



HYPERBRANCHED ORGANOSILICON SURFACTANTS AS EMULSIFIERS FOR THE EMULSION POLYMERIZATION OF METHYL METHACRYLATE

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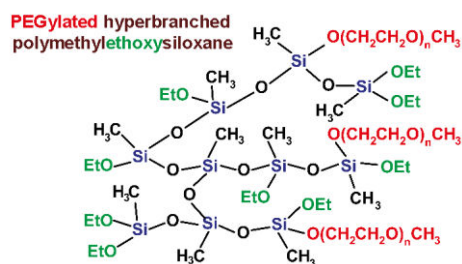
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Abstract

This report is devoted to the investigation of the emulsion polymerization of methyl methacrylate in the presence of PEGylated hyperbranched polymethylethoxysiloxane as an emulsifier. It is shown that its use in the amount of 1–5 wt % affords stable 25–50% poly(methyl methacrylate) dispersions with the controlled particle sizes from 300 to 800 nm and a narrow particle size distribution.

Key words: emulsion polymerization, organosilicon surfactants, polymethylsilsesquioxanes, hyperbranched polymers.



Introduction

Polyacrylic latexes are extensively used in the pulp and paper, textile, paint and varnish industries, as well as medicine [1]. Such a broad application scope places high demands on the latexes in use [2].

Despite a long history of the development, the technology for producing polyacrylic latexes has a number of significant drawbacks, including low stability of the reaction system, the formation of a coagulum, and pollution of wastewater with emulsifiers, most of which are non-biodegradable [3]. A promising alternative to toxic surfactants is the use of organosilicon oligomers [4].

Most of organosilicon surfactants consist of two structural blocks: hydrophobic polydimethylsiloxane moieties and polar groups bound with them. In terms of efficiency, they in many ways surpass the conventional surfactants owing to their structural features. There are reports dealing with the use of linear, dimeric organosilicon surfactants in the emulsion polymerization, while the application of amphiphilic hyperbranched organosilicon compounds in this capacity has not been described.

The goal of this work was to study the emulsion polymerization of methyl methacrylate (MMA) using hyperbranched polymethylethoxysiloxane containing 5 mol % of poly(ethylene glycol) groups (PMEOS–PEG-5) as an emulsifier.

Results and discussion

In industry, polyacrylic latexes are usually obtained with the polymer content of 45–50 wt % using the traditional surfactants [3]. However, the production of concentrated latexes (30–50%) using organosilicon surfactants is unknown in industry.

The polymerization of MMA in the presence of hyperbranched PMEOS–PEG-5 was carried out at the volume ratio of the monomer/water phases equal to 1:1, 1:2, and 1:4. The amount of the surfactant varied from 1 wt % to 5 wt %. Potassium persulfate was used as an initiator in the amount of 1 wt %. Table 1 shows the polymerization conditions and characteristics of the suspensions obtained.

Table 1. Characteristics of PMMA latexes stabilized with PMEOS–PEG-5^a

Exp.	V_m/V_{H_2O}	Surf., wt %	D_i , nm DLS	D , nm SEM	PDI _{DLS}	ζ , mV	P , %
1	1:1	1	810 ± 52	750 ± 239	0.16	-51.6	–
2	1:1	5	460 ± 13	490 ± 71	0.011	-57.7	91
3	1:2	1	530 ± 65	470 ± 49	0.015	-53.8	–
4	1:2	5	510 ± 44	720 ± 60	0.007	-55.4	95
5	1:4	1	330 ± 19	310 ± 19	0.044	-51.5	98

^a the particle sizes were evaluated by averaging the diameter of 500 particles in the SEM micrographs; V_m/V_{H_2O} is the volume ratio of the monomer/water phases; P is the monomer conversion; PDI_{DLS} is the polydispersity index calculated based on the results of dynamic light scattering studies using the formula: $PDI_{DLS} = (SD/Dz)^2$, where SD is the standard deviation, Dz is the intensity-average diameter.

Figure 1 (a–d) shows SEM micrographs of the particles. As can be seen, the resulting particles have a narrow size distribution, which is also confirmed by the PDI_{DLS} values. The highest PDI_{DLS} value of 0.16 was detected for the latex obtained in the first experiment with the volume phase ratio of 1:1 (polymer concentration ~50%), which can be explained by the large amount of the coagulum (~30%).

When the amount of the surfactant was increased from 1 to 5 wt %, the coagulum formation was not observed and the value of PDI_{DLS} was 0.011 (experiment 2). A similar pattern was observed in the experiments 3 and 4, performed at the volume ratio of the phases of 1:2 (polymer concentration ~30%).

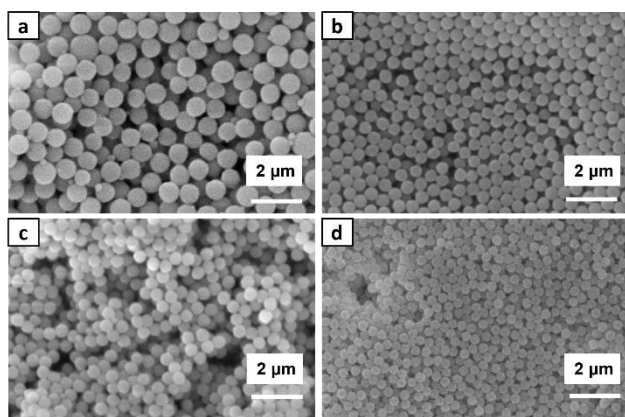


Figure 1. SEM micrographs (JCM-6000 PLUS) of the resulting poly(methyl methacrylate) particles for the following experiments from Table 1: 1 (a), 3 (b), 2 (c), 4 (d).

Based on the data presented in Table 1, it can be concluded that an increase in the latex concentration leads to an increase in the particle sizes. The stable poly(methyl methacrylate) latexes obtained at the phase ratio of 1:1, 1:2, and 1:4 feature the particle diameters of 800, 500, and 270 nm, respectively. The resulting latexes show good aggregation stability, which is confirmed by the values of ζ -potential ($\zeta \leq -50$).

Experimental section

PEGylated hyperbranched polyethoxymethylsiloxane with the degree of substitution of ethoxy groups of 5 mol % (PMEOS-PEG-5) was synthesized according to the published procedure [5, 6].

The emulsion polymerization of methyl methacrylate was carried out in a flask. The monomer and water were degassed twice, then the calculated amount of PMEOS-PEG-5 was added as a surfactant. Potassium persulfate was used in the amount of 1 wt % relative to the monomer. After mixing for 1 min, dispersion was carried out using a magnetic stirrer, resulting in the formation of a stable milky emulsion. Then the reaction mixture was stirred (300 rpm) at a constant temperature (85 ± 0.5 °C) for 2 h.

The latexes obtained in the experiments 1 and 2 were stable for 1 day, those obtained in the experiments 3–5 were stable for 3 days.

The SEM analysis was performed with a JCM-6000 PLUS microscope. The particle sizes, the dispersion degree of the polymer suspension, as well as the electrokinetic potential ζ were determined using a Zetasizer ULTRA particle analyzer (UK).

Conclusions

To summarize the results presented, it was shown that PEGylated hyperbranched polymethylethoxysiloxanes are effective emulsifiers for the emulsion polymerization of MMA and allow for obtaining stable PMMA latexes in a wide range of concentrations (from 25 to 50%) with a narrow particle size distribution. Depending on the synthesis conditions, the diameter of the resulting particles ranged from 300 to 800 nm.

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