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SHORT COMMUNICATION

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Styrene heterophase radical polymerization in the presence of water-soluble polyvinylamides

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Abstract Heterophase polymerization of styrene in the presence of poly-*N*-vinylamides of different structures as stabilizers was investigated. Optimal conditions for preparing of stable polystyrene suspensions with narrow size distribution and the factors affecting the diameter and size distributions of polymer particles were established.

Key words Heterophase polymerization of styrene – suspensions

Introduction

Polymer suspensions with narrow particle size distribution have found a wide range of use in different fields of science, technology and medicine. They are used as calibrating materials and as carriers of biologically-active compounds [1]. Particles of such suspensions show interesting structural properties, creating crystal-like structures [2], however, they should possess narrow size distribution and should be stable during polymerization, storage, and in physiological solutions.

It would be of great value if these systems could create complexes with albumin and dyes.

It is supposed that the structure and properties of colloid "crystals", formed in polymer suspensions, are defined by the contents of low-molecular salt water [2]. In many cases complete deionization of water medium containing dispersed polymer particles is necessary during a number of weeks.

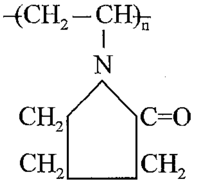
In this connection another problem arises of how to obtain a polymer suspension, the stablity of which is defined not only by electrostatic repulsion of particles, but also by other characteristics of its surface, which could be less sensitive to the presence of dissolved salts. This would additionally promote the range of usage of polymer suspensions, for instance, in electric devices, electronic color sensitive elements, etc. [1, 3].

It is well known that polymer suspensions are received by the heterophase (emulsion or suspension) polymerization of vinyl monomers in the presence of surface-active agents and potassium persulfate as initiator. The following surface-active agents are often used for this process: alkylsulfonate, alkylarylsulfonate [3], alcohols, acids, alkylphenols and polypropylene-glycol with different degrees of oxyethylation [4], polyvinyl alcohol (PVA), cellulose derivatives, gelatine, copolymers of acrylic acids [1, 3] and so on.

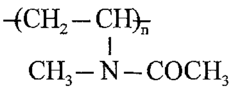
Nevertheless, a great number of problems dealing with synthesis of polymer suspensions with narrow size particle distribution are still unclear, for instance, the physico-chemical principles of nucleating of polymer–monomer particles in this process and their stability to aggregation in water.

In this connection it is interesting to study the influence of chemical structure of surface-active agents of polymer nature, their molecular weight and concentration on kinetics of heterophase polymerization of water-soluble vinyl monomer, size of particles, and their distribution in size. These help to understand peculiarities of heterophase (emulsion and suspension) polymerization of vinyl monomers. That is why this work is aimed at an attempt to research the kinetics of heterophase polymerization of styrene (St) in the presence of new water-soluble polymers from the class of poly-*N*-vinylamides (PVAm). The choice of these polymers is defined by the possibility to change surface-active and complex-forming properties. They possess water solubility with changing structure of a side group and insolubility in styrene. The polyvinylamides undergo no hydrolysis in water during the long-time heating and are nontoxic and ecologically safe polymers.

The following polymers were used in the study:

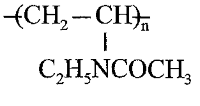


poly-*N*-vinylpyrrolidone (PVP)



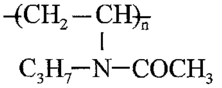
$$\left(CH_2-\underset{\underset{CH_3-N-COCH_3}{|}}{CH}\right)_n$$

poly-*N*-vinyl-*N*-methylacetamide (PVMA)



$$\left(CH_2-\underset{\underset{C_2H_5NCOCH_3}{|}}{CH}\right)_n$$

poly-*N*-vinyl-*N*-ethylacetamide (PVEA)



$$\left(CH_2-\underset{\underset{C_3H_7-N-COCH_3}{|}}{CH}\right)_n$$

poly-*N*-vinyl-*N*-propylacetamide (PVPA)

Molecular weights ($\bar{M}_w$) of PVP, PVMA, PVEA and PVPA are 30×10^3; 15×10^3; 30×10^3 and 30×10^3 respectively.

Experimental

Materials

Styrene (purity 99.6%) was purified before use by distillation under reduced pressure (bp 36 °C/2.6×10^3 Pa) Synthesis of *N*-vinylamides and their polymers was described in [5].

The other commercial reagents (potassium persulphate, PVA) were used without further purification.

Preparation procedure

Required quantities of styrene, poly-*N*-vinylamide and distilled water were charged to a three-neck glass flask equipped with stirrer and were de-oxygenated by bubbling nitrogen for at least 30 min. The nitrogen flow rate was then reduced to a low level and temperature was increased to 70 °C before the addition of potassium persulphate. Reaction mixture was stirred during polymerization. Samples were taken at time intervals to establish the degree of conversion by gravimetry.

