

Bentonite, stabilizer for suspension polymerisation

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Abstract: In suspension polymerizations, stabilizers play a crucial role in the particle formation. An effective stabilizer must be able to maintain complete coverage of the surface by both physical and/or anchoring adsorption. In this work the possibility of using original bentonite and bentonite with a high percentage of montmorillonite, their acid-activated and monocationic forms as mixed stabilizer has been investigated. Styrene was used as the monomer. Beads of polystyrene with spherical or elliptical shape were obtained, depending on form of the used bentonite. The results are discussed in terms of the acidity of the mineral surface, amphiphilic characteristic of the clay and the change of the contact angle between organic / water / mineral phase.

Keywords: bentonite, stabilization, polymerization, surface pressure, acidic surface.

INTRODUCTION

Suspension polymerization of styrene is a widely employed method for producing commercial polystyrene resins (GPPS, EPS, HIPS). Particle size, particle size distribution, particle morphology, molecular masses and molecular mass distribution affect the processing and application characteristics of the polymer.

Suspension polymerization is a free radical process developed for producing polymer as beaded particles. In this process,¹ monomers, containing dissolved initiator, are dispersed, by stirring, as droplets in the continuous phase (water for most monomers) with a dissolved suspension stabilizer and then polymerized. The average size of the beads and the breadth of the size distribution, the particle morphology, molecular mass and molecular mass distribution depend on the size and design of the polymerization equipment (reactor, stirring), and on the chemical properties of the polymerizing system; especially on the type of the suspension stabilizer which hinders coalescence of the monomer droplets and adhesion of the forming beads.^{2,3}

The stabilizer plays a crucial role in the particle formation. An effective stabilizer must be able to maintain complete coverage of the surface by both physical and/or anchoring adsorption.⁴ Three main types of stabilizers are used in suspension polymerization:

- Water soluble organic polymers: natural polymers and synthetic polymers.
- Insoluble finely divided inorganic powders: Mg, Ca, Al salts and clays.
- Mixed stabilizers: organic polymers with inorganic powder or inorganic powders with surfactants.

For the production of PS resins, the most important industrially used stabilizers are gelatin; methyl cellulose; polyacrylic acids and their salts; starch; poly(vinyl alcohol); poly(vinyl pyrrolidone); sulfonated polystyrene; ZnO; alkaline earth phosphates; carbonates and/or silicates (clays).³ Although a number of inorganic powders are used as stabilizers, very limited data can be found for layer compounds of bentonite clays.

In this work the possibility of using bentonite from Ginovci, Republic of Macedonia as a mixed stabilizer for the suspension polymerization of styrene together with methyl cellulose was investigated. Bentonite is a sheet like clay, the main part of which is the mineral montmorillonite, a smectic type of silicate. There are two silicon-oxygen tetrahedral lattices with an aluminium hydroxide octahedral lattice between them in the crystalline structure of montmorillonite. There is a possibility for an exchange reaction between Si^{4+} with Al^{3+} in the tetrahedral lattice and for the substitution of Al^{3+} with Mg^{2+} , Fe^{2+} , and Fe^{3+} , *etc.* in the octahedral position. The negative charge, which appears during these non-stoichiometric exchanges, is compensated for by exchangeable interlayer cations. The important characteristic of montmorillonite, its acidic surface, is mostly due to dissociation of water molecules bound by the interlayer cations.⁵⁻⁹

EXPERIMENTAL

Materials

Styrene (S) and benzoyl peroxide (BP), p.a., commercial products of Merck, were used as received.

Sodium carboxyl methyl cellulose (NaCMe) was a commercial product of M. Blagojević-Lučani, Serbia and Montenegro.

