УДК 691.175.5/.8
МРНТИ 47.09.51

INVESTIGATION OF DIMETHYL DIALLYLAMMONIUM CHLORIDE AND DIMETHYL ACRYLAMIDE SYNTHESIS AND KINETICS

SYRGABEK E.[1], AKHMETZHAN A.[2], TOKTARBAY ZH.[1,4], TASHENOV A.[2], NURAJE N.[3]

[1]Al-Farabi Kazakh National University
[2]L.N.Gumilyov Eurasian National University
[3]Texas Tech University, Lubbock
[4]Specialized gymnasium for gifted children teaching in three languages named after Al-Farabi, Almaty, Kazakhstan

Abstract: *Radical co-polymerization of N, N-dimethyl-N,N-diallyammonium chloride (DMDAAC) with N,N-dimethyl acrylamide (DMAA) has been investigated by the dilatometer technique using ammonium persulfate ($(NH4)_2S_2O_8$) as an initiator. The influences of the molar ratio of DMDAAC to DMAA, concentrations of monomers and initiator, temperature on polymerization rate have been analysed. From these analysis it was found that DMDAAC concentration in monomers composition conversely affects the polymerization rate. Based on the experimental results, the polymerization mechanisms were discussed in more detail.*

Key words: *Radical polymerization, Dimethyl diallylammonium chloride, Dimethyl acrylamide, Kinetics, Activation energy*

ИССЛЕДОВАНИЕ СИНТЕЗА И КИНЕТИКИ ДИМЕТИЛДИАЛЛИЛАММОНИЙ ХЛОРИДА И ДИМЕТИЛ АКРИЛАМИДА

Аннотация: *Радикальная сополимеризация N, N-диметил-N, N-диаллиаммоний хлорида (ДМДААХ) с N, N-диметилакриламидом (ДМАА) была исследована методом дилатометра с использованием персульфата аммония ($(NH4)_2S_2O_8$) в качестве инициатора. Проанализировано влияние молярного отношения ДМДААХ к ДМАА, концентрации мономеров и инициатора, температуры на скорость полимеризации. Из этого анализа было установлено, что концентрация ДМДААХ в составе мономеров, наоборот, влияет на скорость полимеризации. Основываясь на экспериментальных результатах, механизмы полимеризации обсуждались более подробно.*

Ключевые слова: *радикальная полимеризация, диметилдиаллиламмонийхлорид, диметилакриламид, кинетика, энергия активации*

ДИМЕТИЛДИАЛЛИЛАММОНИЙ ХЛОРИДІ МЕН ДИМЕТИЛ АКРИЛАМИДІНІҢ СИНТЕЗІ МЕН КИНЕТИКАСЫН ЗЕРТТЕУ

Аңдатпа: *N, N-диметил-N, N-диаллиаммоний хлоридінің (ДМДААХ) N, N-диметил акриламидімен (ДМАА) радикалды сополимеризациясы аммиак персульфаты ($(NH4)_2S_2O_8$) қатысында дилатометр әдісімен зерттелді. ДМДААХ молярлық қатынасының ДМАА-ға, мономерлер мен бастамашылардың концентрациясы мен температураның полимеризация жылдамдығы-*

на әсері қарастырылды. Осы талдау нәтижесінде ДМДААХ концентрациясы мономерлердің құрамына, керісінше, полимерлену жылдамдығына әсер ететіні анықталды. Эксперимент нәтижелеріне сүйене отырып, полимерлеу тетіктері толығырақ талқыланды.

Түйінді сөздер: *радикалды полимеризация, диметилдиаллиламмоний хлориді, диметил акриламид, кинетика, активация энергиясы*

Introduction

Kinetics of radical polymerization has a long history and it is very useful for large scale polymer production [1, 2]. Homopolymers of dimethyl acrylamide, dimethyl diallylammonium chloride and their copolymers are often used for flocculant production [3], in papermaking [4], medicine [5], in developing hydrogels for heavy metal removal [6, 7], for making sensors [8] etc. due to their simplicity and versatility.

