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Colloidal Systems on the Basis of Novel Reactive Surfmers

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Summary: New anion surfmers of the family of maleic acid asymmetrical esters have been synthesized. Some of its features in the process of emulsion copolymerization with styrene have been studied. The characteristics of covering, obtained on the basis of such latexes of new generation have been investigated as well.

Keywords: emulsion polymerization; latexes; macromonomers; monomers; surface-active substances

Introduction

The problem of latex obtaining with strong stability is important scientific and practical task. Such latexes are useful as polymer carrier for immunodiagnostic obtaining,[1] polymer coverings[2,3] etc. Thus, finding of new methods of regulation of polymer structure as well as morphology and stability of functional particles is very actual assignment. At present there are a lot of research works, in which the authors offer to use reactive surface-active substances for obtaininging latexes with increased stability: initiators (inipars),[4,5] monomers (surfmers).[6–9] The use of such surfmers in the processes of emulsion or dispersion polymerization provide getting polymer colloidal systems with strong aggregative and sedimentation stability.[10–14] It is known, that surface-active derivatives of maleic acid have a set of advantages in comparison with other surfmers. Among other they are not practically able for homopolymerization, that means that they don't create water-soluble polymers (polysoaps) in water phase, but they are able to copolymerize with other monomers.[10] But not enough works are concerned with the study of maleinate surfmers.

The main goal of our work was the synthesis of anion surface-active monomers of the family of maleic acid asymmetrical esters, the study of some features of their emulsion copolymerization with other monomers as well as the properties of obtained latexes.

Experimental Part

Materials

Maleic anhydride of commercial grade was additionally purified by vacuum sublimation. 1-Hexadecanol of analytical grade (''Merck'') was used as received. Methanol (''Aldrich'') was dried by boiling with magnesium swarf with reverse condenser during 2-3 hours and distilled. Triethylamine (''Merck'') was dried over NaOH and distilled. Styrene (''Aldrich'') was distilled under vacuum directly before using. AIBN (''Merck'') was recrystallized from anhydrous methanol. Cetylmaleinate (1) we synthesized by acylation of 1- Hexadecanol with maleic anhydride using known method.[15] After recrystallization from heptane its melting point was 71.5–72.5 °C (lit. 71–72 °C).[15] All experiments were performed using deionized water.

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Analysis Methods

Individuality of the synthesized compounds was verified by thin layer chromatography with plates of Silica gel 60 F_{254} from Merck. The plates were developed in iodine vapour as well as by reflux with solutions of reagents forming colored derivatives: cerium ammonium nitrate – with hydroxyl one. IR spectra were recorded in tetrachloromethane solution with a RS 1000 FT-IR spectrometer (UNICAM Analytische System GmbH). ^{1}H-NMR spectra were recorded using a Brucker 150 spectrometer at working frequency of 300 MHz, substance concentrations of 5 . . . 10%, internal standard – hexamethyldisiloxane. The average molecular weights of obtained copolymers were determined with a gel-permeation chromatograph ''Waters'' (200). Hydrodynamic radii of macromolecules have been measured by the method of dynamic light-scattering using ''Malvern Nano ZS'' with ''red'' laser (wave length - 633 nm). Functional groups in the synthesized substances were determined using the following techniques: carboxylic – potentiometric titration;[16] carbon-carbon double bonds – addition of $Hg(ClO_4)_2$ with following back titration by 0.01 N solution of thioglycolic acid.[17] Process of O- alkylation reaction of synthesized monoester (1) with 1,3-propanesultone was controlled by potentiometric titration of reaction mixture with 0,1 N solution of hydrochloric acid determining the content of triethylammonia salt of monoalkyl maleic in the reaction mixture (1).