Natural bentonite from Ginovci, Macedonia (B) had the following chemical composition: SiO_2 60.82 %, Al_2O_3 21.32 %, Fe_2O_3 3.21 %, MgO 4.11 %, CaO 2.03 %, Na_2O 0.40 %, K_2O 0.40 %, $\text{H}_2\text{O} + \text{CO}_2$ 8.06 %. The montmorillonite content of the bentonite is approx. 85 % and has a monoclinic structure. Ca^{2+} and Mg^{2+} are the most abundant natural interlayer cations.⁸

The fraction less than 2 μm (M) was obtained from the natural bentonite after removing part of the non-clay minerals, by the method of Vasilev and Goncaruk.⁶

Acid-activated bentonites were products of the acid activation of the natural bentonite with 10 and 15 % of HCl and H_2SO_4 (labelled as B-10Cl, B-15Cl, B-10S, B-15S, respectively).¹⁰ Homoionic bentonites were obtained by ion exchange reaction of the natural cations with Co^{2+} , Ni^{2+} , Cu^{2+} , Fe^{3+} , Al^{3+} cations, by treating the natural bentonite and the fraction under 2 μm with the chlorides of the corresponding cations at a concentration of 1 geq/dm^3 (B- Co^{2+} , B- Ni^{2+} , B- Cu^{2+} , B- Fe^{3+} , B- Al^{3+} and M- Co^{2+} , M- Ni^{2+} , M- Cu^{2+} , M- Fe^{3+} , M- Al^{3+}).¹¹

Methods

As a criterion of the surface characteristic (the ratio hydrophilic/hydrophobic), the surface pressure of the adsorbed film (π) was calculated from the water vapor adsorption isotherm, discussed in a previous paper.⁵

The acidic characteristics of the surfaces were determined by potentiometric titration of a 0.5 % water suspension with 0.1 mol/dm^3 NaOH, until pH 9 was attained.⁷

The polymerization of styrene was carried out in a three-necked round glass flask of 500 cm^3 , equipped with a stirrer, condenser and funnel. The polymerization reactions were performed by the conventional, labo-

ratory method. The operating parameters for the synthesis and the ratio of components were kept constants except the mass % of bentonite and NaCMe, which are given in Table I. The obtained pearls were washed several times and then dried. The stabilizer (bentonite) was separated from the liquid phase by filtration.

TABLE I. Mass part of components

Components	Synthesis		
	I	II	III
Styrene	100	100	100
Water	500	500	500
B.P.	1.4	1.4	1.4
NaCMe	0.1	0.1	0.1
Bentonite	10	5	2.5

Operating parameters: $t = 94\text{ }^{\circ}\text{C}$; $\tau = 5\text{ h}$; $\text{rpm} = 500\text{ min}^{-1}$

Analysis

The samples of PS produced under various experimental conditions were analyzed by the sieve analysis method and optical microscopy. The molecular weight of the polymers was determined by gel permeation chromatography (GPC) and viscometry. Toluene was used as the solvent for the viscosity measurements at 25 $^{\circ}\text{C}$. The GPC chromatograms were taken using a Perkin-Elmer instrument (UV-detector) in tetrahydrofuran. The elution rate at 25 $^{\circ}\text{C}$ was 1.2 cm^3/min . A BIO PSKGMHG-styragel column was used. The GPC was calibrated using polystyrene samples.

RESULTS AND DISCUSSION

Polymerization of styrene was carried out in accordance to the standard laboratory procedure. All the variables were constant except for the form of the bentonite and the ratio bentonite/ NaCMe. Polystyrene beads were obtained with homoionic bentonite B (B-Cu²⁺, B-Fe³⁺, B-Al³⁺), homoionic bentonite M (M-Cu²⁺, M-Fe³⁺, M-Al³⁺) and acidoactivated bentonite (B-10Cl, B-15Cl, B-10S, B-15S). There was no stabilizing effect when the natural materials B, M and the monionic bentonites (B-Co²⁺, B-Ni²⁺) were used.

The different stabilization behavior of the different forms of bentonite can be explained by the change in the acidic characteristic of the bentonite surface and by the different contact angle in the three-phased system: water-monomer-bentonite, due to the exchangeable cations.

The acidic characteristic of the bentonite surfaces was found by potentiometric titration of a clay suspension according to Russu.⁷ Some of the titration curves and their differential forms are presented in Fig. 1. The differential titration curves of the examined bentonites have different shapes. Bentonites such as B, M, B-Co²⁺, B-Ni²⁺ are characterized by one dissociation constant and the other forms of bentonite have polybasic acidic character. These characteristics are in accordance with the results for sheet layer silicates.^{6,7,13} The first minimum of the titration curves is the titration of the H⁺ ions from the Brønsted acidic center, according to the reaction:



