methanol were bought from MERCK company. First, the MMA was washed with the solution 5% NaOH [17, 20] twice to remove inhibitors such as hydroquinone. After that, it was washed with water twice. Then, it was dried with CaCl₂, Na₂CO₃ and CaH₂, and then the MMA was distilled from CaH₂ under nitrogen of atmosphere. The distillate MMA stored at low temperature [17]. 2-HPMA was purified by adopting the method of vacuum distillation. Pure AIBN and BPO were purified by using the crystallization method [21]. Toluene and methanol were used without purification. The specific amounts of monomer, inhibitors and toluene were poured in a three-necked flask. The total volume of solution was 50 ml. That flask was connected to the condenser. After that system was put in an oil bath and temperature was controlled. 1 ml of reaction solution at different time of reaction was taken to measure the concentration of monomer. This solution was added to 10 ml methanol at 0°C. In this condition, polymerization reaction is stopped and the polymer is precipitation. By increasing MeOH, the Eligomers were solutions and there were no problems. The precipitated polymer was separated from solution by centrifuging. The absorption of the solution was measured for MMA and 2-HPMA respectively at λ_{max} (286 nm) Figure 1 and λ_{max} (295 nm) [20]. The concentration MMA was measured by calibration curve. The model of UV system was 1601 PC

Schimadzu.

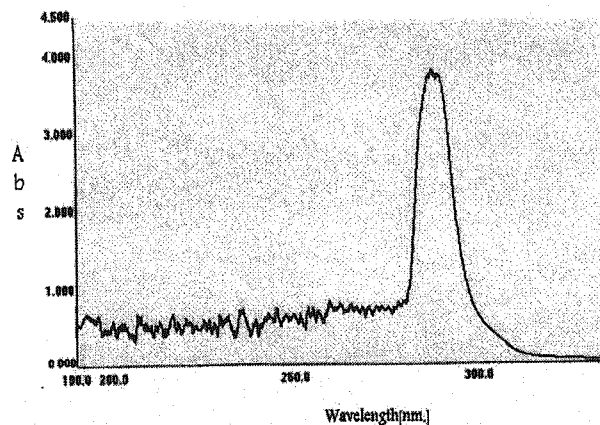


Figure 1: curve of UV spectrum of MMA.

3. RESULTS AND DISCUSSION

The changes in absorption of monomers in λ_{max} were linear in the range of 10^{-5} to 10^{-1} M concentration of monomers. At first the rate of polymerization of monomers in constant concentration of AIBN and BPO measured. Figures 2 and 3 show the percent of conversion of monomer during the time of reaction in constant concentration of AIBN or monomer and Figure 4 shows these conversions for BPO and monomers.

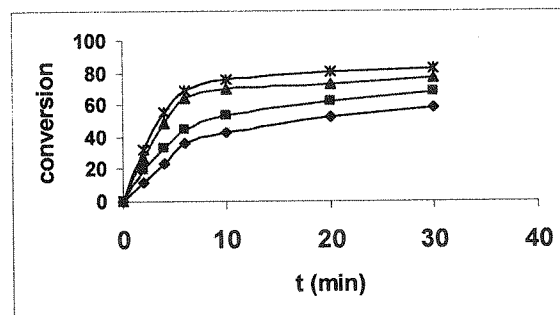


Figure 2: The relation between the rate of polymerization concentration of initiator (AIBN): [AIBN]= 37.2×10^{-4} M, (\diamond) 27.72×10^{-3} M, (\blacksquare) 55.44×10^{-3} M, (\blacktriangle) 11.09×10^{-2} M, ($*$) 22.18×10^{-2} M.

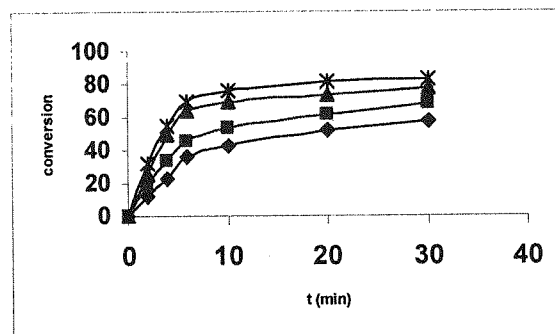


Figure 3: The relation between the rate of polymerization in concentrations of 2-HPMA and constant concentrations of initiator (AIBN) and constant concentration of 2-HPMA: [2-HPMA]= 22.18×10^{-2} M, (\diamond) 24.8×10^{-4} M, (\blacksquare) 37.2×10^{-4} M, (\blacktriangle) 49.6×10^{-4} M, ($*$) 74.4×10^{-4} M.

