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Emulsion polymerization of styrene in the presence of carbohydrate-based amphiphiles

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Summary

Novel amphiphilic N-alkyl-, N-decenyl-, and N-alkyl-N'-methyl-semicarbazones of maltose and maltotriose with C_nH_{2n+1} alkyl chains and n=8,9,10,11,12,16 were applied as emulsifiers in styrene emulsion polymerization. Surfactant properties, emulsion polymerization, and rheology were examined as a function of amphiphile molecular architectures. Both critical micelle concentration and average polystyrene particle size increased with decreasing alkyl chain length. Using N-methyl-N-[11-(acryloylamino)-undecanoyl]-glucamine comonomer in a starved feed emulsion polymerization process, it was possible to prepare uniform polystyrene latex with glucamide surface .

Introduction

For many years polysaccharides, e.g., starch, dextrins, and cellulose derivatives, are being applied as protective colloids in emulsion polymerization to achieve steric stabilization of synthetic polymer latex and to promote film formation in coating applications. Recently, the quest for biodegradable detergents has stimulated again the development of novel amphiphilic sugar derivatives [1]. Examples of amphiphilic sugar and oligosaccharide derivatives useful as non-ionic emulsifiers are esters derived from fatty acids and sorbitol or saccharose respectively, N-alkyl glucamides, and alkylpolyglucosides[2] where long-chain alcohols derived from fatty acids are coupled with saccharides via acetal-linkage. Among such amphiphiles amphiphilic carbohydrates containing amide linkages are outstanding with respect to formation of self-assemblies. According to Pfannemüller [3] carbohydrate amphiphiles, prepared by reaction of aldonic acid lactones of glucose and maltose with various N-alkyl amines, form stable monolayers and other highly ordered aggregates in aqueous solution due to the presence of hydrogen bridges. Gels were found to be composed of a loose network of regularly twisted helical strands. Similar observations were reported by Fuhrhop [4,5] who found dihelical fibers several micrometers in length and gels which resulted from spontaneous aggregation of N-octyl L- and D-glucamides. This self-assembly was attributed to a chiral bilayer effect typical for chiral saccharide units in contrast to racemic saccharides. Numerous patents claim the use of amphiphilic carbohydrates in emulsion polymerization, although little is published concerning basic correlation between emulsion polymerization and amphiphile molecular architectures. Acrylic amphiphilic carbohydrates, e.g., hexylmethacrylate-terminated disaccharide [6], were used as macromonomers in free-radical solution polymerization. In emulsifier-free styrene and methylmethacrylate emulsion polymerization copolymerization of such amphiphilic disaccharide methacrylates afforded polystyrene latexes covered with disaccharide species [7].

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Objective of our research is to further exploit the potential of polymers from renewable resources, especially oligo- and polysaccharides, in emulsion polymerization. Two routes are being explored to compatibilize synthetic and native polymers: (A) novel carbohydrate amphiphiles as non-ionic emulsifiers, and (B) acrylic amphiphilic sugar and polysaccharide derivatives as comonomers in emulsion polymerization. We have examined novel N-alkyl and N-alkyl-N'-methyl semicarbazones of maltose and maltotriose as non-ionic emulsifiers in styrene emulsion polymerization in order to understand the influence of alkyl chain length and amphiphile concentration on critical micelle concentration, latex particles sizes, particle size distributions, and rheology. Moreover, acrylamide-functional amphiphilic derivatives of glucamine such as N-methyl-N-[11-(acryloylamino)-undecanoyl)-glucamine was applied as comonomer in emulsion polymerization to afford latexes with functional surfaces containing covalently bonded glucamide.

Experimental

Materials: styrene was purified by vacuum distillation. Potassium persulfate was used as initiator as received from Fluka AG.

*N-alkyl and N-alkyl-N'-methyl semicarbazones of maltose (**Cn,CnM**) and maltotriose (**CnT**, **CnMT**)*: preparation, characterization and self-assembly formation of the amphiphiles listed in Table 1 are reported elsewhere [8].