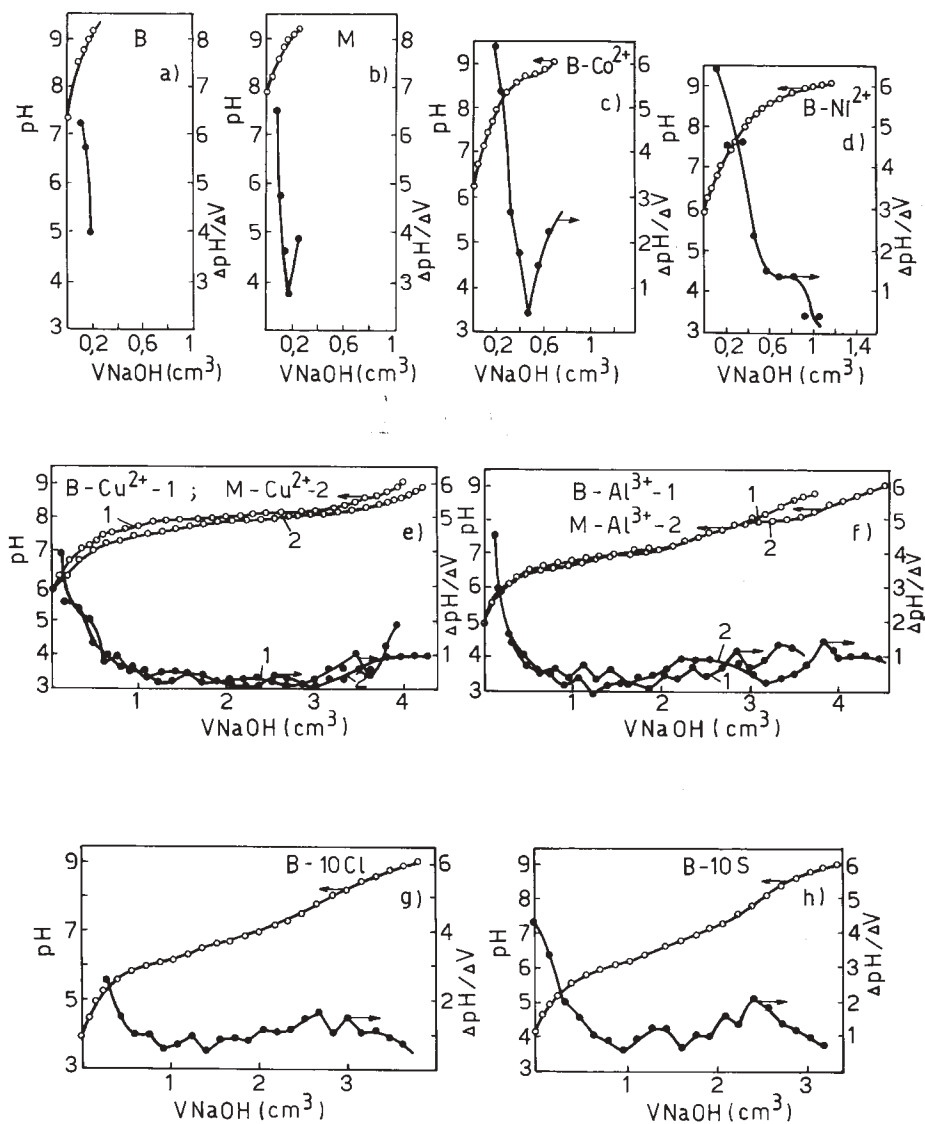
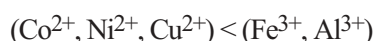


Fig. 1. Titration curves of different bentonites. a) B; b) M; c) B-Co²⁺; d) B-Ni²⁺; e) B-Cu²⁺, M-Cu²⁺; f) B-Al³⁺, M-Al³⁺; g) B-10Cl; h) B-10S.

The radii, charge and nature of the exchangeable cations (Me) influence the strength of the Brønsted centers. The second and third maximum on the differential curves are due to the titration of partly protonized H⁺ from the Si-OH groups and to the water held by the aluminium atoms of the side chain of the sheets.