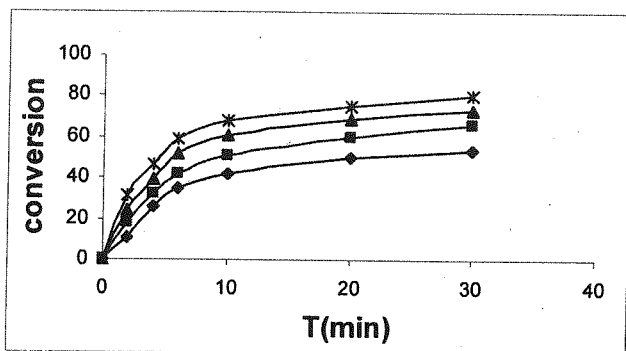


Figure 4: The relation between the rate of polymerization in concentrations of MMA and constant concentration of initiator BPO : [BPO] = 1.52×10^{-3} M, (\diamond) 18.77×10^{-3} M, (\blacksquare) 37.55×10^{-3} M, (\blacktriangle) 7.51×10^{-2} M, ($*$) 15.02×10^{-2} M.

The rate reaction of polymerization is : $R_p = k[M]^\alpha [I]^\beta$
 Here α and β are order of reaction with respect to the concentration of respectively monomer and AIBN. The orders of reaction (α , β) were determined by initial rate method [22]. In this method the rate is measured at the beginning of the reaction for several different initial values of the concentration of monomer: $R_p = k' [M]^\alpha$
 Taking logarithms: $R_p = \ln k' + \alpha \ln [M]$.

For a series of initial concentrations, a plot of logarithms of the initial rates against the logarithms of the initial concentration of monomer should be a straight line with slope α (Figures 5 and 7). In this method, it was found that the rate law is: $R_p = [M]^1 [AIBN]^{1/2}$ it is first order in monomer, and half order in AIBN initial. As shown in tables 1-8 and figures 5-12, the rate constant of these reactions were found [22]:

$$k_{R(\text{MMA} \& \text{AIBN})} = 1.75 \text{ mol}^{-1/2} \text{ lit}^{1/2} \text{ min}^{-1}$$

$$k_{R(\text{2-HPMA} \& \text{AIBN})} = 0.432 \text{ mol}^{-1/2} \text{ lit}^{1/2} \text{ min}^{-1}$$

$$k_{R(\text{MMA} \& \text{BPO})} = 0.21 \text{ mol}^{-1/2} \text{ lit}^{1/2} \text{ min}^{-1}$$

$$k_{R(\text{2-HPMA} \& \text{BPO})} = 0.173 \text{ mol}^{-1/2} \text{ lit}^{1/2} \text{ min}^{-1}$$

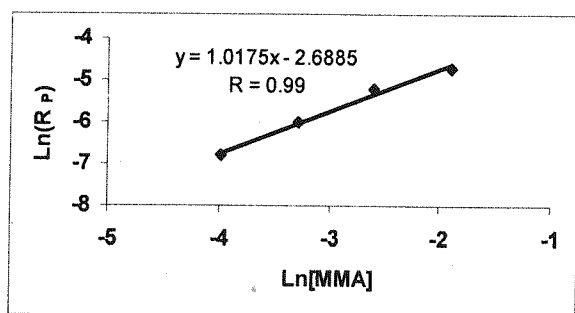


Figure 5: The plot of $\ln(R_p)$ against of $\ln[\text{MMA}]$ in poly. MMA & AIBN.

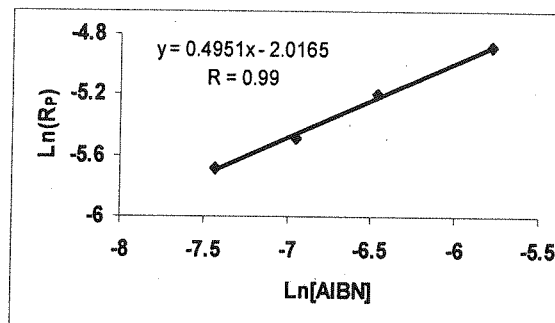


Figure 6: The plot of $\ln(R_p)$ versus of $\ln[\text{AIBN}]$ in poly. MMA & AIBN.

