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## KINETICS OF PARTICLE FORMATION IN THE GRAFT POLYMERIZATION OF ACRYLIC MONOMERS ONTO POLYSACCHARIDES

### Summary

The kinetics of polymer particle formation and distribution of acrylic monomers between a solution and polymer particles at the graft polymerization of acrylic monomers onto polysaccharides have been investigated. The polyacrylic particle number increased at the first stage of polymerization of soluble monomers. At the second stage of polymerization, the number of particles was always constant. The concentration of adsorbed monomer decreased during the polymerization process. The monomer concentration in dispersed phase was higher than in solution.

The mathematical model taking into account the rate of monomer polymerization, aggregation of oligomer radicals and their conformation changes, adsorption of monomer in the polymer particles has been proposed. Based on the experimental results, some constants of the process were calculated.

### Introduction

At the graft polymerization of acrylic esters onto water soluble polysaccharides, the stable core-shell polymer dispersions are formed [1-3]. The stability of dispersions is associated with the amphiphility of the graft copolymers, where the nucleus of the polymer particle is formed by polyacrylic chains and its shell is formed by the soluble polysaccharide chains bound chemically to the nucleus. The degree of adsorption saturation of such particles, determined by adsorption titration with sodium oleate is about 70–90%. The grafting degree with respect to acrylic polymer increases from 30 to 100% when the initial concentration of monomer in the reaction mixture decreases. On the other hand, the part of polysaccharide chemically bound with polyacrylate decreases in this case.

Investigation of the kinetics of polymerization of acrylic monomers onto water soluble polysaccharides showed [4, 5] that the first stage of the process is the reaction between the initiator radical with polysaccharide macromolecule and initiation of the graft polymerization. In this stage, the efficiency of the grafting reaches 100%. The homopolymer of acrylic monomers is formed in the second stage of polymerization, when the polymer particles have been formed. The efficiency of grafting decreases till to minimum.

## Materials and methods

The acrylic monomers, methyl acrylate, methyl methacrylate and butyl acrylate were purified by rectification. Ammonium peroxydisulfate, used as initiator of the polymerization, was recrystallized twice from water. Carboxymethyl cellulose was purified by precipitation with hydrochloric acid from water solution. Industrial water soluble potato starch was used without purification.

The average particle radius was determined by the nephelometric method and calculated by the Shifrin-Slonim equation [6].

The monomer concentration was determined by the bromide-bromate method. The monomer concentration in solution was determined after centrifugation of dispersed phase. The concentration of monomer, adsorbed in the polymer particles was calculated according to equation:

$$c_a = c_t - c \quad (1)$$

where  $c_t$  was the total concentration of monomer and  $c$  was the concentration of monomer in solution after centrifugation.

The molecular mass of polyacrylate chains, extracted by toluene from the graft copolymer, was determined by the viscosimetric method [7].

## Results and discussion

Investigation of the particle size during the monomer polymerization at the initial concentration of monomer 18–70 g/l showed that the radius of polymer particles was practically constant for methyl acrylate (Fig. 1) and butyl acrylate. An increase in the initial monomer concentration in the reaction mixture led to an increase in the radius of polymer particles at the constant concentration of polysaccharide. The particle radii increased slightly with decrease in the initial polysaccharide concentration.

The monomer concentration in solution was practically constant during polymerization for butyl acrylate graft polymerization onto starch. In this case, on polymerization monomer formed mostly monomer droplets or monomer - polymer particles. At the same time, methyl acrylate was practically soluble in water within the concentra-

tion region investigated. In course of polymerization the concentration of methyl acrylate in solution as well as the concentration of adsorbed monomer decreased (Fig. 2).

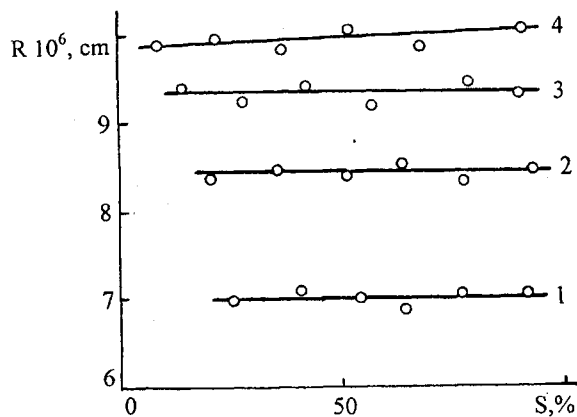


Fig. 1. Relationship between average radius of polymer particles and monomer conversion in the graft polymerization of methylacrylate onto starch at the initial monomer concentration of 18 (1), 37 (2), 54 (3) and 72 g/l (4).