Bentonite B, bentonite M, B-Co²⁺, B-Ni²⁺ reach the end point (pH 9) after the addition of a very small volume of NaOH, while the bentonites B-Cu²⁺, B-Fe³⁺, B-Al³⁺, M-Cu²⁺, M-Fe³⁺, M-Al³⁺ and acidoactivated B-10Cl, B-10S consumed more NaOH. Ac-

cordingly, the bentonites can be divided into two main groups, Table II. This confirms the more pronounced acidic character of the surfaces of the group 2 bentonites, compared to those of group one. The different acidity of the surfaces of the bentonites is due to the different proton donating ability of the exchangeable cations, present in the inter-layer space of the bentonite. Literature data⁹ on the influence of cations on the acidic characteristic gives:



which corresponds to the results given in Table II.

TABLE II. Volume of NaOH consumed during the titration of a 0.5 % bentonite water suspension

Group	Bentonite sample	$V_{\text{NaOH}} / \text{cm}^3$
I	B	0.17
	M	0.17
	B-Co ²⁺	0.70
	B-Ni ²⁺	1.00
II	B-10S	3.30
	B-15S	1.90
	B-10Cl	3.70
	B-15Cl	1.80
	B-Cu ²⁺	4.00
	B-Al ³⁺	4.50
	B-Fe ³⁺	5.00

The second difference which causes the bentonite to act in a different way during a suspension polymerization is the value of the contact angle. Monomer and water wet the solid phase, bentonite, as illustrated in Fig. 2. Complete wetting occurs when the contact angle $\alpha = 0^\circ$ (hydrophilic) or $\alpha = 180^\circ$ (hydrophobic). If the contact angle lies between these two values, the solid phase has amphiphilic characteristics, which is typical for clay minerals. It has been suggested that inorganic powders are effective stabilizers for suspension polymerization if the contact angle $\alpha > 50^\circ$ (such as NiO, CaCO₃, CaO, Al₂O₃ and Al(OH)₃); when the angle is less than 50°, the droplet stability is reduced and the dispersion breaks.³ With the entrance of cations of different sizes and charges into the interlayer space, the hydrophilic characteristic and the ratio hydrophilic/hydrophobic is changed. It is well-known that hydrophobic organic substances show no or a little affinity towards the hydrophilic surfaces of minerals in the presence of water.¹⁵

Most of the hydrophilic centers placed on the side chain of the mineral are obtained by termination of tetrahedral or octahedral sheets. Their surface is more hydrophilic in comparison with the basal side, a tetrahedral sheet based on oxygen triads. The electrostatic fields of the hydrophobic properties of clays are due to the Si—O—Si groups, while the aluminium side provides a surface of hydroxyl groups.¹² It is possible by isomorphic substitu-

SYSTEM water - monomer - bentonite

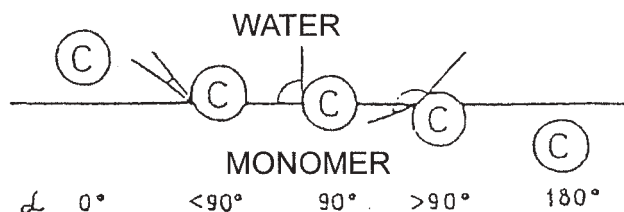


Fig. 2. Contact angles between the solid surface (C) and the interface water-monomer.

tions to develop a net negative charge on the triple layer, compensated by interlayer cations. In such a way the clay particles have a structure like a micelle of hydrophobic salt.

The change of the contact angle can be discussed in terms of the change of the surface free energy of the particles, ΔF . The bigger the surface free energy of particles, the bigger the surface wetted by water is. The surface free energy can be expressed as follows:

$$-\Delta F = \pi = -\frac{RT}{S} \int_0^p a d \ln p$$

where: a – quantity of adsorbate per unit mass of adsorbent, S – specific surface, p – water vapor pressure, R – universal gas constant, T – temperature, K.

