

L.R. Harutyunyan^a, *R.S. Harutyunyan*^b

ON THE MECHANISM OF ACRYLAMIDE EMULSION POLYMERIZATION WITH THE PARTICIPATION OF ITS DIMERS

^a Armenian National Agrarian University, Yerevan, Armenia

^b Yerevan State University, Yerevan, Armenia

The role of both dimeric and monomeric forms of acrylamide monomer in the process of polymerization in emulsions initiated by different type of initiators was discussed and the reasons for the reaction order with respect to monomer greater than unity were elucidated for acrylamide free radical polymerization in emulsions. The emulsion polymerization mechanism of acrylamide is discussed separately for the processes initiated by water-soluble initiator and oil-soluble initiator. The main difference in two cases is the distribution of acrylamide and initiator in aqueous and toluene phases. In the case of using water-soluble initiator, the initiator and acrylamide are in the same phase, whereas the molecules of the initiator and acrylamide are distributed between different phases in the case of using oil-soluble initiator. As a result, the participation of the dimers in the process of acrylamide emulsion polymerization is more efficient for the system where water-soluble initiator is used. For that system, it is suggested that both dimers and monomers of acrylamide participate in the propagation reaction at relatively low concentrations of acrylamide, which explains the value of the reaction order with respect to monomer greater than unity.

Keywords: acrylamide, emulsion polymerization, polymerization mechanism, water-soluble initiator, potassium persulfate, oil-soluble initiator, 2,2'-azobisisobutyronitrile.

DOI: 10.32434/0321-4095-2021-136-3-50-56

Introduction

Emulsion polymerization (EP) of acrylamide (AA) for the synthesis of polyacrylamide (PAA) with different characteristics and with different copolymers is a topical issue due to the application of PAA and copolymers of PAA in different fields, especially in pharmacy and environmentally friendly technologies [1–8]. The main procedure for the polymerization of AA and other non-saturated amides is free radical polymerization that can be carried out by well-known methods in mass, in solution, in suspension and in emulsion [9–12]. Each method has its features which predetermine the properties of produced polymers and the field of their application. In particular, polymerization in emulsions makes possible to perform the polymerization process with a high rate and to synthesize the polymers with a high molecular weight [9–12].

To understand the mechanism of polymerization in emulsions, one has consider, in which form the monomer is present in a reaction system. It is known that AA can exist in solution

both in monomeric and dimeric forms, which affects the polymerization kinetics [9]:



In polar solvents, equilibrium shifts to the left, whereas it shifts to the right in non-polar solvents. Different factors affect equilibrium (1), in particular, colloid-chemical properties of reaction medium and the presence of additives [9]. The analysis of literature data has shown that in aqueous phase in the presence of emulsion polymerization system (EPS) components, monomeric form prevails at the concentrations of AA less than 0.7 mol L⁻¹, while dimeric form prevails at the concentrations of AA greater than 0.7 mol L⁻¹ [9]. This fact is very important and strongly influences on the kinetics and mechanism of AA emulsion polymerization.

This work is an attempt to disclose the role of AA dimers in EP process and reveal the differences in EP mechanism of AA in emulsion system (ES) initiated by different type initiators.

Experimental

Materials

Acrylamide (AA, $\text{CH}_2=\text{CHCONH}_2$, suitable for electrophoresis, $\geq 99.0\%$, Sigma-Aldrich), initiators potassium persulfate (PP, $\text{K}_2\text{S}_2\text{O}_8$, ACS reagent, $\geq 99.0\%$, Sigma-Aldrich) and 2,2'-azobisisobutyronitrile (AIBN, $(\text{CH}_3)_2\text{C}(\text{CN})\text{N}=\text{NC}(\text{CH}_3)_2\text{CN}$, $\geq 98.0\%$ (GC), Sigma-Aldrich), emulsifier lecithin (from egg yolk, type XVI-E, (TLC), lyophilized powder, 99.0% , Sigma-Aldrich), toluene ($\text{C}_6\text{H}_5\text{CH}_3$, ACS reagent, $\geq 99.5\%$, Sigma-Aldrich) were used without further purification. The properties of the used chemicals are listed in Table.