Polymerization kinetics focuses on many factors like polymerization rate, initiator concentration, monomer concentration and temperature [9, 10]. Production of high-quality polymer or copolymer with high production rates requires a detailed and precise knowledge of polymerization kinetics [11]. Thus, due to the industrial application of poly (DMAA-DMDAAC) copolymer, optimization of polymerization process and controlling properties of final copolymer is very important [12]. Usually, dimethylacrylamide is added to DMDAAC in order to increase the molecular weight of copolymers and application of these copolymers depend on copolymer composition. Therefore, issues related to producing copolymers with specific properties and right composition, and their dependency on the reaction conditions can be solved from investigation of the polymerization kinetics [13].

Usually, kinetics of polymerization is investigated by different methods such as 1H-NMR spectroscopy [14], differential scanning calorimetry [15,16], Polarographic Study [17], Electrochemical method [18], gravimetry [19] and dilatometry [20]. In this study to investigate the kinetics of free radical co-polymerization experimentally, we used the dilatometric method due to its simplicity and effectiveness [21, 22]. Moreover, in this method the equation of polymerization rate can be easily calculated by polymer and monomer mixture composition difference [23, 24]. The aim of this work is to obtain the kinetic equation for co-polymerization of poly (N, N-dimethyl-N,N-diallyammonium chloride-co-N,N-dimethylacrylamide) (DMDAAC-DMAA) by mentioned method and to investigate the influences of various parameters on the kinetics of polymerization. The co-polymerization equation is also proposed.

EXPERIMENTAL

Materials

The monomers DMDAAC (65 wt. % in water, density 1.183 g/mL) and DMAA (purity 99.5 wt %, density 0.962 g/mL) were purchased from Sigma Aldrich (USA). $AgNO_3$ (purity 99.8 wt %), and $(NH_4)_2S_2O_8$ (purity 99.7 wt %) were kindly provided by “Labor Pharma” Ltd. (Kazakhstan). Acetone (purity 99.9 wt %) and other organic chemicals were purchased from “Labchimprom” Ltd. (Kazakhstan). Argon with purity of 99.995 wt % was received from “Ikhsan” Ltd. (Kazakhstan). For all kinetic study glass dilatometers with capillary diameter of 1 mm were used. Distilled water with a conductivity 2.4 mS/cm at 20°C was used in all experiments.

Copolymerization

The co-polymerization reaction of DMDAAC with DMAA was carried out at different molar ratios of monomers in the presence of ammonium persulfate initiator. The total molar concentration of monomers in the mixture was equal to 5 mol/l. After purging with argon gas for 20 min, the ampule containing monomers was sealed and placed in a water bath heated at 60°C. The reaction time was controlled to give conversions less than 10 wt %. Then the copolymers were washed and precipitated with fresh acetone. This operation was repeated three times to remove the unreacted monomers. The copolymers were finally dried under vacuum at 40°C until constant weight.

Kinetics of co-polymerization

In this experiment, the rate of polymerization was measured using dilatometers. The dilatometric method is based on a change in the volume of the reaction mixture during the polymerization of monomers. It works such a way that the dilatometer is placed in a constant temperature bath and the volume change of the polymerizing system, which is quantitatively related to the percent conversion, is controlled with time.

Initially, dilatometers in which the co-polymerization reactions will be carried out, are cleaned and thoroughly dried. The formation of a polymer is associated with an increase in the density, consequently with decrease in the volume of the reaction mixture, which occurs during polymerization of monomers.

The degree of conversion of monomers A

$$A = \frac{\Delta V}{VK'} * 100\% \qquad (1)$$

(%) is calculated from formula (1):

where V – is the initial volume of the reaction mixture at the polymerization temperature;

ΔV – change in the volume of the reaction mixture over a given period of time;

$$K' = K_1''\omega + K_2''(1-\omega) \qquad (2)$$

K' – is the contraction factor for co-polymerization, which is found from equation (2):

where K''1 and K''2 are contraction factors for the homo-polymerization of DMDAAC and DMAA, respectively;

$$K_1'', K_2'' = \frac{\rho_p - \rho_m}{\rho_m} \qquad (3)$$

ω – is the DMDAAC content in the starting monomer mixture. The values of K''1 and K''2 were found from the formula (3):

where ρ_m and ρ_p are the density of the monomer and polymer, respectively, g/cm3.

Results and discussion

Kinetics of co-polymerization

In this study, the influences of various polymerization parameters, including the molar ratio of DMDAAC to DMAA, monomer [M] and initiator [I] concentrations to the rate of the reaction were investigated.