Characterization

The latex particles was cleaned by means of ultra-filtration tehcniques using Amicon filtration device. The size of latex particles and their polydipersity were determined in cleaned latexes with Coulter Model 4MP apparatus by averaging 10 independent measurements. The particle size thus determined was the weight average d_w. Accuracy of the method was checked by evaluation of SEM micrographs.

Results and their discussion

The influence of the structure of PVAm on the kinetics of styrene polymerization and the properties of polymer suspensions

The kinetic curves of heterophase radical polymerization of styrene being received in the presence of PVAm of different structure are shown in Fig. 1. It is clear that styrene polymerization goes on practically without induction period with the constant rate up to 50% conversion. Under the styrene conversion higher than 50% conversion, sharp growth of rate is detected in presence of all PVAm apparently due to gel-effect. The structure of PVAm was found to affect the polymerization kinetics. The initial rate of polymerization, Vo, decreases when going from PVMA, PVP to PVEA and PVPA (see Fig. 1, Table 1). In the presence of PVMA, PVEA, and PVPA the reaction terminates during 4; 5 and 7 h respectively.

The data on Vo, quantity of coagulum, the size of particles, their distribution in size and stability of suspensions in salt solutions are represented in Table 1. Table 2 gives the data of the interphase tension of well-known polymer stabilizer (polyvinyl alcohol) and PVAm used.

It is clear that in the presence of PVAm stable suspensions with rather narrow distribution of particles by size can be synthesized. At the same time, in the presence of PVA the reaction system is unstable. Particles having wide distribution by size was formed at high content of coagulum in the reactin system (Table 1).

These results prove that in contrast to the traditional stabilizers (PVA, gelatine, etc.) polymers mentioned above affect the conditions of formation of polymer–monomer particles during the process of heterophase polymerization, supplying high strength of adsorption layer and narrowing the size distribution of particles.

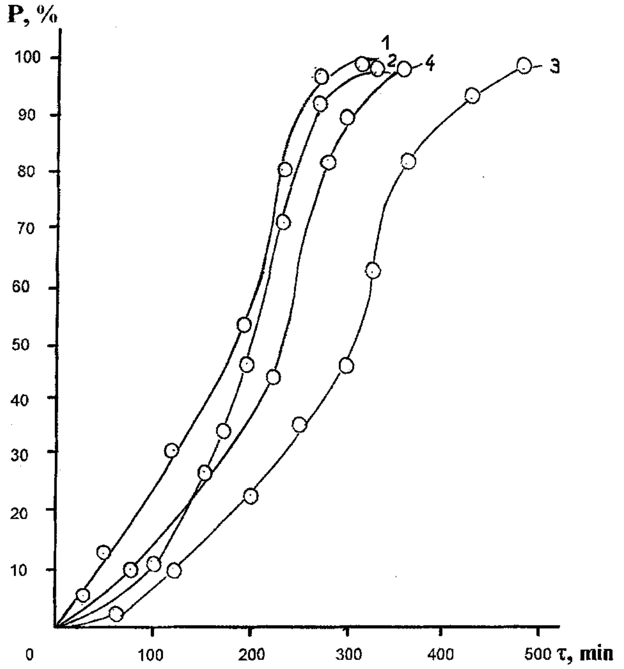


Fig. 1 Kinetic curves of styrene polymerization reaction in the presence of stabilizer: (1) PVMA; (2) PVEA; (3) PVPA; (4)-PVP. Conditions of polymerization: volume ratio of monomer: water is 1:9; concentrations of potassiumpersulphate and PVAm are 1% wt to monomer, PVMA concentration is 1% wt to monomer at 70 °C

It is important to note that in the presence of PVAm unlike PVA the process of polymerization goes on in such a way that the formed drops of monomer–polymer particles preserve their size and stability from the beginning of polymerization (5–6% conversion) until the complete conversion of monomer into polymer (Table 3). In other words the coalescence stage of particles is evidently absent because of the appearance of a layer of PVAm macromolecules on the surface of these particles.

It is known that during polymerization initiated with potassium persulfate, carboxylic groups are formed on the end of polymer chains, they orient on the surface of particles and help their stabilization.

In addition, macromolecules of PVP and PVMA form complexes with aromatic compounds, containing SO_3 and COOH groups, for example, with anilinonaphtalene-8-sulfonate sodium [6].

