Dilatometric Research of Copolymerization of Acrylamide with N-Vinyl-Lactams

U. MIRZAEV, I.ISMAILOV, M.MIRZAEVA

Departament of Chemistry, Tashkent State Technical University named after Beruni, Uzbekistan

Abstract

In article with the help of dilatometric method there is studied kinetics copolymerization of acrylamide with N-vinyl-pyrolydon and N-vinyl-caprolactam. As well as the dependency of the output copolymers from concentration of the initiator, temperature and from source correlations of monomers is studied. The got results indicate the radical mechanism initiation of copolymerization and flow of breakaway chain on bi-molecular type. At the study of the reactions of copolymerization there is installed a main factor that influencing upon composition structure and characteristic of synthesized copolymers, is a source correlation monomer in reactionary mixture and is herewith shown that AA in reactions of copolymerization with VP and VKL shows the greater activity, than the second so-monomer.

Keywords: acrylamide, caprolactam, pyrolydon, copolymer, peroxysulphatepotassium,, dilatometry

Introduction

Water-soluble polymers are broadly used in present time on base acrylamide (AA) [1]. In this group enters the polyacrylamide (PAA) – non-ionone polymer, and its anionic derived, for instance, partly hydrolyzed PAA and cationic derived, for instance poly-vinyl-amine, as well as copolymers AA with different ionone and non-ionone monomers [2]. The most broadly used water-soluble polymers AA as phloculants for efficient peelings of natural and industrial sewages, catching and separations of ions of heavy metal and toxic material that promotes the decision of the ecological problem protection of environment and in particular natural basins from contamination [3]. The perspective application of polymers and copolymers AA are using them in agricultures, as structure-forming of ground, film-forming for seeds, fertilizers, insecticides, herbicides and fungicide [4, 5].

Materials and Methods

Acrylamide, N-vinylcaprolactam, N-vinylpyrolidon, peroxysulphate potassium, copolymer acrylamide - vinylcaprolactam, acrylamide –vinylpyrolidon,

Results and Discussion

Methods of dilatometer.

In this article there are considered some kinetic regularities of joint polymerization AA with N-vinyl-caprolactam (VC) and N-vinyl-pyrolydon (VP). The kinetics of radical copolymerization AA - VCl and AA-VP researched with the dilatometric method in presence of initiator of peroxysulphate potassium in water solution. As is well known, under the kinetic study of the reactions of copolymerization of dilatometric method there is necessary to know the value of the factor contraction, characterizing maximum change of the volume of reactionary mixture under determined degree of the conversion (q) mixture monomer in copolymer. For this purpose, the dependency of the factor of contraction was studied from source correlation monomer (Figure.1) at copolymerization.

As can be seen from Figure.1 factor ofcontraction to linear depends on composition monomer mixture that enables define the degree of the conversion monomer at copolymerization under any

correlations of component. There is installed that under q=10-15% observed linear dependency of degree of conversions from time.
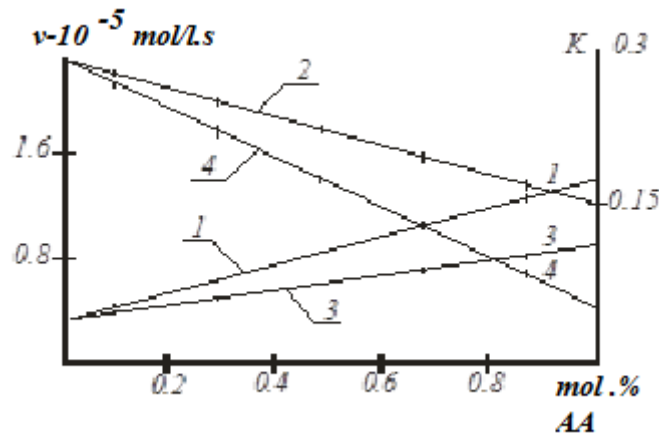

Figure.1. The dependency to initial velocity of copolymerization AA-VP (1), AA-VCL (3) and factor of contraction for copolymer AA-VP (4) and AA-VCL (2) from source composition of monomer under $60^o C$.

For determination of the initial velocities of copolymerization AA with VP and VCL was studied dependency of velocities of copolymerization from source correlation of monomer. The dependency was builton the base of results to initial velocity of copolymerization from composition of monomer mixture which is present at Figure. 1. As can be seen from presented data, the initial velocity of copolymerization depends on composition of monomer mixture and increases with improving the contents AA in source mixture that is bound obviously, with greater activity of acrylamide in contrast with VP and VCL in reaction of the growing chain.