Effect of the molar ratio of DMDAAC to DMAA on co-polymerization

For DMDAAC copolymers, the cationic degree of the product can change the property of the polymer notably. Increasing the cationic degree of DMDAAC copolymers by increasing DMDAAC content leads to wider applicability of the material in water treatment processes.

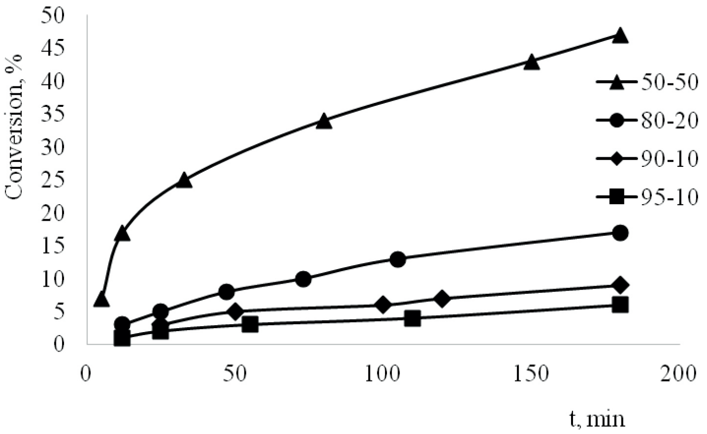

Fig. 1 – Conversion vs. time curves at different molar ratios of DMDAAC to DMAA; conditions: [M]= 5M, T =60°C, [I] = 0.03% (monomer)

As can be seen from the Fig 1, the greater the mole fraction of DMAA in the original monomer mixture, the higher is conversion. This is due to the fact, that the reactivity of the DMAA monomer is higher, as the monomer DMDAAC is not active due to the steric hindrance of molecular structure [12].

Effect of polymerization temperature on co-polymerization

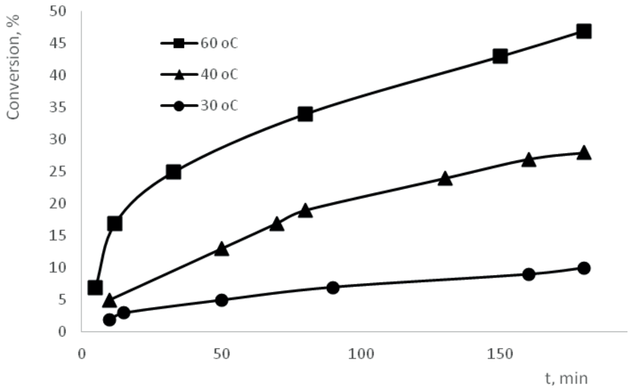

Fig. 2 – Conversion vs. time curves at different temperature; conditions: [M]= 5M, MDMDAAC:MDMAA=50:50, [I] = 0.03% (monomer)

The effect of temperature on the polymerization rate is shown in Fig.2. With increasing temperature, the initiation process accelerates, which subsequently increases the concentration of radicals, finally resulting in an increase of the polymerization rate.

Effect of initiator concentration on co-polymerization

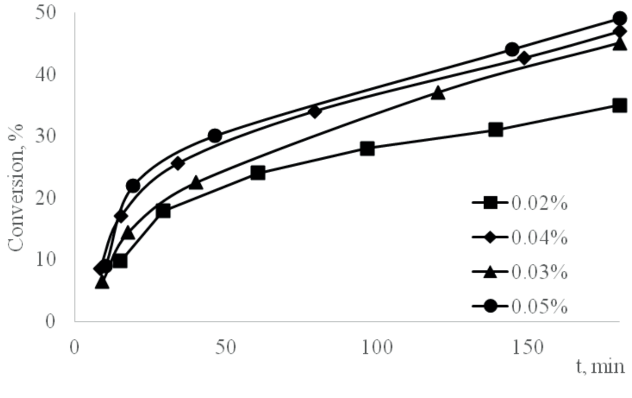

Fig. 3 – Conversion vs. time curves at different initiator concentration; conditions: [M]= 5M, T =60°C, MDMDAAC:MDMAA=50:50

In figure 3 it was found that conversion and the rate of polymerization increase with increasing initiator concentration. Consequently, this result leads to make assumption that termination of bimolecular interaction of polymer radicals slightly decreases due to the bulky molecular structure and positive charge of DMDAAC [26].