Methods

The rate of polymerization was determined by dilatometric method at 323.15 K and $V_{\text{water}}:V_{\text{toluene}}=1:2$. The dilatometer was filled up under vacuum after degassing ($\sim 10^{-4}$ MPa). Under the stream of high purity helium, the dilatometer was separated from installation and placed in a thermostat. The volume of dilatometer was 5.6 mL, the height change in the dilatometer capillary tube was measured with accuracy of ± 0.5 mm. The temperature was controlled within ± 0.5 K. The emulsion was prepared by magnetic-shaker stirring with constant rate.

Results and discussion

It is well known that the rate of polymerization (R_p) for AA is described in stationary conditions by the following relation:

$$R_p = k [I]^n [M]^m, \quad (2)$$

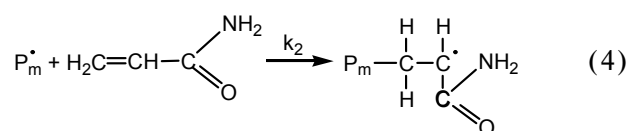
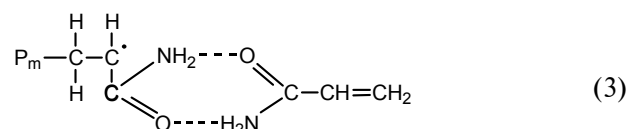
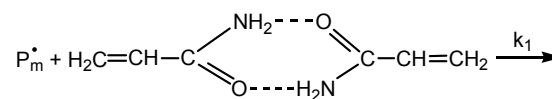
where $[I]$ and $[M]$ are the concentrations of initiator and monomer, respectively; n and m are the reaction order with respect to initiator and monomer, respectively.

Commonly, $n=0.5$ and it is the constant for many systems, but the order with respect to monomer is varied depending on monomer concentration [1,9,10,13]. Analysis of AA EP kinetics data allows elucidating the mechanism of AA polymerization in ES based on AA existing form in a reaction system. The most important problem is to understand in

which locus elementary reactions occur and elucidate the effect of a medium on the kinetics of reactions. At first, it is related to initiator homolysis and reactions of chain initiation. To establish the locus of each elementary reaction, it is also important to take into account the distribution of the initiator, monomer and other components in the polymerization system. Of course, the type of initiator has significant importance for kinetics and mechanism of EP, therefore the mechanisms of polymerization of AA in emulsions initiated by water-soluble and oil-soluble initiators should be discussed separately.

Polymerization of AA initiated by water-soluble potassium persulfate (PP)

It is known that homolysis of PP occurs in the aqueous phase where AA also is present; therefore, all elementary reactions of polymerization occur in an aqueous medium. As was mentioned, AA is present in an aqueous phase both in the monomeric and dimeric forms and can participate in elementary reactions in both forms. For the kinetics of EP, the participation of dimers in chain growth reaction is especially important. Let's assume that propagation reaction of growing radicals (P_m^\bullet) with dimers and monomers of AA proceeds simultaneously (as parallel reactions):



Specification of the chemicals used

Chemical	Source	CASRN	Purification method	Final purity *
acrylamide	Sigma-Aldrich	79-06-1	none	$\geq 99.0\%$
potassium persulfate	Sigma-Aldrich	7727-21-1	none	$\geq 99.0\%$
2,2'-azobisisobutyronitrile	Sigma-Aldrich	78-67-1	none	$\geq 98.0\%$
lecithin	Sigma-Aldrich	8002-43-5	none	$\geq 99.0\%$
toluene	Sigma-Aldrich	108-88-3	none	$\geq 99.5\%$

Note: * Declared by supplier.