By increasing concentration monomer (Figures 5 and 7), initiators (Figures 6 and 8) and temperature (Figures 14, 15, 17 and 18), rate of reaction was increased.

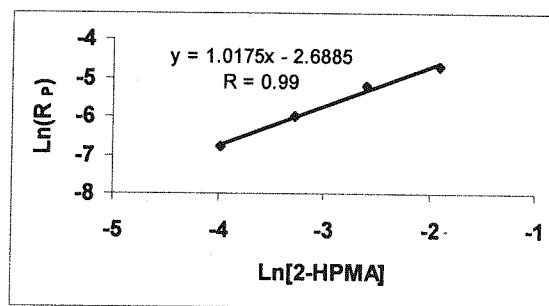


Figure 7: The plot of $\ln(R_p)$ against of $\ln[\text{2-HPMA}]$ in poly.2-HPMA & AIBN.

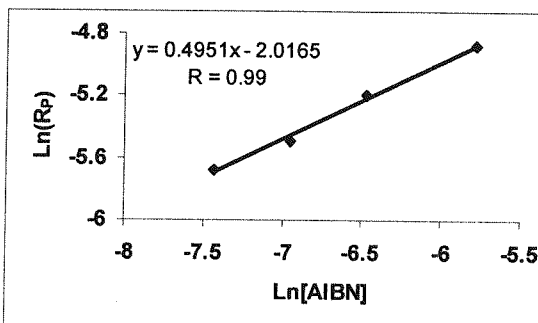


Figure 8: The plot of $\ln(R_p)$ versus of $\ln[\text{AIBN}]$ in poly.2-HPMA & AIBN.

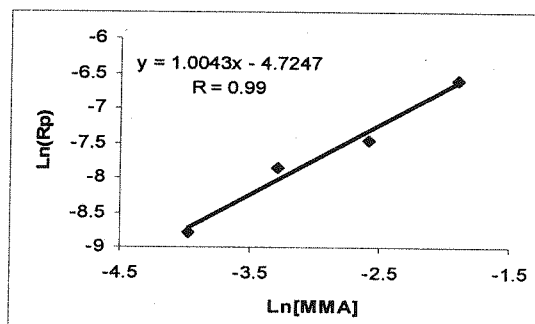


Figure 9: The plot of $\ln(R_p)$ against of $\ln[\text{MMA}]$ in poly. MMA & BPO.

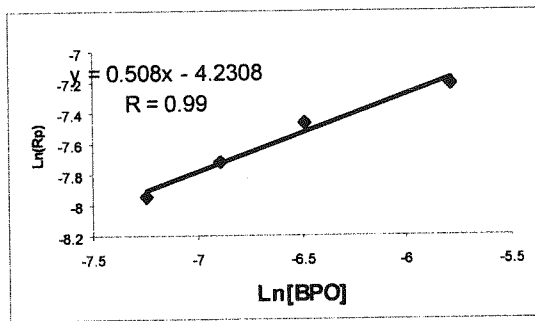


Figure 10: The plot of $\text{Ln}(R_p)$ versus of $\text{Ln}[\text{BPO}]$ in poly. MMA & BPO.

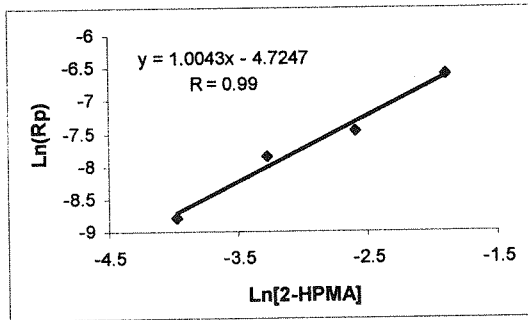


Figure 11: The plot of $\text{Ln}(R_p)$ against of $\text{Ln}[2\text{-HPMA}]$ in poly.2-HPMA & BPO.