Effect of monomer concentration on co-polymerization

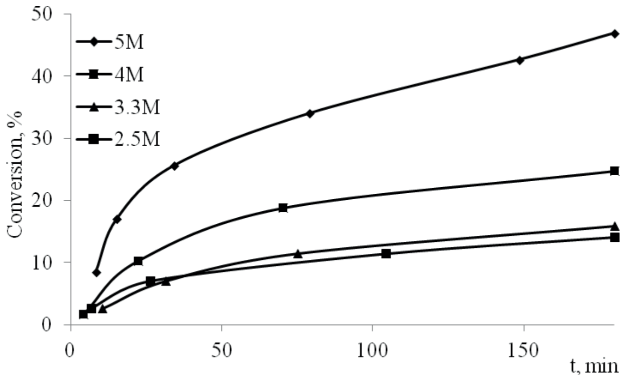

Fig. 4 – Conversion vs. time curves at different monomer concentration, conditions: MDMDAAC:MDMAA=50:50, T =60°C, [I] = 0.03% (monomer)

Figure 4 illustrates the dependence of monomer concentration on polymerization conversion and rate.

From these figures it can be seen, that with increasing monomer concentration, polymerization conversion and rate also increase. This may be due to formation of more active centers which leads to more interactions between radicals [25,26].

Conclusion

Aqueous radical polymerization of DMDAAC-DMAA has been prepared by free radical polymerization in the presence of ammonium persulfate initiator which was studied by dilatometry method. The kinetics of radical polymerization were discussed as well. It was found that the polymerization rate decreases with the increase of DMDAAC composition in the copolymer due to the bulky molecular structure and positive charge, resulting in the significant steric hindrance and electrical repulsion.

REFERENCES

1. Moad G, Solomon DH. Inroduction. In: Moad G, Solomon DH. The Chemistry of Radical Polymerization; 2nd ed. Oxford: Elsevier; 2006. p. 1-9.
2. Nesvadba P. Radical Polymerization in Industry. In: Chatgilialoglu C, Studer A, editors. Encyclopedia of Radicals in Chemistry, Biology and Materials. Vol 4. Chichester: John Wiley & Sons, Ltd; 2012. p. 1701-1736.
3. K.Zh. Abdiyev, Z. Toktarbay, A.Zh. Zhenissova, M.B. Zhursumbaeva, R.N. Kainazarova, N. Nuraje, The New effective FlocculantsndashCopolymers of N,N-dimethyl-N,N-diallyl-ammonium Chloride and N,N-dimethylacrylamide, Colloids and Surfaces A: Physicochemical and Engineering Aspects (2015)
4. N. Maximova, M. Цsterberg, K. Koljonen and P. Stenius, Lignin adsorption on cellulose fibre surfaces: effect on surface chemistry, surface morphology and paper strength, Cellulose. 8 (2001) 113-125.5.
5. Matthew P. Mullarney, Thomas A.P. Seery, R.A. Weiss Drug diffusion in hydrophobically modified N,N-dimethylacrylamide hydrogels// Polymer 47 (2006) 3845–3855
6. Vijay Shankar Pandey, Shiv Kumar Verma, Mithilesh Yadav, Kunj Behari Studies on graft co-polymerization of gellan gum with N,N-dimethylacrylamide by the redox system// International Journal of Biological Macromolecules 70 (2014) 108–115
7. A.L. Ramos-Jacques, J.A. Lujan-Montelongo, Silva-Cuevas, M. Cortez-Valadez, M. Estevez, A.R. Hernandez-Martínez Lead (II) removal by poly(N,N-dimethylacrylamide-co-2-hydroxyethyl methacrylate)// European Polymer Journal 101 (2018) 262–272
8. Hideaki Tokuyama, Eri Kitamura, Yoshimi Seida Detection of AU(III) ions using a poly(N,N-dimethylacrylamide)-coated QCM sensor// Talanta 146 (2016) 507–509
9. Nowers, J.R., Narasimhan, B., “The effect of interpenetrating polymer network formation on polymerization kinetics in an epoxy[hyphen (true graphic)]acrylate system”, Polymer, 47 (4), 1108-1118 (2006).
10. Choi, E.C., Jin, S.M., Park, Y.J., Kim, Y., “Polymerization kinetics for the preparation of poly(p-divinylbenzene) via a miniemulsion polymerization process”, J. Chin. Inst. Chem. Eng., 39 (5), 483-488 (2008).
11. Cutie SS, Smith PB, Henton DE, Staples TL, Powell C (1997) Acrylic acid polymerization kinetics. J Polym Sci Part B Polym Phys 35:2029–204712.
12. K. Zh. Abdiyev, Zh. Toktarbay, A. Zh. Zhenissova, M. B. Zhursumbaeva, and R. N. Kainazarova Copolymerization of N,N-dimethyll-N,N-diallylammonium Chloride with N,N-dimethylacrylamide// Polymer Science, Ser. B, 2015, Vol. 57, No. 3, pp. 217–223.
13. Rintoul I, Wandrey C (2005) Approach to predict copolymer compositions in case of variable monomer reactivity. Macromolecules 38:8108–8115
14. Mahdi Abdollahi, Parisa Alamdari, Hadis Koolivand, Farshid Ziaee A comprehensive study on the kinetics of aqueous free-radical homo- and co-polymerization of acrylamide and diallyldimethylammonium chloride by online 1H-NMR spectroscopy// J Polym Res (2013) 20:239.
15. E. Nadim, H. Bouhendi, F. Ziaee, R. Bazhrang Kinetic study of 2-acrylamido-2-methylpropanesulfonic acid in free-radical polymerization method by differential scanning calorimetry// Polym. Bull. (2012) 68:405–414.
16. Pham Q-Thai, Hsu Y-Jung, Wang F-Ming, Chern C-Shyan, Mechanisms and kinetics of non-isothermal polymerization of N,N-bismaleimide-4,4-diphenylmethane with 2-thiobarbituric acid, Thermochimica Acta (2018), ***https://doi.org/10.1016/j.tca.2018.08.01617***.