We suppose that the appearance from the beginning of polymerization of the end SO_3 groups and the existence of benzene circles of polystyrene chains which are distributed on the surface of polymer–monomer particles favors the attraction of PVAm macromolecules to the surface of particles due to electrostatic and hydrophobic interaction. As a result, the surface of drops is covered with PVAm macromolecules which, in turn, are hydrated markedly with water molecules interacting with amide groups. In this case, the size of the particles and their stability during the polymerization process are defined not only with changing interphase tension but also by the strength of the interphase layer and the concentration of PVAm on the surface layer due to the approach of macromolecules to the surface of particles and forming of the complex with end groups. The difference in the rate of polymerization in the presence of PVAm is defined by the distinction in the size of the particles which are formed in their presence.

Table 1 Styrene polymerization rate, quantity of coagulum, size of particles and stability of polymer suspensions in the presence of PVAm of different structure (conditions of polymerization: volume ratio of monomer : water is 1 : 9; concentrations of potassiumpersulphate and PVAm are 1% wt to monomer, 70 °C)

Stabilizer	Rate of polymerization %/min	Average diameter of particles d, mkm	Coefficient of polydispersity D_w/D_n	Coagulum %	Stability in NaCl solution C_{NaCl}, M.***	Stability during storage 3 months
PVMA	0.28	0.350	1.010	0	0.3	stable
PVEA	0.28	0.350	1.035	0	0.3	stable
PVPA	0.16	0.650	1.014	0	0.3	stable
PVP	0.32	0.300	1.010	0	0.3	stable
PVA*	0.30	0.180	1.450	5	0.0	non stable
PVA**	0.65	0.175	1.430	2	0.0	non stable

*volume ratio of monomer: water is 1 : 6.

**volume ratio of monomer : water is 1 : 6, concentration is PVA is 2% wt to monomer.

***limiting salt concentration without aggregation in polystyrene suspension.

Large particles (0.65 mkm) appear in the presence of PVAm with *N*-propyl substitute, small particles (0.3 mkm) being formed in the presence of PVAm with *N*-methyl or *N*-ethyl substitute. That is why the rate of polymerization in the presence of the latter noticeably exceeds the rate observed in the presence of PVMA.

Thus, we can conclude that the use of PVAm of different structure makes possible the change of particle sizes of polymer suspensions.

The influence of the concentration and molecular weight of PMVA on the parameters of the heterophase styrene polymerization

The data concerning the influence of the PVMA concentration on polymerization rate, diameter of particles and molecular weight of polystyrene are represented in Table 4. It is seen that the change of the stabilizer concentration in water significantly affects all characteristics of the process. An increase of PVAm concentration (40 times) leads to a decrease of particle diameter by 4.2 times (from 0.84 to 0.2 mkm) with narrowing of the size distribution from 1.7 to 1.02 and increasing aggregative stability with salt influence.

Table 2 The value of interphase tension on boarder water//o-xylol in the presence of PVAm and PVA (limiting concentration of polymer is 4% wt to water)

Polymer	σ_{12} mN/m
PVMA	22.0
PVEA	23.0
PVPA	21.5
PVP	20.7
PVA	20.0

Table 3 Polystyrene particle sizes being stabilized by PVAm with monomer conversion (conditions of polymerization: volume ratio of monomer: water is 1: 9; concentrations of potassium persulphate and PVAm are 1% wt to monomer; 70 °C)

Stabilizer	Conversion of monomer %	Average diameter of particles, mkm
PVMA	10.0	0.30
	15.0	0.30
	50.0	0.30
	99.7	0.35
PVEA	10.0	0.25
	15.0	0.30
	50.0	0.30
	99.8	0.35
PVPA	10.0	0.50
	15.0	0.50
	50.0	0.65
	99.8	0.65

Molecular weight of PVMA from 26×10^3 to 565×10^3 practically does not affect the initial rate of polymerization of styrene, the size of particles on their size distribution (Table 5). It is significant that the increase of $\bar{M}_w$ of the polymer does not result in a growth of coagulum content in the reaction system. This important fact shows that the use of PVMA prevents the association of polystyrene particles because of the high hydrophilicity of these macromolecules. PVMA with $\bar{M}_w \approx 30 \times 10^3$ is the best stabilizer of heterophase styrene polymerization. Polymer suspension, being prepared in the presence of such PVMA, is characterised by the most narrow size distribution (polydispersity coefficient is 1.01).

The absence of the influence of $\bar{M}_w$ of stabilizer on the particles size is probably connected with the fact that separate fragments of a macromolecule are exposed to the particle surface. The chainlinks close to the surface of a droplet create a hydrophilic "coat" which interrupts coalescence of droplets.

An increase of initiator concentration leads to an increase in the rate of polymerization reaction (Table 6). The order of the reaction under the initiator is 0.5, indicating the square chain termination reaction. It is important to note that the size of particles and their distribution of size remain practically unchangeable at constant PVMA concentration with increasing concentration of initiator (15-fold). $\bar{M}_w$ of polystyrene goes down from 380×10^3 to 61×10^3.