The reactivity of the dimer is lower than monomer [9], therefore $k_1 < k_2$. The rate of reactions (3) and (4) can be expressed by the following expressions:

$$R_1 = k_1 [P_m] [M]^2, \quad (5)$$

$$R_2 = k_2 [P_m] [M]. \quad (6)$$

The overall rate of the process is summed up from (5) and (6) as follows:

$$R_p = R_1 + R_2 = k_1 [P_m] [M]^2 + k_2 [P_m] [M]. \quad (7)$$

Then, two extreme cases should be considered:

1) the dimers are practically absent in the system when $[AA] < 0.7 \text{ mol L}^{-1}$, and the rate of polymerization is expressed by the following equation:

$$R_p = k_2 [P_m] [M]. \quad (8)$$

In this case, the reaction order with respect to monomer is equal 1, which has been established in a number of publications [1,10,11,13]. Our data also confirm this conclusion (Fig. 1, curve 3).

2) the dimers prevail in the system when $[AA] > 0.7 \text{ mol L}^{-1}$, and the rate of polymerization is expressed by the following equation:

$$R_p = k_1 [P_m] [M]^2. \quad (9)$$

As follows from Eq. (9), the reaction order with respect to monomer is equal to 2. In practice at $[AA] > 0.7 \text{ mol L}^{-1}$, the reaction order with respect to AA is always greater than unity, however less than 2, and can reach 2 only in the ideal case. As follows from Fig. 1, the reaction order with respect to AA equal 1 at $[AA] > 0.8 \text{ mol L}^{-1}$ in an aqueous medium, as opposed to the emulsion.

Thus, for AA polymerization, the value of reaction order with respect to AA is greater than unity and the behavior of polymerization rate at $[AA] > 1.0 \text{ mol L}^{-1}$ can be explained on the basis of the above mentioned kinetic scheme. As follows from Eq. (3), that the dimers of AA can exist within macromolecules of PAA, which, principally, can start the propagation of polymer chains and, as a result, the branched polymeric structures can be formed. They can also be the cause of the formation of partially cross-linked polymeric structures. Apparently, the mentioned factors are the fundamental reasons for PAA solubility decreasing at relatively high concentrations of AA; thus, about 15% of PAA is not solubilized in water at $[AA] = 1.5 \text{ mol L}^{-1}$, and about 30% of PAA is not solubilized in water at $[AA] = 2.0 \text{ mol L}^{-1}$. These facts can explain the observable gel-effect at relatively high concentrations of AA [9]. The separation of side monomeric molecules from the polymer chain also must not be excluded. The probability of such separation increases under the local influence of the released energy in the polymerization process. In that case, the reaction order with respect to monomer

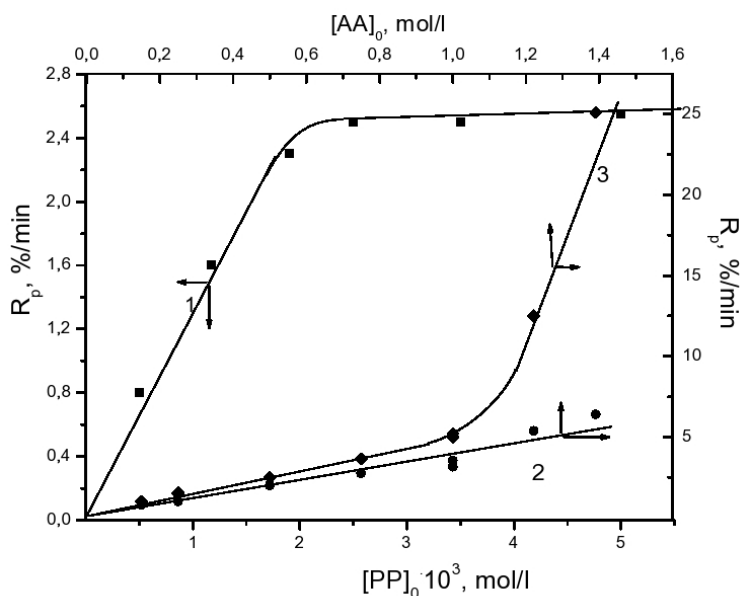
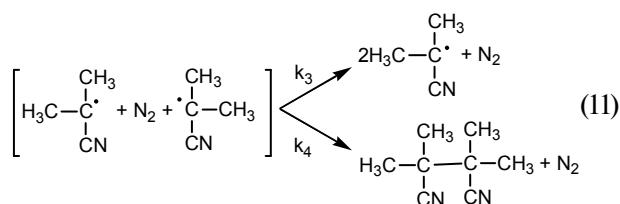
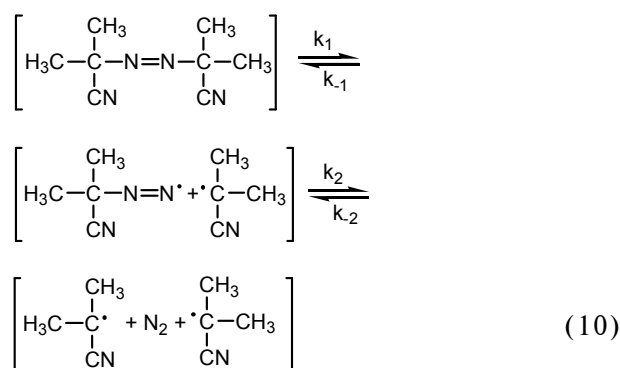