For the reason determinations of the order to reactions on initiator, is studied kinetics under constant concentration monomer AA: VP, AA: VCL and different concentration of the initiator under 600C. The gained data (Figure. 2 a, b) witnesses that in both events with increase the concentrations of the initiator grow the velocity of radical copolymerization.
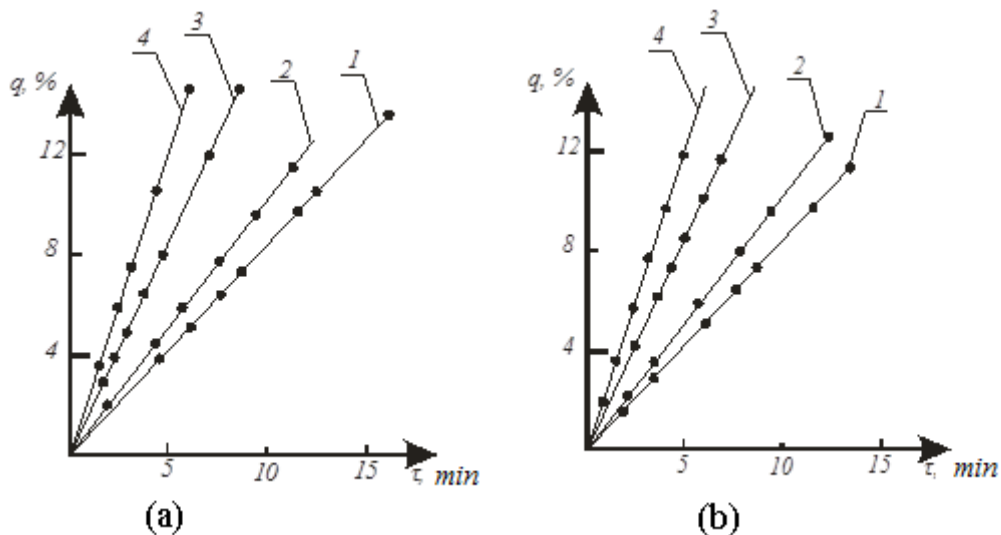

Figure. *2*. The dependency of the copolymers output AA-VP (a) and AA-VCL (b) from length of the reactions (the correlations M_1: M_2 – 50 : 50 mole%; [M] = 0.48 mole/l; t = 60^oC) under different concentration of the initiator (1-4), according a - $2,83 \cdot 10^{-5}$; $5,66 \cdot 10^{-5}$;$11.3 \cdot 10^{-5}$; $17.0 \cdot 10^{-5}$mole/l. b - 1,85·10-4; 3.2·10-4; 5.55·10-4 ; 9.26·10-4 mole/l.

The order to reactions on initiator, found on the grounds of logarithm dependencies to velocities of copolymerization from concentration of the initiator, turned out to be equal 0,5±0,01 и 0,51±0,01 for AA-VP and AA-VCL accordingly (the Figure.3 a,b). It is indicative of radical mechanism of initialization of copolymerization and flowing breakaway chain on bimolecular type.
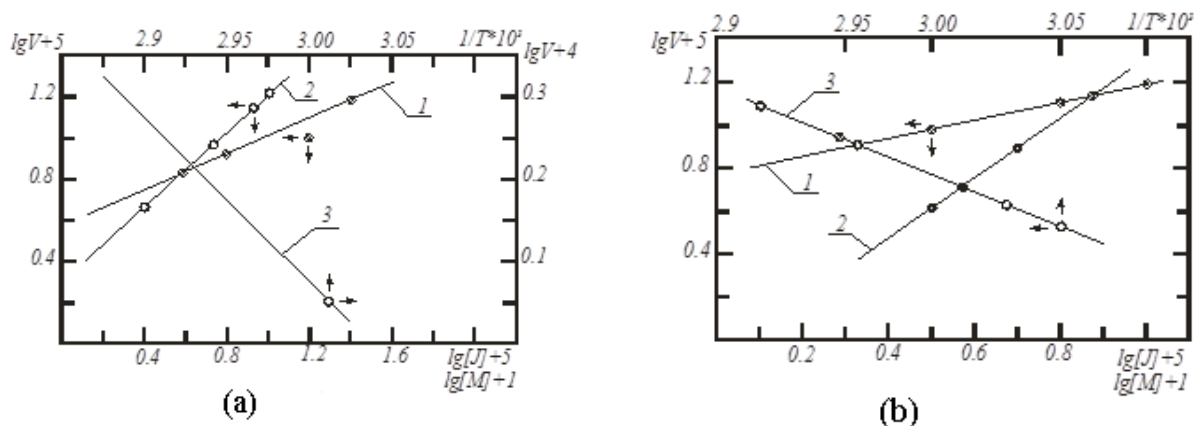

Figure.*3*. The logarithmic dependency of velocities of copolymerization AA-VP (a) and AA-VCL (b) from concentration of the initiator (1), monomer (2) and inverse temperature (3).