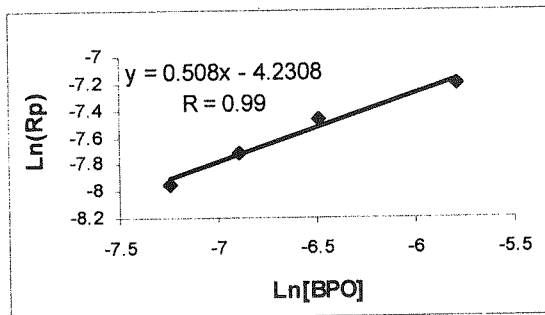


Figure 12: The plot of $\text{Ln}(R_p)$ versus of $\text{Ln}[\text{BPO}]$ in poly.2-HPMA & BPO.

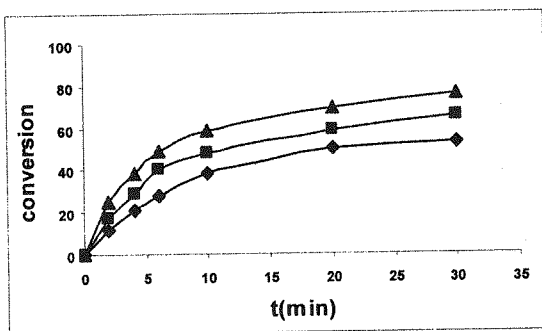


Figure 13: The relation between the rate of polymerization of reaction and temperature in constant concentration of reactants: $[\text{AIBN}] = 1.55 \times 10^{-3} \text{ M}$, $[\text{MMA}] = 18.77 \times 10^{-3} \text{ M}$, (\diamond) 65°C , (\blacksquare) 70°C , (\blacktriangle) 75°C .

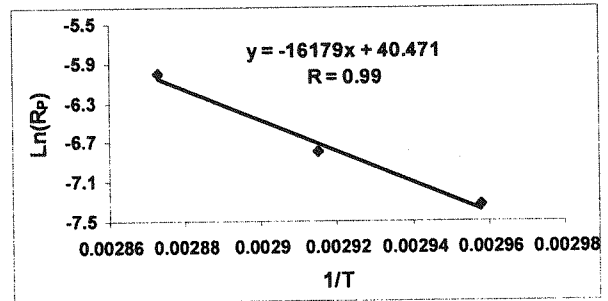


Figure 14: The plot of $\text{Ln}(R_p)$ versus of $1/T$ in poly. MMA & AIBN, (\diamond) 65°C , (\blacksquare) 70°C , (\blacktriangle) 75°C .

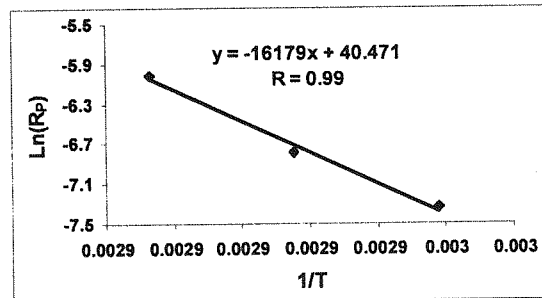


Figure 15: The plot of $\text{Ln}(R_p)$ versus of $1/T$ in poly. 2-HPMA & AIBN.

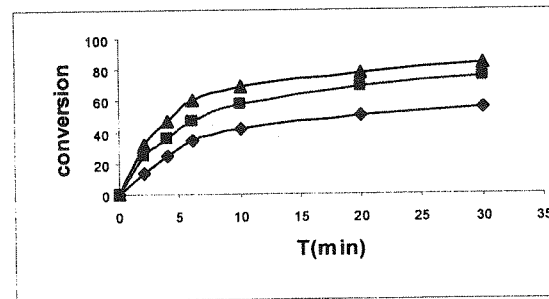


Figure 16: The relation between the rate of polymerization of reaction and temperature in constant concentration of reactants: $[\text{PBO}] = 15.02 \times 10^{-4} \text{ M}$, $[\text{MMA}] = 15.02 \times 10^{-2} \text{ M}$, (\diamond) 70°C , (\blacksquare) 80°C , (\blacktriangle) 90°C .

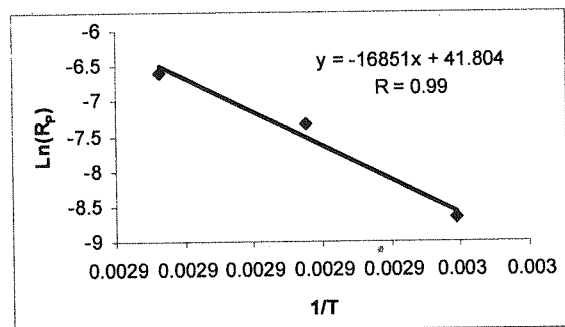


Figure 17: The plot of $\text{Ln}(R_p)$ versus of $1/T$ in poly. MMA & BPO.