Synthesis of Surfmers

Triethylammonia 3-[(Z)-4-cetyloxy-4-oxy-2-butenoyleoxy]-1-propanesulfonate. **2.** 2.1 g (0.021 mol) of triethylamine were added to the solution of 6.8 g (0.02 mol) of cetylmaleinate (1) and 2.45 g (0.02 mol) of 1,3-propane sultone in 10 ml of dimethylformamide and held it during 48 hours at the temperature of 20–25 °C. After distillation under vacuum solvent we have obtained 11.2 g of target product (quantitative yield). IR spectrum, cm^{-1}: 1090 and 1250 (C–O), 1635 (C=C), 1730 (C=O), 1240 and 1045 (SO_2). ^{1}H-NMR ($CDCl_3$), δ, ppm.: 0.98 t (3H, CH_3), 1.37 t (9H, 3CH_3), 1.45 m. (26H, $(CH_2)_{13}CH_3$), 1.70 m. (2H, $C\underline{H}_2$–$C_{14}H_{29}$), 2.20 m (2H, $C\underline{H}_2CH_2SO_3^-$), 2.95 t (2H, $CH_2SO_3^-$), 3.15 q (6H, $N(CH_2CH_3)_3$), 4.24 t (2H, $C(O)OCH_2$–$C_{15}H_{31}$), 4.33 t (2H, $COOC\underline{H}_2CH_2CH_2SO_3^-$), 6.22 d (J = 12.3 Hz, 2H, HC=CH), 10.40 s (1H, $^+$NH). It was determined, %: C 61.63; H 10.16; N 2.57; S 5.61. $C_{29}H_{57}NO_7S$, ca., % C 61.78; H 10.19; N 2.48; S 5.69.

Synthesis of Polystyrene Latexes

Polymerization was carried out in argon atmosphere at 70 °C at continuous stirring with mechanic stirrer. The solution of surfmer 2 (1–5% with respect to styrene mass) in 50.0 g of water, were charged into reactor and degassed during 30 minutes at 70 °C. Afterwards 5.0 g of styrene were added and emulsion polymerization was initiated with adding 0.05 g of ammonia persulphate, dissolved in 2.0 g of water. The process was carried out at three different styrene-to-surfmer ratios (Table 1). Monomer conversion was controlled gravimetrically by estimation of non-volatile residue (NVR).[18]

Results and Discussion

Surface-Active Monomer Getting

The synthesis of surface-active monomer – maleic acid derivative containing hydrophobic aliphatic fragment and hydrophilic sulfonate group, situated at opposite sides of double bond, was carried out in two stages (Scheme 1). Firstly as a result of acylation of cetyl alcohol by maleic anhydride monoalkylmaleate was synthesized (1). Target asymmetrical dialkylmaleinate, that contains sulfonate group was synthesized by further O-alkylation of obtained monoester of maleic acid (1) with 1,3-propanesulton in the presence of triethylamine (mole ratio was 1:1:1.05 respectively) in the solution of dimethylformamide. Practically complete conversion of reagents was reached after ageing the reaction mixture during 48 hours 48 at ambient temperature.

Table 1.
Characteristics of polystyrolene latexes, stabilized by anion surface-active monomer (2).

No of latex	[Styrene]: [Surfmer], parts w/w	Polymerization time, hours	NVR, %	Conversion, %	Particle diameter, nm	TFC, mmol KCl/l
1	100:1.02	10[a)]	5.84[b)]	67.0	205	110
2	100:3.18	5	7.52	84.2	185	160
3	100:5.00	3	8.26	89.2	95	330

[a)] In 5 hours after polymerization beginning additionally 0.05 g of peroxysulphate of ammonia dissolved in 2.0 g of water were added;

[b)] Great amount of coagulum has been formed.

Monomer (2) is a paste-like substance of white colour, it dissolves well in dimethylformamide, ethanol, other polar organic dissolvents and can be restrictedly dissolved in water. Structure of obtained substances is confirmed by data of IR and ^{1}H-NMR spectroscopy.