Fig. 1. Dependence of AA polymerization rate on concentration of PP (1) and AA (2 and 3) in aqueous solution (2) and in emulsion (1 and 3). $[AA]_0 = 0.5 \text{ mol L}^{-1}$, $[PP]_0 = 5 \cdot 10^{-3} \text{ mol L}^{-1}$, $[Le]_0 = 3\%$, $T = 323.15 \text{ K}$ (curves 1 and 2)

must not differ from unity, which is established for homogenous polymerization of AA in aqueous solutions [9,11,13]. Particularly, it is established that the reaction order with respect to AA remains to be unity in homogenous system at $[AA] \leq 2.0 \text{ mol L}^{-1}$, while the reaction order with respect to AA is greater than unity at higher concentrations of AA. It is obviously caused by the formation of more stable dimeric forms at relatively high concentrations of AA in water. As can be concluded from our earlier studies [9,2,14] and literature data [10,13], the threshold concentration of dimerization in emulsions is relatively low, which explains the value of reaction order with respect to AA greater than unity at relatively low concentration of AA.

Polymerization of AA initiated by oil-soluble 2,2'-azobisisobutyronitrile (AIBN)

As shown in ref. [9], the oil-soluble initiator AIBN practically does not transfer from toluene (i.e. organic phase) to aqueous phase and, at the same time, AA does not transfer from aqueous phase to toluene practically (AIBN is in disperse phase and AA is in continuous phase). Thus, the homolysis of AIBN occurs in organic phase where the molecules of AA are practically absent. The decay of AIBN can be presented by the following general scheme:



It should be noted that the constant of AIBN decay rate does not practically depend on the polarity of a solvent [13,15]. The effect of medium on the decay of AIBN is explained by the theory of cage effect [11,13,15]. It is suggested that the changes in

the values of AIBN decay rate constant, which is detected by the replacement of one solvent by other, is a result of the cage effect on the recombination of formed radicals. Due to the replacement of one solvent by other, the fraction of radicals, which has time to recombine in the «cage», changes depending on the properties of solvent and reaction system. It was shown in ref. [9,12] that the rate of AIBN decay decreases with an increase in the viscosity of a solvent. It was also reported [9,12] that the rate of AIBN homolysis decreases in ES as compared with the homogenous system. At the same time, the decrease in the rate of homolysis becomes more significant with an increase in the size of discrete particles. In general, it is due to the effect of emulsion properties on the cage effect. The R radicals, formed due to AIBN decay, are more mobile and relatively easily diffuse into the surface layer of emulsion droplets or polymer-monomer particles (PMP), where the molecules of AA can also exist together with molecules of emulsifier [9,12]. It is suggested that is where the act of initiation proceeds. At the same time, the dependence of initiation rate (R_i) on the AIBN concentration is expressed as the first order-like kinetic equation, regardless of the type of emulsion [12]:

$$R_i = k_i [AIBN]. \quad (12)$$

As the reaction of AIBN homolysis is slightly sensitive to solute properties, thus, independently the molecules of AIBN are within discrete or continuous phase, the energetic and kinetic characteristics of AIBN homolysis will be practically the same. However, the efficiency of the initiation of AIBN within discrete particles is lower than within homogenous system [14]. The particles RM^\bullet (primary single radicals) and RM_x^\bullet (oligomeric radicals) are more hydrophilic than R and the probability of their transfer to an aqueous phase is more realistic. The mobility of the molecules of the adsorption (surface) layers on discrete particles (emulsion droplets, PMP) [9–13] and the existence of dynamic equilibrium of the adsorbed molecules within the layer and continuous phase will also contribute to this.

Naturally, the number of R^\bullet and RM^\bullet in a surface layer is limited and mainly depends on the specific surface of discrete particles and characteristics of adsorption layer molecules. Obviously, this is a basic reason for the independence of polymerization rate (R_p) from the AIBN concentration at its relatively high concentrations (Fig. 2). It can be suggested that the formed RM radicals are in the interfacial

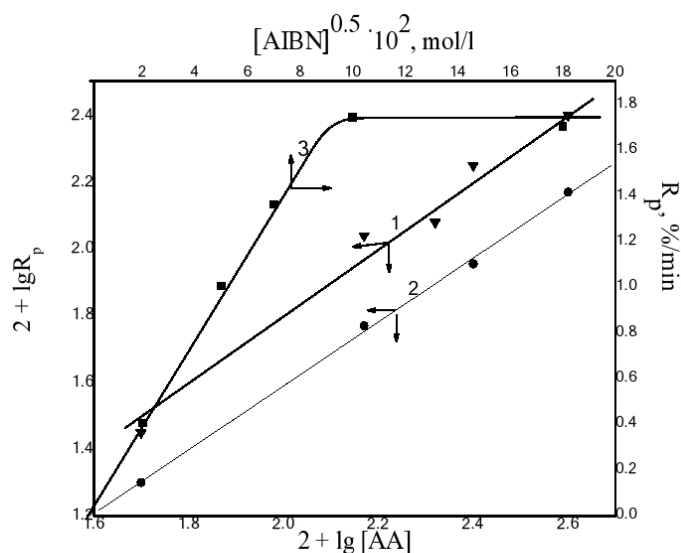


Fig. 2. Dependence of AA polymerization rate on concentration of AA (1 and 2) and AIBN (3). $[AIBN]=5 \cdot 10^{-3} \text{ mol L}^{-1}$ (1 and 2), $[AA]=0.5 \text{ mol L}^{-1}$ (3), $[Le]_0=3\%$, $V_{\text{water}}:V_{\text{toluene}}=1:2$, $T=323.15 \text{ K}$

layer and they are not transferred into the bulk of aqueous medium where the growth of polymer chains mainly occurs. When carrying out the process under constant conditions, the surface of the interface layer, which is limited through the put of radicals formed due to AIBN homolysis, is not practically changed, and, thus, the detected dependence of R_p on the AIBN concentration (Fig. 2, curve 3) is quite expected.

If we compare the data concerning the AA EP initiated by water-soluble PP (Fig. 1) with those relating to the AA EP initiated by oil-soluble AIBN (Fig. 2), we can conclude that the values of R_p when applying PP are higher than in the case of AIBN under comparable conditions. It is important that there is no change in R_p vs. $[AA]$ curve behavior at comparable high concentrations of AA for the ES initiated by AIBN, which was detected for the ES initiated by PP. Probably, the chance of a transfer of dimer into interfacial layer for the discussed system is significantly low than for molecules of AA.

Conclusions

The present paper reveals that the mechanism of AA EP is highly depending on the type of the used initiator. The dimeric form of AA prevails in the discussed system in the case of EPS where water-soluble PP is used as an initiator at the $[AA]<0.7 \text{ mol L}^{-1}$, and, as a result, the reaction order with respect to monomer is greater than unity. However, at the $[AA]>0.7 \text{ mol L}^{-1}$, the amount of dimers of AA in EPS becomes lower and the reaction order with respect to AA remains within the unity.