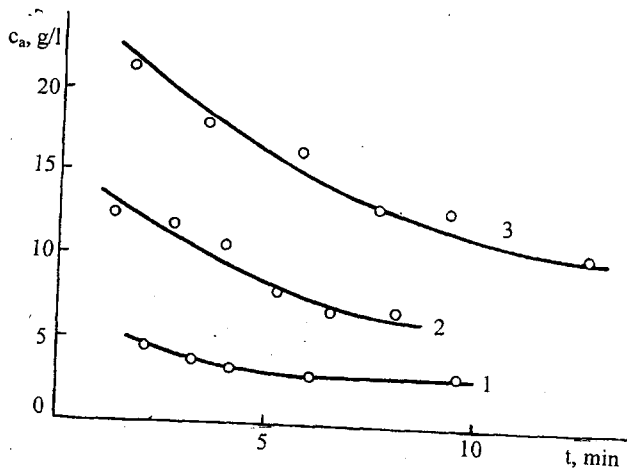


Fig. 2. Plot of the adsorbed monomer concentration vs time at the graft polymerization of methylacrylate onto carboxymethyl cellulose at the initial monomer concentration of 40 (1), 61 (2) and 82 g/l (3).

The change of the total concentration of monomer in the reaction mixture proceeded according to first order kinetics with respect to the monomer:

$$d[M]_t/dt = -k_e[M]_t \quad (2)$$

where  $k_e$  was the effective rate constant of polymerization.

For methyl acrylate, methyl methacrylate and butyl acrylate the molecular mass of polyacrylic chains of graft copolymer increased with the initial concentration of monomer in the reaction mixture. The linear relationship between the volume of polymer particles and molecular mass is showed in Fig. 3. Evidently, it was associated with an increase in the monomer concentration in the monomer - polymer particles. The monomer content in the unit volume of disperse phase rose with increase in the initial monomer concentration in the reaction mixture (Fig. 4). It was higher than the monomer concentration in the solution during the methyl acrylate polymerization. Evidently, the large oligomer radicals adsorbed the monomer from water solution. A high monomer concentration around the oligomer radical its solubility in water - monomer mixture increased and the flexibility of polyacrylic chains also increased.

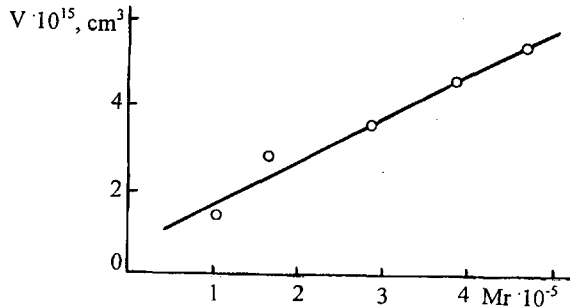


Fig. 3. Relationship between particle volume and molecular mass of polymethylacrylate at the graft polymerization of methylacrylate onto carboxymethyl cellulose.

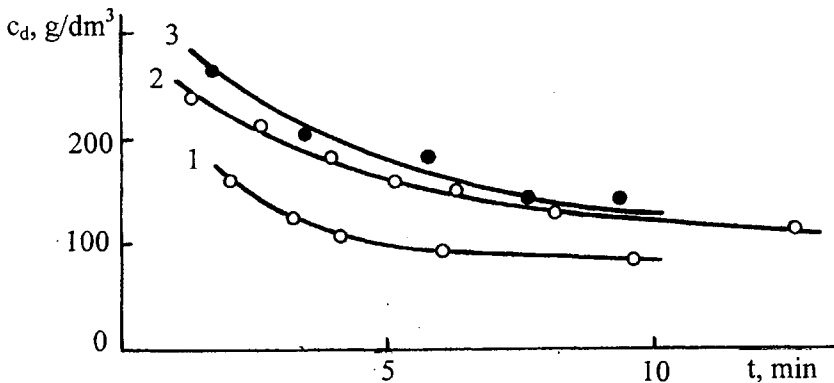


Fig. 4. Plot of the mass of monomer adsorbed in the unit volume of dispersed phase vs time for the graft polymerization of methylacrylate onto carboxymethyl cellulose at the initial monomer concentration of 40 (1), 61 (2) and 82 g/l (3).

The number of polymer particles in the unit volume of dispersion increased at the initial stage of methyl acrylate polymerization (Fig. 5), reaching maximum in 10 min. and then it remained practically constant. Therefore, the particle aggregation did not proceed until the high monomer conversion was achieved. For all monomers the number of particles in the unit volume of the reaction mixture increased with the initial monomer concentration.