The temperature effect of polymerization reaction was investigated. It is found that the plot of $\text{Ln}(R_p)$ against $1/T$ gives a straight line (Figures 15 and 18) [22]. The slope of this line is $(-E_a/R)$. The activation energy and the pre-exponential factors (A) of reactions are: 134.5, 140 kJ/mol

respectively and the pre-exponential factors (A) are [22]:

$$E_{a(MMA \& AIBN)} = 134.4 \text{ kJ/mol,}$$

$$A_{(MMA \& AIBN)} = 2.26 \times 10^{20} \text{ mol}^{-1/2} \text{ lit}^{1/2} \text{ min}^{-1}$$

$$E_{a(MMA \& BPO)} = 140 \text{ kJ/mol,}$$

$$A_{(MMA \& BPO)} = 2.17 \times 10^{20} \text{ mol}^{-1/2} \text{ lit}^{1/2} \text{ min}^{-1}$$

$$E_{a(2\text{-HPMA} \& AIBN)} = 170.45 \text{ kJ/mol,}$$

$$A_{(2\text{-HPMA} \& AIBN)} = 7.2 \times 10^{24} \text{ mol}^{-1/2} \text{ lit}^{1/2} \text{ min}^{-1}$$

$$E_{a(2\text{-HPMA} \& BPO)} = 172.99 \text{ kJ/mol,}$$

$$A_{(2\text{-HPMA} \& BPO)} = 6.88 \times 10^{24} \text{ mol}^{-1/2} \text{ lit}^{1/2} \text{ min}^{-1}$$

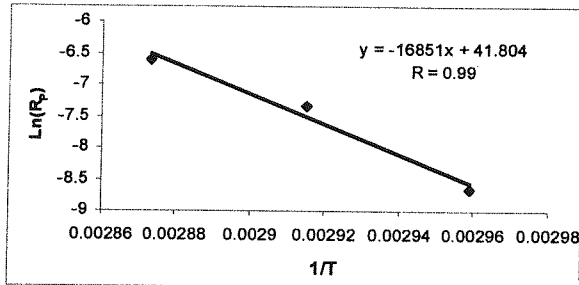


Figure 18: The plot of $\ln(R_p)$ versus of $1/T$ in poly. 2-HPMA & BPO.

A. Define standard entropy of activation ΔS^\ddagger

Similar to previously report [22], we can consider:

$$A = (kT/h) e^{(n+(\Delta S^\ddagger/R))}$$

$$\Delta S^\ddagger_{(MMA \& AIBN)} = 101.1 \text{ J/K mol, } \Delta S^\ddagger_{(2\text{-HPMA} \& AIBN)} = 187.19 \text{ J/K mol}$$

$$\Delta S^\ddagger_{(MMA \& BPO)} = 101.02 \text{ J/K mol, } \Delta S^\ddagger_{(2\text{-HPMA} \& BPO)} = 186.81 \text{ J/K mol}$$

B. Define standard Gibbs free energy of activation ΔG^\ddagger

As previously reported [22], we can consider:

$$k_R = (kT/h) e^{(-\Delta G^\ddagger/RT)}$$

$$\Delta G^\ddagger_{(MMA \& AIBN)} = 95.96 \text{ k J/K mol, } \Delta G^\ddagger_{(2\text{-HPMA} \& AIBN)} = 101.43 \text{ k J/K mol}$$

$$\Delta G^\ddagger_{(MMA \& BPO)} = 104.11 \text{ k J/K mol, } \Delta G^\ddagger_{(2\text{-HPMA} \& BPO)} = 100.6 \text{ k J/K mol}$$

C. Define standard enthalpy of activation ΔH^\ddagger

Similar to previously report [22], we can consider:

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$$

$$\Delta H^\ddagger_{(MMA \& AIBN)} = 131.15 \text{ k J/K mol,}$$

$$\Delta H^\ddagger_{(2\text{-HPMA} \& AIBN)} = 167.5 \text{ k J/K mol}$$

$$\Delta H^\ddagger_{(MMA \& BPO)} = 135.8 \text{ k J/K mol,}$$

$$\Delta H^\ddagger_{(2\text{-HPMA} \& BPO)} = 105.66 \text{ k J/K mol}$$

TABLE 1

AVERAGE OF POLYMERIZATION IN DIFFERENT IN DIFFERENT CONCENTRATIONS OF AIBN.