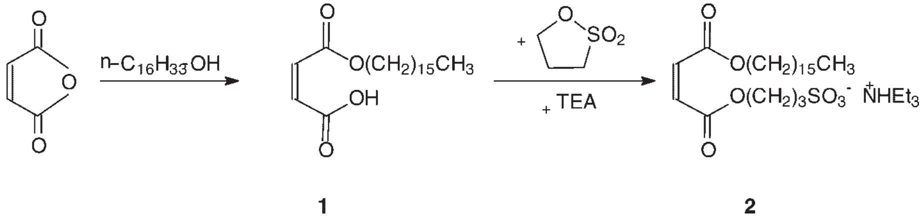
Study of Peculiarities of Emulsion Copolymerization

The possibility of the utilization of synthesized anion surfmers, that contain hydrophobic cetyl mixer and hydrophilic sulfonate group for obtaining polystyrene latexes as well as the influence of surfmer amount on the stability of latex and latex particle size have been studied.

Polystyrene latexes were synthesized via styrene emulsion polymerization at weight ratio [styrene]:[water] = 1:10.4 in argon atmosphere. Quantity of surfmer (2) introduced into reaction mixture was varied from 1 to 5% with respect to styrene weight. Polymerization was initiated by adding ammonia peroxysulphate. Composition of initial reagents and the properties of obtained latexes are shown in the Table 1.

One can see that the quantity of surfmer (2) in the composition of reaction mixture has exceptional effect on the process of styrene emulsion polymerization as well as on the properties of synthesized latexes. In the case of little quantity of surface-active maleate (1% with respect to styrene weight) polymerization has low speed that is confirmed by low styrene conversion (only 67%) after 10 hours. After surfmer increase up to 5% with respect to styrene 90% conversion has been reached after 3 hours of emulsion polymerization process. Increasing the concentration of surface- active substance in reaction mixture causes the enhancement of micelle quantity in the system, and as a result quantity of polymer- monomer particles, in which polymer chain growth takes place. Thus, the increase of latex particle quantity allows to reach higher styrene conversion within short time.

From the data presented in the Table 1, one can see that the rise of surface-active monomer concentration results in the decrease of latex particle size. From our point of view the explanation is as follows. The increase of surfmer content in the composition of reaction mixture provides its adsorption and grafting to larger area of surface of polystyrene latex particles. Obviously the enhancement of polymer–



Scheme 1.

water phase boundary results in the decrease of latex parts size (approximately from 200 to 100 nm). On the other hand, increasing quantity of anion maleate surfmer, grafted to surface of polystyrene latex particles, increases aggregate stability of obtained latex due to electrostatic stabilization of particles. This conclusion is proved by the increase of threshold of fast coagulation (TFC) by electrolyte with the increase surfmer concentration from 1 to 5% with respect to styrene weight.

The effect of introduction method of surface-active maleate in reaction mixture on the properties of obtained latexes. It is known[19] that the technique of obtaining of initial monomer emulsion can predetermine the diameter and size distribution of polymer dispersion particles. During these studies styrene to maleate ratio was constant for all experiments and was 10:1. As initiators we used water-soluble ammonia persulphate or oil-soluble 2,2′- azobisisobutyronitrile, quantity of initiator – 10% with respect to monomer weight (Scheme 2).

We have determined that the choice of the phase of initial emulsion, in which surfmer was dissolved influences strongly the characteristics of obtained dispersion.

In the case of maleate surfmer (2) introduction into styrene and further emulsification of resulted mixture in water phase as a result of polymerization we have got latexes with narrow particle size distribution. In this case the nature of used initiator practically didn't influence the latex particle size distribution.