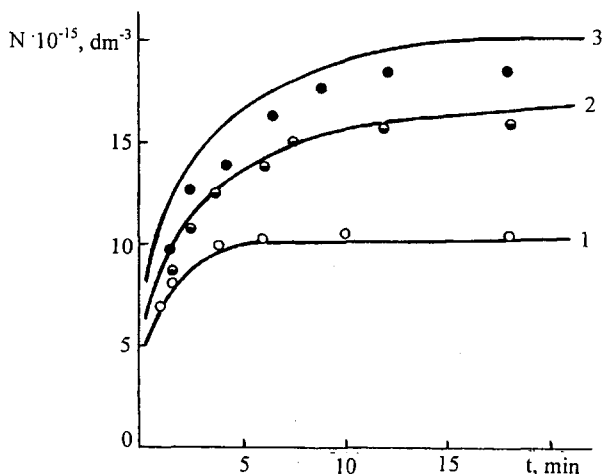


Fig. 5. Plot of the particle number in unit volume of dispersion vs time for the graft polymerization of methylacrylate onto starch at the initial monomer concentration of 40 (1), 61 (2) and 82 g/l (3). Curves are calculated according to Eq. (6).

Experimental data showed that the graft polymerization of monomers low soluble in water proceeded within monomer droplets. The initiation of polymerization passed through the stage of adsorption of polysaccharide radical on the surface of monomer droplets. The efficiency of polymerization initiation was very low. Initiation of polymerization of water soluble monomers proceeded in the aqueous solution. In this case, the dispersed primary particle consisted of polyacrylic chains, a monomer and water in the initial stage of polymerization. The monomer content in the dispersed phase was below 30%, and the content of polyacrylate in it did not exceed 20% at the initial stage of the process. Then the monomer diffused into the polymer particles from the reaction medium and water diffused from the particles. The polymerization process proceeded generally in particles in the second stage of polymerization.

The rate of a change of a polymer particle number in the unit volume of dispersion as a function of monomer and initiator concentration could be described by equation:

$$dN/dt = k_{ad}N_A N \left\{ F_1/2 - [F_1^2/4 + 2k_dfk_i[S_2O_8^{2-}][M]/k_{ag}]^{1/2} \right\} + 2k_dfk_iN_A[M][S_2O_8^{2-}] \quad (3)$$

where  $k_d$ ,  $f$ ,  $k_i$ , and  $[M]$  were the rate constant of initiator decomposition, the initiation efficiency, the rate constant of initiation of polymerization, and  $[M]$  is the monomer concentration in water phase, respectively,  $k_{ad}$ ,  $N$ ,  $k_{ag}$  and  $k_f$  were the rate constant of oligomer radical adsorption onto polymer particles, the particle number in unit volume of dispersion the rate constant of oligomer radical aggregation leading to the particle formation, and the rate constant of a conformation changes of oligomer radical that leads to particle formation, respectively.  $F_1 = k_f/k_{ag} + k_{ad}N/k_{ag}$

The rate of a change of the concentration of monomer, adsorbed in polymer particles, could be expressed by equation:

$$d[M_a]/dt = k_c V[M] dN/dt + k_{di} S N [M] ([M_s] - [M_a]) - k_n [M_a] \quad (4)$$

where  $k_c$ ,  $k_{di}$ ,  $S$ , and  $[M_s]$  were the coefficient, the rate constant of diffusion, the surface area of one particle, and the monomer concentration when the particle is total saturated with monomer, respectively,  $[M_a]$  and  $k_n$  were the concentration of the adsorbed monomer and the rate constant of polymerization, respectively.

Under condition of  $c = [M]Mr$  and  $F_3 = 2k_d f k_i N [M] [S_2O_8^{2-}] / k_e \gg dN/d[M]$ , one can obtain Eq. (5) From Eqs.(2) and (3):

$$N dN/dc = -k_f F_3 / (k_{ad} Mr) - k_{ag} k_e F_3^2 / (Mr^2 k_{ad}^2 N_A) c / N \quad (5)$$

As it is shown in Fig. 6, experimental data on the kinetics of particle formation at the methyl acrylate graft polymerization follow a linearity according to Eq.(5). Correlation coefficient was 0.971. From the intercept on the axis of ordinate,  $k_f F_3 / (k_{ad} Mr) = (7 \pm 2) \cdot 10^{29} \text{ l}^{-1} \text{ g}^{-1}$ , and from the tangent of the slope angle of straight line,  $k_{ag} k_e F_3^2 / (k_{ad}^2 N_A Mr^2) = (7.7 \pm 0.6) \cdot 10^{44} \text{ l}^{-1} \text{ g}^{-2}$ .

Obtained ratios of rate constants provided the number of polymer particles in the unit volume of dispersion during polymerization according to the Eq. (6).

$$N = \left\{ 3 \int_0^{\infty} [k_{ag} k_e^2 F_3^2 / (Mr^3 k_{ad}^2 N_A) c_0^2 \exp(-2k_e t) + k_f k_e F_3 / (Mr^2 k_{ad}) N c_0 \exp(-k_e t)] dt \right\}^{1/3} \quad (6)$$

where  $c = c_0 \exp(-k_e t)$ .