At the same time, as the oil-soluble initiator AIBN and water-soluble AA are distributed in different phases and the transfer of each components molecules to other phase is limited, the form of AA molecules does not play decisive role in the participation of EP, and, as a result, the reaction order of polymerization with respect to AA is always equal to unity.

REFERENCES

1. *Mohsin M.A., Attia N.F.* Inverse emulsion polymerization for the synthesis of high molecular weight polyacrylamide and its application as sand stabilizer // *Int. J. Polym. Sci.* – 2015. – Vol.2015. – Article No. 436583.
2. *Asadi S., Tabani H., Nojavan S.* Application of polyacrylamide gel as a new membrane in electromembrane extraction for the quantification of basic drugs in breast milk and wastewater samples // *J. Pharm. Biomed. Anal.* – 2018. – Vol.151. – P.178-185.
3. *Application of polyacrylamide (PAM) through lay-flat polyethylene tubing: effects on infiltration, erosion, N and P transport, and corn yield / McNeal J.P., Krutz L.J., Locke M.A., Kenty M.M., Atwill R.L., Pickelmann D.M., Bryant C.J., Wood C.W., Golden B.R., Cox M.S.* // *J. Environ. Qual.* – 2017. – Vol.46. – P.855-861.
4. *Application of polyacrylamide to reduce phosphorus losses from a Chinese purple soil: a laboratory and field investigation / Jiang T., Teng L., Wei S., Deng L., Luo Z., Chen Y., Flanagan D.C.* // *J. Environ. Manage.* – 2010. – Vol.91. – P.1437-1445.

5. *Polyacrylamide* degradation and its implications in environmental systems / Xiong B., Loss R.D., Shields D., Pawlik T., Hochreiter R., Zydney A.L., Kumar M. // *npj Clean Water*. – 2018. – Vol.1. – Article No. 17.

6. *Synthesis* and viscosimetric behavior of poly(acrylamide-co-2-acrylamido-2-methylpropanesulfonate) obtained by conventional and adiabatic gel process via RAFT/MADIX polymerization / Mejia A., Rodriguez L., Schmitt C., Andreu N., Favero C., Braun O., Dupuis G., Deniau E., Reynaud S., Grassl B. // *ACS Omega*. – 2019. – Vol.4. – P.11119-11125.

7. *Tischenkova M.O., Filin V.M., Ivashchenko N.G.* Use of polyacrylamides of a series ECOFLOC for dust suppression in ash and sludge collectors of thermal power plants // *Voprosy Khimii i Khimicheskoi Tekhnologii*. – 2019. – No. 6. – P.236-240.

8. *Synthesis* and properties of polymer matrices based on cross-linked polyacrylamide and β -cyclodextrin-containing pseudorotaxane / Orel L.A., Sinelnikov S.I., Kobrina L.V., Shtompel V.I., Riabov S.V. // *Voprosy Khimii i Khimicheskoi Tekhnologii*. – 2017. – No. 5. – P.3-10.

9. *Chain* initiation mechanism of acrylamide polymerisation in direct and inverse emulsions / Beylerian N.M., Grigoryan M.V., Grigoryan J.D., Harutyunyan R.S. // *Oxid. Commun.* – 2002. – Vol.25. – No. 3. – P.395-405.

10. *Capek I., Fialova L., Berek D.* On the kinetics of inverse emulsion polymerization of acrylamide // *Des. Monomers Polym.* – 2008. – Vol.11. – P.123-137.

11. *Moad G., Solomon D.H.* The chemistry of free radical polymerization, 2nd Edition. – Amsterdam: Elsevier Science Ltd, 2005.

12. *Acrylamide* emulsion polymerization kinetics dependence on radical generation loci / Grigorian J.D., Grigorian M.V., Chshmaritian J.H., Harutyunyan R.S., Beylerian N.M. // *Oxid. Commun.* – 2006. – Vol.29. – No. 2. – P.427-442.