The change of the surface free energy is equal to the surface pressure of the adsorbed film π . The value of π can be calculated from adsorption isotherms, discussed in a previous paper.⁷ This can be observed as a relative measure of the contact angle for the bentonites, presented in Table III. The criterion value of surface pressure is assumed to be 45 mN/m. Bentonites belonging to the first group with a surface pressure $\pi \leq 45$ mN/m have a hydrophilic/hydrophobic ratio suitable to enable them to act as stabilizer, the other with $\pi \geq 45$ mN/m are not suitable. Tarasevic has reported a value of $\pi_{\text{fob}} < 70$ mN/m $< \pi_{\text{fil}}$ for caolinite and talc.¹²

TABLE III. Surface pressure of the adsorbed films (π)

Group	Bentonite sample	$\pi/\text{mN m}^{-1}$
I	B	50.5
	B-Cu ²⁺	50.7
	B-Co ²⁺	49.0
	B-Ni ²⁺	47.7
II	B-10S	43.3
	B-10Cl	42.7
	B-Al ³⁺	34.2
	B-Fe ³⁺	32.5

If the hydrophilic properties are more expressed, then their surfaces are much more easily soaked by water compared to the organic phase. In such cases the adhesion of the benton-

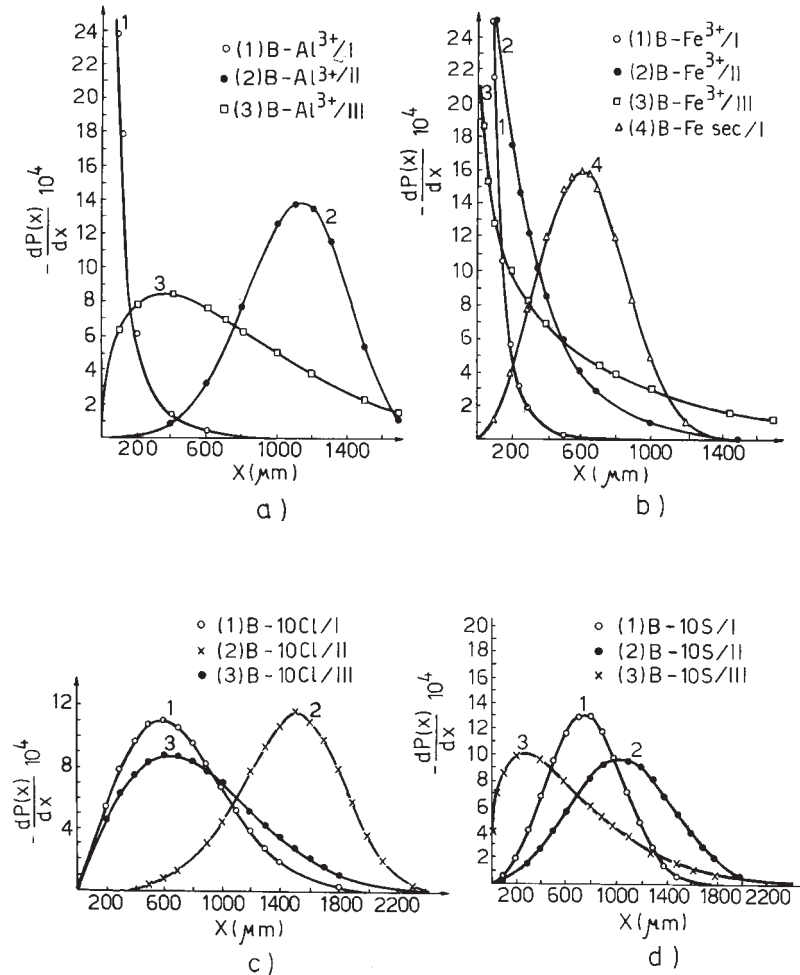


Fig. 3. Particle size distribution curves. a) B-Al³⁺; b) B-Fe³⁺; c) B-10Cl; d) B-10S.

ite around the styrene droplets lowers, and the resulting effect is the linkage of the dispersed organic phase into a unique mass. The bentonites which are characterized with a surface pressure of the adsorbed film of the interface bentonite-water $\pi < 45$ mN/m are useful as stabilizers. An exception is bentonite B-Cu²⁺ with a surface pressure of 50.7 mN/m that can be used as a stabilizer, but according to the adsorption characteristics belongs to the other group (Table II).⁹ It can be supposed that the stabilizer forms a film with a molecular dimension around the droplets of the monomer and in that way prevents their adhesion.