17. E. E. Ergozhin, B. A. Mukhitdinova, S. A. Shoinbekova, A. I. Nikitina, and B. M. Nuranbaeva Kinetics of Radical Polymerization of a Monomer Derived from Monoethanolamine Vinyl Ether and 1,4-Benzoquinone: A Polarographic Study// Russian Journal of Applied Chemistry, Vol. 76, No. 3, 2003, pp. 460 – 463.
18. Marco Fantin, Abdirisak A. Isse, Nicola Bortolamei, Krzysztof Matyjaszewski, Armando Gennaro Electrochemical approaches to the determination of rate constants for the activation step in atom transfer radical polymerization// Electrochimica Acta 222 (2016) 393–401.
19. Hong-Ru Lin Solution polymerization of acrylamide using potassium persulfate as an initiator: kinetic studies, temperature and pH dependence// European Polymer Journal 37 (2001) 1507-1510.
20. LIAO Liewen, YUE Hangbo, and CUI Yingde Crosslink Polymerization Kinetics and Mechanism of Hydrogels Composed of Acrylic Acid and 2-Acrylamido-2-methylpropane Sulfonic Acid// Chinese Journal of Chemical Engineering, 19(2) 285-291 (2011)
21. De, Gee A., Davidson, C., Smith, A., “A modified dilatometer for continuous recording of volumetric polymerization shrinkage of composite restorative materials”, J. Dent., 9 (1), 36-42 (1981).
22. Watts, D., Cash, A., “Determination of polymerization shrinkage kinetics in visible-light-cured materials: Methods development”, Dent. Mater., 7 (4), 281-287 (1991).
23. Venhoven, B., De, Gee A., Davidson, C., “Polymerization contraction and conversion of light-curing BisGMA-based methacrylate resins”, Biomaterials, 14 (11), 871-875 (1993).
24. Braga, R.R., Ferracane, J.L., “Contraction stress related to degree of conversion and reaction kinetics”, J. Dent. Res., 81 (2), 114-118 (2002). 25. Yebol Dauletov, Kaldybek Abdiyev, Zhexenbek Toktarbay, Nurxat Nuraje, Maryamgul Zhursumbaeva, and Bagdaulet Kenzhaliyev Radical Polymerization and Kinetics of N,N-diallyl-N,N-dimethylammonium Chloride and Vinyl Ether of Monoethanolamine// Fibers and Polymers 2018, Vol.19, No.10, 2023-202926. Kezhen Bi, Yuejun Zhang Kinetic Study of the Polymerization of Dimethyldiallylammonium Chloride and Acrylamide// J Appl Polym Sci – 2012, Vol.125, -1636–1641.