For determination order of reactions on monomer polymerization was realized under constant contents of the initiator and different concentration of monomer. The got results (Figure. 4 a,b) show that with increase of total amount of monomer in the system of copolymer output greatly increases.

As a result of calculation of the order of reactions on monomer, realizable on logarithmic dependency of the velocities of copolymerization from concentration monomer forms 1,5 and 1,53 for systems AA-VP and AA-VCL accordingly (pic.3 a,b). Under radical polymerization the majority of vinyl monomer orders of reaction on monomer usually close to one. However, it's known the much reactions of polymerization of vinyl monomer, characterized with dependency to velocities, polymerization from [M] in the degree greater 1.
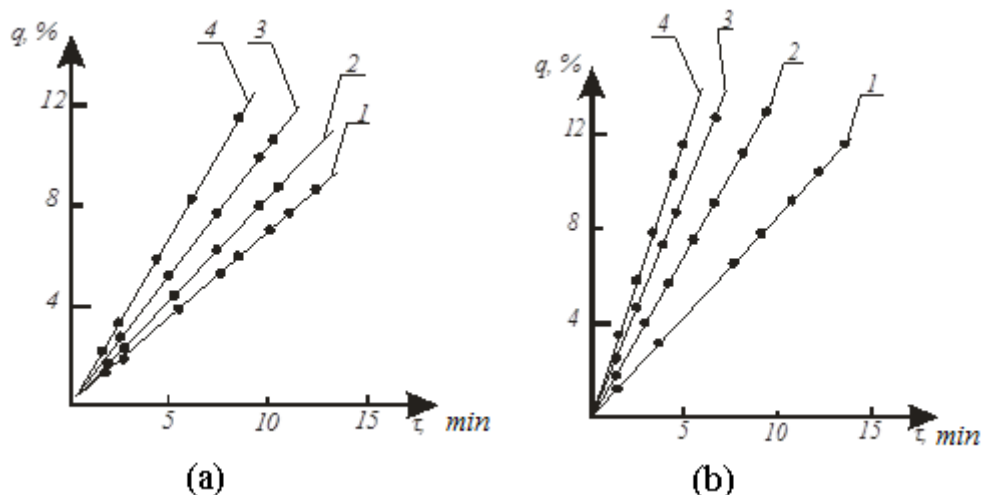

Figure. *4*. The dependency of the copolymer output AA-VP (a) and AA-VCL (b) from length of the reactions under different source correlations of monomer: a -1-4 contents AA in source mixture, accordingly: 0.24; 0.42; 0.56; 0.63 mole/l., [J]- 11,33·10^{-5}mole/l; t=60° Cb-1-4 contents AA in source mixture, accordingly: 0.29; 0.38; 0.48; 0.67 mole/l., [J]-1.85·10^{-4}mole/l; t=65°C

The deflection of the order to reactions on monomer from one can be conditioned different factor. Under the system that we study the deflection order to reactions on monomer will possible explain the

possibility of forming the hydrogen relationships between functional group monomer, as can serves the reason of the deflection of the order to reactions on monomer.

For study of the influence of the temperature on reactions of copolymerization process conducted under different temperature. The Experimental data has shown that with increasing the temperature the reactions output of copolymers increases. The total energy of activations E for velocity of copolymerization AA with VP and VCL found the graphic way, building to dependencies LgV from 1/T (Figure. 3 a, b) Found importance for copolymers AA-VP and AA-VCL, accordingly, forms 16,15kkal/mole and 17,8kkal/mole.

The suitable method of the determination of velocities if initializing is a so-called method of the acceptor, based on using strong inhibitor. At introduction to reactionary mixture of the inhibitor exists the inductive period during which the polymerization practically does not occur in consequence of interaction radical with molecule of the inhibitor. Length of induction period depends on amount of the inhibitor of system. Knowing the length of induction period, the importance of the velocity of initializingiseasy to define from the known correlationsVin=α [x] / τ ind. -where [x] - aconcentration of the inhibitor, τ ind.- length of induction period, α- stoichiometric factor, showing number of the ragged reactionary chains under the waste of one molecule of the inhibitor.