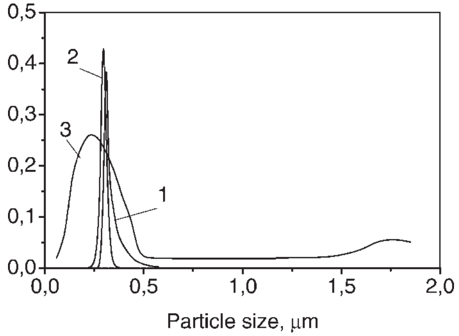
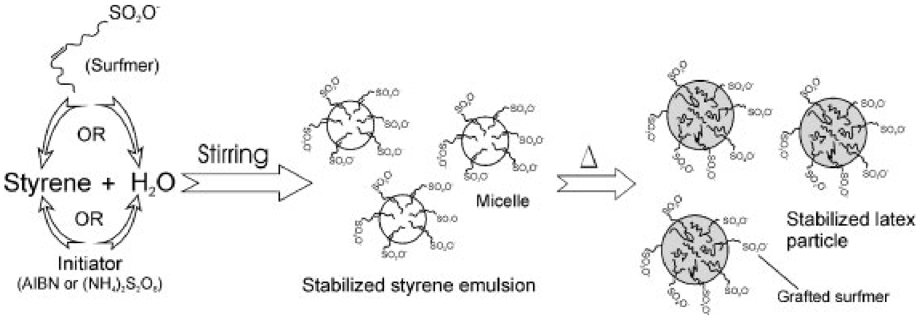


Figure 1.

Size distribution of particles obtained during emulsion copolymerization of styrene and surfmer **2**. 1-surfmer was dissolved in styrene, initiator AP; 2 - surfmer was dissolved in styrene, initiator – AIBN; 3 – surfmer was dissolved in water, initiator – AP.

After surfmer introduction into water phase a wide particle size distribution was observed, and also we have found the presence of fraction of the particles with too big size (more then 1.5 μm), which obviously are the agglomerates. The results of these studies are shown in Figure 1.

From our point of view, size polydispersity of latex particles, which were obtained after surfmer dissolving in water phase can be explained as follows: due to amphiphilic nature of surfmer (2) it can dissolve in both: water and hydrophobic monomer, in particular in styrene. But it is too polar, that's why its transfer through phase boundary from hydrophobic monomer phase into water goes more intensive as compared with the transfer from water phase into organic one. As a result breaking



Scheme 2.

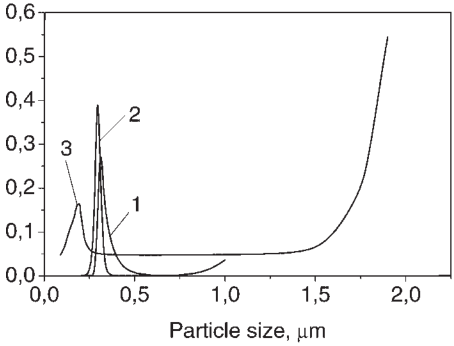


Figure 2.
Particle size distribution after 2 months of latex storage: 1 – surfmer was dissolved in styrene, initiator – AP; 2 – surfmer was dissolved in styrene, initiator – AIBN; 3 – surfmer was dissolved in water, initiator – AP.

and microemulsification of styrene droplets is more effective in the case, when surfmer is dissolved in monomer but not in the water.

It has been established that water dispersion (latexes) obtained in the presence of surfmer (2), dissolved in styrene possess higher stability as compared with latexes obtained in the case of introduction of surface-active monomer into water phase. The latter have the inclination to particle agglomeration during storage. As one can see in Figure 2, in latexes, obtained with surfmer dissolved in hydrophobic monomer mixture the change of particle size distribution is negligible. At the same time for polystyrene dispersions, obtained after surfmer (2) introduction into water phase, we can see pronounced enlargement of content of big size particle fraction with time. Evidently, the increase of the stability of the first type latex is caused with more effective grafting of polymerizable surmers (2) to surface of latex particles as compared with latexes of the 2-nd type.

Thus, experimental results, presented above, confirm the appropriateness of the application of anion surfmers as reactive surface-active substances in the process of emulsion polymerization of conventional monomers for latex particle stabilization and size control.

Conclusion

We developed method of synthesis of new sulfonate surfmers of the family of asymmetrical maleic acid esters that allow to obtain target surfmers with practically quantitative yield.

It was shown that the use of synthesized surfmer for emulsion polymerization of styrene allows to obtain stable latex with narrow size distribution without using other surfactants. The concentration of introduced surfmer allows to control size of latex particles.

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