Let us to suppose that physico–chemical factors affect the change of particle size for the heterophase styrene polymerization process in the presence of stabilizers. The emulsion of styrene consists of large drops with middle diameters of particles (10 mkm). Already at the start of particle formation (5 –10% of conversion) monomer–polymer particles are formed with lesser size (0.2 – 0.6 mkm) in

Table 4 Concentration effect of PVMA on styrene rate polymerization and characteristics of polystyrene suspensions (conditions of polymerization: volume ratio of monomer : water is 1 : 9; concentration of potassium persulphate is 1% wt to monomer; 70 °C)

Concentration of PVMA %wt to monomer	Rate of polymerization %/min	Average diameter of particles mkm	Coefficient of polydispersity $\bar{D}_w/\bar{D}_n$	Molecular weight of styrene M_η, $\times 10^{-3}$	Stability in NaCl solution C_{NaCl}, M
0.10	0.05	0.84	1.680	106.3	0.15
0.25	0.15	0.78	1.008	138.5	0.20
0.50	0.23	0.76	1.040	162.6	0.30
1.00	0.28	0.35	1.010	172.3	0.30
2.00	0.41	0.25	1.050	185.2	0.30
4.00	0.62	0.20	1.040	191.4	0.30

Table 5 Polymerization rate and characteristics of polystyrene suspensions in the presence of PVMA with different molecular weight (conditions of polymerization: volume ratio of monomer: water is 1:9; concentration of potassium persulphate is 1% wt to monomer; is 70 °C)

Molecular weight of PVMA $\bar{M}_w \times 10^{-3}$	Rate of polymerization %/min	Coagulum %	Average diameter of particles $\bar{d}$, mkm	Coefficient of polydispersity $\bar{D}_w/\bar{D}_n$	Molecular weight of polystyrene $\bar{M}_\eta \times 10^{-3}$	Stability in NaCl solution C_{NaCl}, M
26	0.33	0.0	0.35	1.01	172	0.3
36	0.31	0.9	0.35	1.01	178	0.3
60	0.32	2.0	0.30	1.02	185	0.3
81	0.33	1.1	0.30	1.05	180	0.3
100	0.36	1.8	0.30	1.05	182	0.3
565	0.32	1.6	0.33	1.20	175	0.3

Table 6 Styrene polymerization rate and characteristics of polystyrene suspensions at different concentrations of potassium persulphate (conditions of polymerization: volume ratio of monomer: water is 1:9, PVMA concentration is 1% wt to monomer; 70 °C)

Concentration of potassium persulphate % wt to monomer	Rate of polymerization, Vo %/min	Average diameter of particles $\bar{d}$, mkm	Coefficient of polydispersity $\bar{D}_w/\bar{D}_n$	Molecular weight of styrene $\bar{M}_\eta \times 10^{-3}$	Stability in NaCl solution C_{NaCl}, M
0.25	0.13	0.35	1.08	380.5	0.3
0.50	0.19	0.35	1.03	290.5	0.3
1.00	0.28	0.35	1.01	172.0	0.3
2.00	0.44	0.35	1.03	79.8	0.3
4.00	0.62	0.30	1.06	61.3	0.3

comparison with the size of drops of styrene emulsion (Table 4). The size of particles is defined both by the nature of stabilizers and their concentration (Tables 1 and 4). It is advantageous that size of these particles remains constant up to complete conversion of monomer, causing the narrow size distribution.

The transformation of a large particle into a small one can be understood on the basis of the following speculation. After interaction of a persulfate radical with a styrene molecule on the surface of large drops, the propagation chain reaction starts. We assume that the large constant of the propagating reaction rate (145 l/mol s), the great heat of polymerization (18 kcal/mol) and the low heat conductivity of styrene (0.3×10^{-3} cal/cm s degree) create the conditions for local superheating close to the drop surface. This results in a heat explosion process with expulsion of small droplets. It is evident that the process of such explosive formation of droplets depends on the presence of polymer stabilizers, for example, PVMA interacting with end sulfo groups of polystyrene macromolecules followed by a change of interphase tension on the boundary water/styrene.

The size of particles is defined by the concentration of stabilizer in water, as is found (Table 5). At small concentration of stabilizer ($< 1\%$ wt to monomer), when the surface of the emulsion drops is only partially covered with macromolecules of stabilizer, particles with diameters 0.7–0.8 mkm are formed. The wide size distribution of particles is evidently connected with coalescence of particles. At large concentration of stabilizer emulsion drops reduce to smaller droplets (0.2–0.35 mkm diameters) and their size distribution is narrow.

Thus, water soluble poly-*N*-vinylamides can be used as stabilizers of heterophase polymerization of styrene. With changing the structure of PVAm and their concentration, the rate of polymerization, size of particles, and their size distribution can be regulated.

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