The results obtained from the sieve screen analysis are presented in the differential form using the Rosin-Rammler equation. The shape and width of the differential distribution curve depend on the used stabilizer and its concentration. The average particle size lies in the range of 0.063–1.6 mm. As an illustration, some of the size distribution curves are presented in Fig. 3. Particles with the smallest size and narrowest distribution were ob-

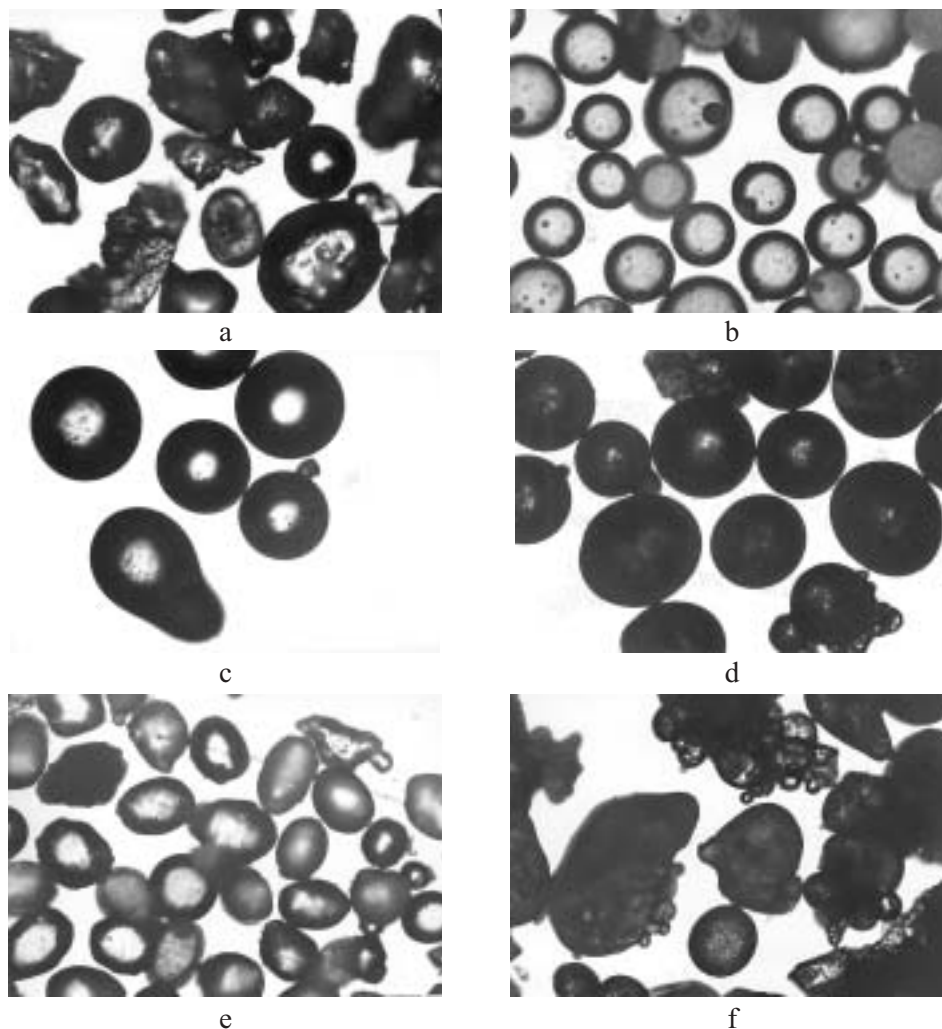


Fig. 4. Microscopic pictures of PS beads obtained with different bentonites. a) B-Cu²⁺/I; b) B-Al³⁺/I; c) B-10Cl/I; d) B-10S/I; e) B-Fe³⁺/I; f) B-Fe³⁺/I (sec).

tained by using B-Al³⁺, B-Fe³⁺ and acidoactivated bentonite, according to the conditions of syntheses I and III. During the synthesis II, beads with the biggest size were formed, regardless of the used stabilizers, probably as a result of the unfavourable ratio of the activated bentonite/NaCMe.

The optical microscopic pictures presented in Fig. 4 show a difference in the shape of particles, depending on the used stabilizer and the ratio of the activated bentonite/NaCMe. Particles having a spherical shape and well defined border were formed using B-Al³⁺ and acidoactivated bentonites according to syntheses I. Elliptical beads are obtained using B-Fe³⁺, while in the presence of B-Cu²⁺ the pearls have an irregular shape, some of them are sticky and agglomerated.