13. *Chern C.S.* Emulsion polymerization mechanism and kinetics // *Prog. Polym. Sci.* – 2006. – Vol.31. – P.443-486.

14. *On the initiation* mechanism of acrylamide polymerisation in aqueous solutions initiated by potassium persulfate / Beylerian N.M., Ruckenstein E., Harutyunyan R.S., Grigoryan J.D., Grigoryan V.V., Hagopyan R.M., Asaturyan R.A. // *Oxid. Commun.* – 2002. – Vol.25. – No. 3. – P.383-394.

15. *Al-Moameri H., Jaf L., Suppes G.J.* Viscosity-dependent frequency factor for modeling polymerization kinetics // *RSC Adv.* – 2017. – Vol.7. – P.26583-26592.

Received 11.11.2020

ПРО МЕХАНІЗМ ЕМУЛЬСІЙНОЇ ПОЛІМЕРИЗАЦІЇ АКРИЛАМІДУ ЗА УЧАСТЮ ЙОГО ДИМЕРІВ

Л.Р. Арутюнян, Р.С. Арутюнян

Обговорено значення димерних і мономерних форм акриламідного мономеру в процесі полімеризації в емульсіях, що ініційована різними типами ініціаторів. Висвітлені причини порядків реакції за мономером, більших одиниці, для вільно радикальної полімеризації акриламід у емульсіях. Механізм емульсійної полімеризації обговорено окремо для процесів, ініційованих водно-розчинними ініціатором і масло-розчинним ініціатором. Основна відмінність в обох випадках є розподіл акриламід і ініціатора в водній і толуольній фазах. У випадку використання водно-розчинного ініціатора ініціатор і акриламід знаходяться в одній фазі, тоді як молекули ініціатора і акриламід розподілені між двома різними фазами у випадку використання масло-розчинного ініціатора. У результаті участь димерів в процесі емульсійної полімеризації акриламід більш дієва для систем, де використовується водно-розчинний ініціатор. Для таких систем як димери, так і мономер акриламід беруть участь в розповсюдженні реакції при відносно низьких концентраціях акриламід, що і пояснює величину порядку реакції по мономеру, більшу за одиницю.

Ключові слова: акриламід, емульсійна полімеризація, механізм полімеризації, водно-розчинний ініціатор, калій персульфат, масло-розчинний ініціатор, 2,2'-азобіс(ізобутиронітріл).

ON THE MECHANISM OF ACRYLAMIDE EMULSION POLYMERIZATION WITH THE PARTICIPATION OF ITS DIMERS

L.R. Harutyunyan^{a,}, R.S. Harutyunyan^b*

^a *Armenian National Agrarian University, Yerevan, Armenia*

^b *Yerevan State University, Yerevan, Armenia*

* e-mail: l.harutyunyan@anau.am

The role of both dimeric and monomeric forms of acrylamide monomer in the process of polymerization in emulsions initiated by different type of initiators was discussed and the reasons for the reaction order with respect to monomer greater than unity were elucidated for acrylamide free radical polymerization in emulsions. The emulsion polymerization mechanism of acrylamide is discussed separately for the processes initiated by water-soluble initiator and oil-soluble initiator. The main difference in two cases is the distribution of acrylamide and initiator in aqueous and toluene phases. In the case of using water-soluble initiator, the initiator and acrylamide are in the same phase, whereas the molecules of the initiator and acrylamide are distributed between different phases in the case of using oil-soluble initiator. As a result, the participation of the dimers in the process of acrylamide emulsion polymerization is more efficient for the system where water-soluble initiator is used. For that system, it is suggested that both dimers and monomers of acrylamide participate in the propagation reaction at relatively low concentrations of acrylamide, which explains the value of the reaction order with respect to monomer greater than unity.

Keywords: acrylamide; emulsion polymerization; polymerization mechanism; water-soluble initiator; potassium persulfate; oil-soluble initiator; 2,2'-azobisisobutyronitrile.