[MMA] mol lit ⁻¹	mol lit ⁻¹ min ⁻¹
18.77×10^{-3}	$.25 \times 10^{-4}$
37.55×10^{-3}	24.54×10^{-4}
7.51×10^{-2}	5.17×10^{-4}
15.02×10^{-2}	1.05×10^{-4}

TABLE 2

AVERAGE OF POLYMERIZATION IN DIFFERENT CONCENTRATIONS OF 2-HPMA AND CONSTANT CONCENTRATION OF AIBN.

[2-HPMA] mol lit ⁻¹	R_p mol lit ⁻¹ min ⁻¹
27.72×10^{-3}	7.1×10^{-4}
55.44×10^{-3}	11.25×10^{-4}
11.09×10^{-2}	24.54×10^{-4}
22.18×10^{-2}	60.36×10^{-4}

TABLE 3

AVERAGE OF POLYMERIZATION IN DIFFERENT CONCENTRATIONS OF MMA AND CONSTANT CONCENTRATION BPO.

[MMA] mol lit ⁻¹	R_p mol lit ⁻¹ min ⁻¹
18.77×10^{-3}	15.38×10^{-3}
37.55×10^{-3}	38.97×10^{-3}
7.51×10^{-2}	57.56×10^{-3}
15.02×10^{-2}	13.6×10^{-2}

TABLE 4

AVERAGE OF POLYMERIZATION MMA IN DIFFERENT CONCENTRATIONS OF BPO.

[BPO] mol lit ⁻¹	R_p mol lit ⁻¹ min ⁻¹
71.73×10^{-4}	35.26×10^{-4}
10.18×10^{-4}	44.39×10^{-4}
15.2×10^{-4}	57.56×10^{-4}
30.6×10^{-4}	73.91×10^{-4}

TABLE 5

AVERAGE OF POLYMERIZATION MMA IN DIFFERENT CONCENTRATIONS OF BPO.

[BPO] mol lit ⁻¹	R_p mol lit ⁻¹ min ⁻¹
24.8×10^{-4}	18.18×10^{-4}
37.2×10^{-4}	20.09×10^{-4}
49.6×10^{-4}	25.04×10^{-4}
74.4×10^{-4}	31.2×10^{-4}

TABLE 6

AVERAGE OF POLYMERIZATION IN DIFFERENT TEMPERATURES IN CONSTANT CONCENTRATIONS OF MMA AND AIBN.

T(k)	R_p mol lit ⁻¹ min ⁻¹
338	6.49×10^{-4}
343	11.25×10^{-4}
348	24.54×10^{-4}

TABLE 7
AVERAGE OF POLYMERIZATION IN DIFFERENT
TEMPERATURES IN CONSTANT CONCENTRATIONS OF
2-HPMA AND AIBN.

T(k)	R_p mol lit ⁻¹ min ⁻¹
343	93.03×10^{-4}
353	60.36×10^{-4}
363	27.32×10^{-3}

TABLE 8
AVERAGE OF POLYMERIZATION IN DIFFERENT
TEMPERATURES IN CONSTANT CONCENTRATIONS 2-
HPMA AND BPO.

T(k)	R_p mol lit ⁻¹ min ⁻¹
343	53.03×10^{-5}
353	20.09×10^{-4}
363	16.57×10^{-3}

4. CONCLUSION

In this method, it was found that law is: $R_p = k[M]^1[I]^{1/2}$ it is first order in monomer, and half order in initiators by initial rate method. By increasing concentration of monomer, initiators and temperature, rate of reaction was increased. The activation energy of reaction of MMA with AIBN and BPO were 134.5 and 140 kJ/mol, respectively. The activation energy of reaction of 2-HPMA with AIBN and BPO are respectively 170.45, 172.99 kJ/mol. The pre-exponential factors (A), rate constants, Standards entropy, enthalpy and Gibbs free energy changes of these reactions were defined.