Fig. 6 shows that calculated curves properly describe the experimental data.

The rate of a change of the concentration of adsorbed monomer was described by Eq.(4). Eq.(4), if  $k_n = k_e$ , can be transformed into equation:

$$Y = k_d c_s / k_e + k_c X \quad (7)$$

where  $Y = c_a / (c_s F_4)$ ,  $X = VN / (SF_4)$ ,  $F_4 = \int_{c_0}^0 (N/c dc)$ ,  $c_s = [M_s]Mr$ .

$F_4$  was calculated by means of numerical integration taking into account the rate constant ratios found above and

$$S = 4\pi R^2 \text{ and } V = 4/3 \pi R^3 \quad (8)$$

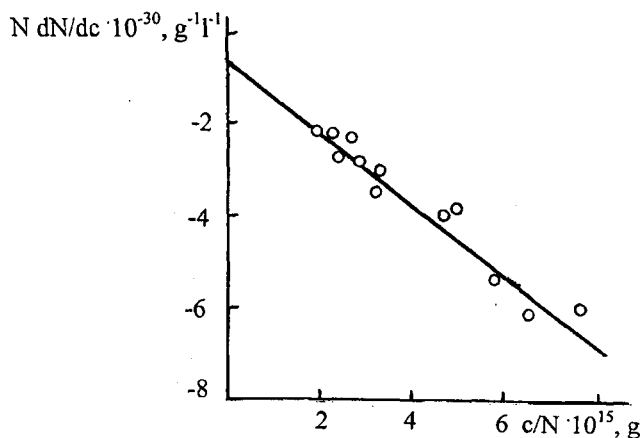


Fig. 6. Relationship between particle number in unit volume of dispersion and monomer concentration in solution when plotted according to Eq. (5) for the graft polymerization of methylacrylate.

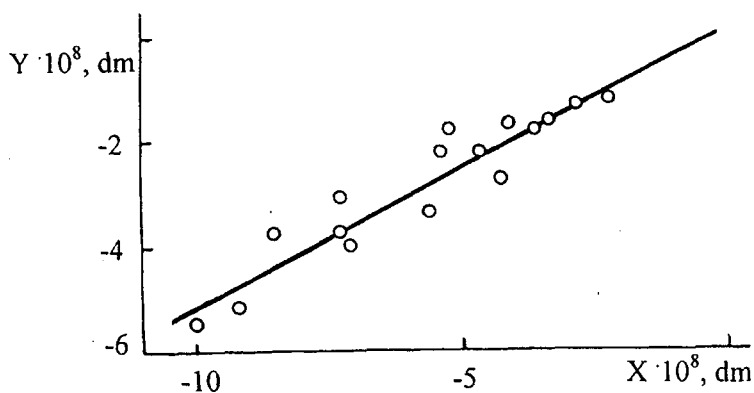


Fig. 7. Relationship between the concentration of adsorbed monomer and the monomer concentration in solution when plotted according to Eq. (7) for the graft polymerization of methylacrylate.

As showed in Fig. 7, experimental data of a change of adsorbed monomer concentration followed the straight line according to Eq. (7) with the correlation coefficient of 0.937. The intercept on the axis of ordinate was close to zero. Thus, the value of  $k_{d,c_s}$  was below of experimental error. From the tangent of the slope of straight line,  $k_c = (5.2 \pm 0.5) \cdot 10^{-3}$ .

Therefore, monomer adsorption proceeded as the process of particle formation at low initial monomer concentration in the reaction mixture. Monomer concentration in particle was higher than in water phase for water soluble monomers.

## References

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### KINETYKA TWORZENIA CZĄSTECZEK W SZCZEPIONEJ POLIMERYZACJI MONOMERÓW AKRYLOWYCH Z POLISACHARYDAMI

#### Streszczenie

Badano kinetykę tworzenia polimerycznych cząsteczek i rozdział monomerów akrylowych pomiędzy roztwór i cząsteczki polimeru w trakcie szczepionej polimeryzacji monomerów akrylowych ze skrobią. Liczba cząsteczek poliakrylowych wzrastała w pierwszym etapie polimeryzacji rozpuszczanych monomerów. W drugim etapie polimeryzacji liczba tych cząsteczek utrzymywała się na stałym poziomie. Stężenie adsorbowanego monomeru malało w trakcie polimeryzacji. Stężenie monomeru w fazie zdyspergowanej było wyższe niż w roztworze.

Zaproponowano matematyczny model uwzględniający szybkość polimeryzacji agregację rodników oligomerowych i ich zmiany konformacyjne oraz adsorpcję monomeru w cząsteczkach polimerów. W oparciu o wyniki doświadczeń obliczono niektóre stałe procesu. ❖