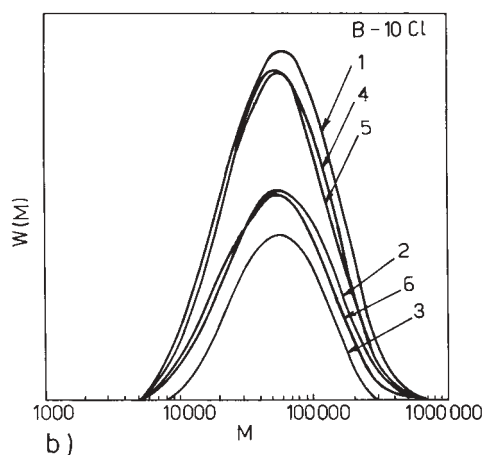
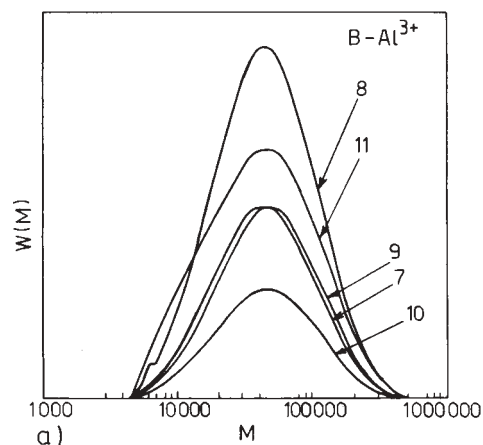


Fig. 5. MWD curves of PS fractions from sieve analyses. a) B-Al³⁺; b) B-10Cl.

The multiple use of activated bentonite as a stabilizer was investigated with the B-Fe³⁺ form of bentonite, separated from synthesis I, by adding a new portion of NaCMe. Although a dispersed product was obtained, optical microscopy shows agglomerates of irregular size, (B-Fe³⁺ sec), Fig. 4, f.

The average molecular masses measured by viscosimetric ($[\eta] = 1.7 \times 10^{-4} Mv^{0.69}$)¹⁶ and GPC methods, are in good agreement. The molecular mass distributions, Fig. 5, are similar. They have the same values of the lowest and highest molecular masses. The exception is curve 8 with a narrower distribution, but with the same value for the average molecular mass. All the curves are unimodal, which excluded the presence of polystyrene emulsions in the product, which was confirmed as well by optical microscopy.

CONCLUSIONS

The suspension polymerization of styrene can be carried out in the presence of acid-activated, Fe³⁺, Al³⁺ and Cu²⁺ monocationic bentonites. The change of ratio hydro-

phobic/hydrophilic depends on the charge and radius of the exchangeable cation, as a result of which a change in the acidity of the bentonite surface occurs. According to these two factors, a separation of bentonites into two main groups can be made. Bentonites that can be used as stabilizers for the suspension polymerization of styrene are characterized by a surface pressure of the absorbed film of the interface bentonite-water of less than 45 mN/m, and the consumption of more than 1.8 cm³ of a solution of NaOH during potentiometric titration. The second group consists of the bentonites with $\pi > 45$ mN/m and a consumption of less than 1 cm³ of NaOH solution. The potentiometric titration can serve as a primary and very simple method for the characterization of a bentonite.

ИЗВОД

БЕНТОНИТ, СТАБИЛИЗАТОР СУСПЕНЗИОНЕ ПОЛИМЕРИЗАЦИЈЕ

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Стабилизатори имају пресудну улогу при формирању честица код суспензионе полимеризације. Погодан стабилизатор треба да обезбеди комплетну покривеност површине адсорбованим молекулима. У овом раду испитивана је могућност примене природног бентонита, бентонита са високим садржајем монторијонита, као и њихових киселоактивнираних и монокатјонских облика. Сви наведени облици бентонита испитивани су заједно са Na-карбоксиметил-целулозом, у виду мешаних стабилизатора. Стирен је примењен као мономер, за праћење реакције полимеризације. У зависности од вида коришћеног бентонита, добивене су сферичне или елиптичне перле полистирена. Резултати су дискутовани у односу на киселост површине минерала, амфибилне карактеристике глине као и у односу на промене контактне угла између органске /водене/ чврсте фазе.

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