5. REFERENCES

- [1] M. Save, J.V. Weaver, S.P. Armes, *Macromolecules* vol. 35, pp. 1152-1159, 2002.
- [2] A.L. Lewis, Z.L. Cumming, P.W. Stratfort, *Biomaterials* vol. 22, pp. 99-111, 2001.
- [3] M.J. Park, S.M. Ahn, H. Rhee., *J. Appl. Polym. Sci.* Vol. 78, pp. 2554, 2000.
- [4] R.A. Hutchinson, S. Beuermann, D.A. Paquet Jr., J.H. McMinn, C.Jackson, *Macromolecules* vol. 31, pp. 1542-1547, 1999.
- [5] S.G. Yeates, S.N. Richards, *Surf. Coat. Int.* vol. 10, pp. 437-442, 1996.
- [6] M. Park, S. Ahn, R. HK *J. Apl. Polym.Sci* vol. 78 pp. 2554-2564, 2000.
- [7] J. Shen, G. Wang, M. Yang, Y. Zheng, *Polym. Inter.* Vol. 28, pp. 75-79, 1992.
- [8] F. Garcia, M. EL *J. Apl. Polym.Sci* vol. 35, pp. 1961-1965, 1997.
- [9] J. Wang, T. Grimaud, K. Matyjaszewski, *Macromolecules* vol. 30, pp. 6507-6512, 1997.
- [10] N. Lavrov, *Russ. J. of Appl. Chem.* Vol. 71, pp. 1234-1236, 1998.
- [11] S. Nagarajan, S. Kumari, K. Srinivasan, *J. Apl. Polym.Sci* vol. 63, pp.565-571, 1997.
- [12] N. Lavrov *Russ. J. of Appl. Chem.* Vol. 68, pp. 922-924, 1995.
- [13] E. Madruga, F. Garcia, *Macromolecule Chem. And Phys.* Vol. 197, 1996.
- [14] M.J. Park, S.M. Ahn, H.K. Rhee. *J. Apl. Polym.Sci.*, vol. 78, 2554-2564, 2000.
- [15] A.Goto, K.Sato, Y.Tsuj, T. Fukuda, G. Moad, E. Rizzardo, San H. Thang. *Macromolecules*, vol. 34, pp. 402-408, 2001.
- [16] C. Cascavel, I. Poinescu, *Polymer Degradation and Stability*, vol. 48, pp. 55-60, 1995.
- [17] K. Demirelli, M.F. Coskun, E. Kaya, M. Coskum, *Polymer Degration and Stability*, vol. 78, pp. 333-339, 2002.
- [18] H. Sasaki, T. Nagano, K. Sakanaka, S. Kawakami, K. Nishida, J. Nakamura, N. Ichikawa, J. Iwashita, T. Nakamura, M. Nakashima, *Journal of Controlled Release*, vol. 92, pp. 241-247, 2003.
- [19] S. Kammer, K. Albinsky, B. Sander, S. Wartewig, *Polymer*, vol. 40, pp.1131-1137, 1999.
- [20] L. Wojnarovits, E. Takacs, *Radiation physics and chemistry* vol. 55, pp. 639-644, 1999.
- [21] M. Stickler, E. Dumont, *Makromol. Chem.*, Vol. 87, pp. 2663-2673, 1986.
- [22] J.H. Ward, N.A. Peppas, *Macromolecules*, Vol. 33, pp. 5137-5142, 2000.



Instruction to authors

a: *Amirkabir Journal of Science and Technology* appears quarterly and contains papers describing original investigations in all areas of physical sciences and engineering that have not been published earlier or submitted for possible publication elsewhere. Review papers in specialized fields are also considered for publication.

b: Papers in both Persian and English will be considered for possible publication

c: Manuscripts should be prepared based on the template given in www.akujournal.com.

d: The title of the paper should be concise and informative. It is highly desirable to divide the paper into different sections, such as Introduction, Problem Statements, Experiments, Results, Discussion, and Conclusion. All papers should have an Abstract both in Persian and English.

Amirkabir Journal of Science & Technology
Vol.19/ No. 68- E(MPC) / Spring - Summer 2008

ISSN. 1015-0951

Director & Editor-In-Chief: Prof. S. K. Y. Nikraves, Ph.D.

Co-Editor-In-Chief & Assistant Director: Prof. M. B. Menhaj, Ph.D.

Address for correspondence:

Amirkabir University of Tech., Office of Vice Chancellor in
Research Affairs, Tehran 15. Iran.

Tel: 0098-21-66491123

Fax: 0098-21-66491123

Web site: www.akujournal.com

Email Address: Info@akujournal.com