The value τ inddefinedfrom kinetic crooked dependencies of the leaving the polymer from length of copolymerization at the various concentration of inhibitor (pic.5).As inhibitor there is used 2,2; 6,6- tetramethyl - 4 - oxylperidine - 1 oxyltanan.
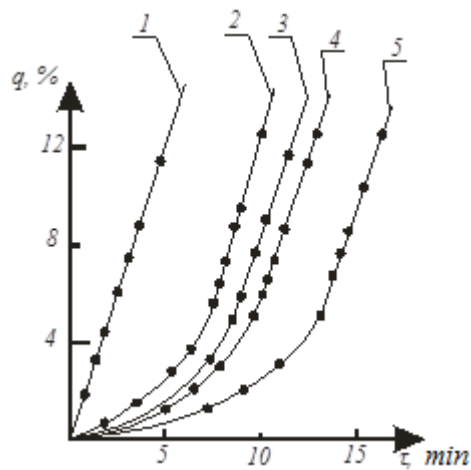

Figure. 5. The dependency of the output of copolymers AA-VP from length of time under different concentration of the inhibitor
[J]=11.33·10-5 mole/l;
[M]= 0.42 mole/l; t=65o C
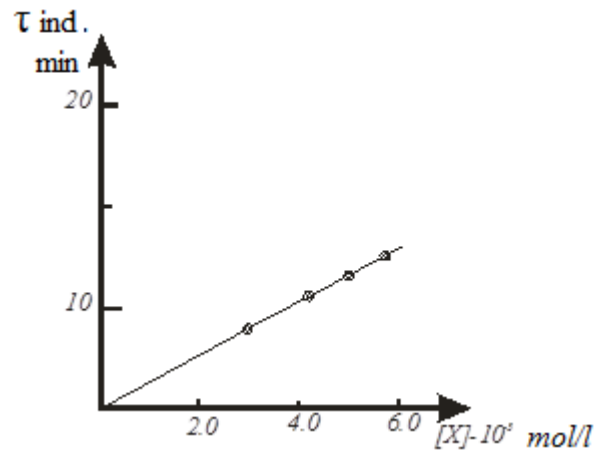1-5 concentrations of inhibitor accordingly
0; 2.88; 4.21; 4.81; 5.66·10-5 mol/l.

Figure. 6. The dependency induction period from concentration of the inhibitorundercopolymerizationAA-VP.

As can be seen from Figure..5 on kinetic crooked dependency output of copolymers from length of copolymerization in witness of inhibitor exist the induction period. Its length is proportional to the initial concentration of the inhibitor (Figure. 6), a velocity of copolymerization after completion of inhibitionthe velocities of the process is equal to the absence of the inhibitor. Linearity of dependencies of induction period from concentration of the inhibitor is indicative of efficiency of the used inhibitor.

Conclusions

Thereby, there isstudied main kinetic regularities of copolymerization AA with VP and VCL. The process is characterized by bimolecular breakaway of the polymeric chains, running on mechanism of the recombination. At study of the reactions of copolymerization there is installed that main factor, influencing upon composition structure and characteristic of synthesized copolymers, is a source correlation of monomer in reactionary mixture, and herewith shown that AA in reactions of copolymerization with VP and VCL shows the greater activity, than the second somonomer. As well as, accordingto the kineticsof copolymerization AA with VP and VCLthere are received equations to velocities of copolymerization: $V=k[J]^{0.5}[m]^{1.5}$forAA-VP, $V=k[J]^{0.51}[m]^{1.53}$forAA – VCL.

References

[1] Polyacrylamide. /Under the edit. V.F.KURENKOVA // M.:Chemistry, 1992. 192 p.
[2] Solovskiy M.V., Nikoliskaya N.V. The Main types of the polymeric carriersofbiologically active material (review)//Journal of plastic masses, 2005. №12.P.51-56.
[3] Zapoliskiy A.K., Baran A.A. The coagulants and flocculants in the process of waterpeelings//L.:Chemistry, 1987.288 p.
[4] Panarin E.F. Biologically active synthetic polymers (review) //Research bordereau SPBGPU, 2007. №2.P. 149-156.
[5] Ponarin E.F. Biologically active polymeric nanosystems//Innovation. 2008, №6. P. 50-53.