REFERENCES

1. Mohsin MA, Attia NF. Inverse emulsion polymerization for the synthesis of high molecular weight polyacrylamide and its application as sand stabilizer. *Int J Polym Sci.* 2015; 2015: 436583. doi: 10.1155/2015/436583.
2. Asadi S, Tabani H, Nojavan S. Application of polyacrylamide gel as a new membrane in electromembrane extraction for the quantification of basic drugs in breast milk and wastewater samples. *J Pharm Biomed Anal.* 2018; 151: 178-185. doi: 10.1016/j.jpba.2018.01.011.
3. Mc Neal JP, Krutz LJ, Locke MA, Kenty MM, Atwill RL, Pickelmann DM, et al. Application of polyacrylamide (PAM) through lay-flat polyethylene tubing: effects on infiltration, erosion, N and P transport, and corn yield. *J Environ Qual.* 2017; 46: 855-861. doi: 10.2134/jeq2016.08.0299.
4. Jiang T, Teng L, Wei S, Deng L, Luo Z, Chen Y, et al. Application of polyacrylamide to reduce phosphorus losses from a Chinese purple soil: a laboratory and field investigation. *J Environ Manage.* 2010; 91: 1437-1445. doi: 10.1016/j.jenvman.2010.02.006.
5. Xiong B, Loss RD, Shields D, Pawlik T, Hochreiter R, Zydny AL, et al. Polyacrylamide degradation and its implications in environmental systems. *npj Clean Water.* 2018; 1: 17. doi: 10.1038/s41545-018-0016-8.
6. Mejia A, Rodriguez L, Schmitt C, Andreu N, Favero C, Braun O, et al. Synthesis and viscosimetric behavior of poly(acrylamide-co-2-acrylamido-2-methylpropanesulfonate) obtained by conventional and adiabatic gel process via RAFT/MADIX polymerization. *ACS Omega.* 2019; 4: 11119-11125. doi: 10.1021/acsomega.9b00975.
7. Tischenkova MO, Filin VN, Ivashchenko NG. Use of polyacrylamides of a series ECOFLOC for dust suppression in ash and sludge collectors of thermal power plants. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2019; (6): 236-240. doi: 10.32434/0321-4095-2019-127-6-236-240.
8. Orel LA, Sinelnikov SI, Kobrina LV, Shtompel VI, Riabov SV. Synthesis and properties of polymer matrices based on cross-linked polyacrylamide and β -cyclodextrin-containing pseudorotaxane. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2017; (5): 3-10.
9. Beylerian NM, Grigoryan MV, Grigoryan JD, Harutyunyan RS. Chain initiation mechanism of acrylamide polymerisation in direct and inverse emulsions. *Oxid Commun.* 2002; 25(3): 395-405.
10. Capek I, Fialova L, Berek D. On the kinetics of inverse emulsion polymerization of acrylamide. *Des Monomers Polym.* 2008; 11: 123-137. doi: 10.1163/156855508X298035.
11. Moad G, Solomon DH. *The chemistry of free radical polymerization.* 2nd edition. Amsterdam: Elsevier Science Ltd; 2005.
12. Grigorian JD, Grigorian MV, Chshmaritian JH, Harutyunyan RS, Beylerian NM. Acrylamide emulsion polymerization kinetics dependence on radical generation loci. *Oxid Commun.* 2006; 29(2): 427-442.
13. Chern CS. Emulsion polymerization mechanism and kinetics. *Prog Polym Sci.* 2006; 31: 443-486. doi: 10.1016/j.progpolymsci.2006.02.001.
14. Beylerian NM, Ruckenstein E, Harutyunyan RS, Grigoryan JD, Grigoryan VV, Hagopyan RM, et al. On the initiation mechanism of acrylamide polymerisation in aqueous solutions initiated by potassium persulfate. *Oxid Commun.* 2002; 25(3): 383-394.
15. Al-Moameri H, Jaf L, Suppes GJ. Viscosity-dependent frequency factor for modeling polymerization kinetics. *RSC Adv.* 2017; 7: 26583-26592. doi: 10.1039/C7RA01242J.