*N-methyl-N-[(11-acryloylamino)-undecanoyl)-glucamine (**AUG**)*: Similar to procedures by Gallot and Marchin [9], 3g (12mmol) 11-acryloylaminoundecanoic acid, 0.2g 2,6-ditert.butyl-cresol and 1.35g (12mmol) N-hydroxy-succinimide were dissolved in dry THF. At 0°C 2,4g N,N'-dicyclohexylcarbodiimide dissolved in 5ml THF was added dropwise. After stirring the reaction mixture 12h at 0°C, urea was filtered off and 4g (80%) of the resulting succinimidylester was recovered. Then a solution of 3.5g (10mmol) succinimidylester in 100ml THF was added dropwise to a stirred solution comprising 1.95g (10mmol) N-methyl-glucamine, 50ml methanol and 3ml (20mmol) triethylamine. After stirring 12h and stripping off the solvent mixture in vacuo, 50ml water was added and acidified with HCl. The precipitate was filtered off, dried, dissolved in methanol and precipitated in diethylether. Yield of the N-methyl-N-[(11-acryloylamino)-undecanoyl)-glucamine was 1.5g (30%).

Emulsion polymerization: In a typical run, 100ml deionized water, which was distilled twice and sparged 30min with nitrogen, was added to a 250ml three-necked round-bottom flask equipped with mechanical stirrer, feed pump, and nitrogen inlet. After adding semicarbazone amphiphiles (cf. Table 1), 0.2g $K_2S_2O_8$ initiator and 0.15g $Na_2HPO_4x7H_2O$ buffer and degassing repeatedly, the solution was heated to 80°C and stirred at 300 r.p.m.. Under nitrogen atmosphere 20ml distilled styrene was fed within 1.5h with constant feed rate of approximately 2ml/min. After 2h, 3.5h and 6h samples were removed to control conversion. After 8h styrene conversion was complete and the latex was filtered over a coarse G1 glass fritte containing glass wool. The resulting latex contained 15.7wt.-% solids as expected on the basis of the feed component. In order to improve stabilization, trace amounts of NaN_3 was added to the dispersion. Accordingly, 1.3wt.-% (with respect to styrene) of the AUG comonomer was added instead of non-functional amphiphiles to prepare glucamide-functional latex.

Characterization: latex particle sizes and particle size distributions were determined using photon correlation spectroscopy (Malvern Zetasizer 3, 5mW He-Ne laser, 633nm at angle of 90°) of diluted latex (10^{-5}g/ml), and transmission electron microscopy (Zeiss CEM 902, 80kV). For TEM imaging carbon-coated grids were dipped in diluted latex (0.01wt.-% solids). Surface tension measurements were performed on a Krüss Digital Tensiometer K10T at 20°C after 30min. Shear viscosity of concentrated dispersions was measured by means of Bohlin CS10 rheometer. In the case of diluted dispersions an Ostwald viscosimeter was used. All measurements were performed at 20°C.

For comparison, as illustrated in Scheme 3, polymerizable acrylic glucamide-based amphiphiles were prepared according to procedures first described by Gallot and Marchin [9]. Here N-methyl-glucamine was reacted with the activated succinidylester resulting from dicyclohexylcarbodiimide-mediated coupling of N-hydroxy-succinimide with 11-acryloylamino-undecanoic acid. In order to investigate basic correlation between amphiphile molecular architectures, critical micelle concentration, and average particle size of polystyrene latex, styrene emulsion polymerization was carried out in the presence of 1.3wt-% (with respect to styrene) of the semicarbazone and 1,1wt.-% $K_2S_2O_8$ initiator and 0.83wt.-% $K_2HPO_4x7H_2O$ buffer. While batch processes gave unacceptable agglomerations, slow feed of styrene to the water solution containing amphiphile, buffer, and initiator afforded quantitative styrene conversion and stable dispersion containing 16wt.-% solids. Preferably this starved-feed emulsion polymerization was carried out 12 hours at 80°C. Latex particle sizes were analyzed by means of photon correlation spectroscopy and transmission electron microscopy. Fig. 1 shows a typical TEM image of polystyrene latex obtained in the presence of 1,3wt.-% N-decenyl-N'-methyl-semicarbazone of maltose (**C10UM**).

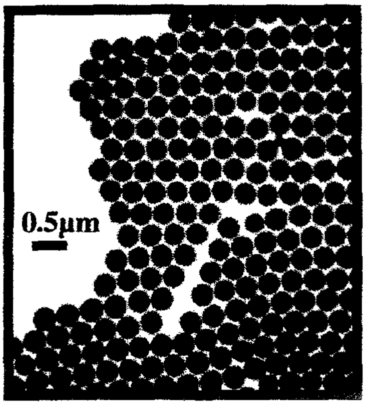

Fig.1 TEM image of polystyrene latex prepared in the presence of **C10UM**

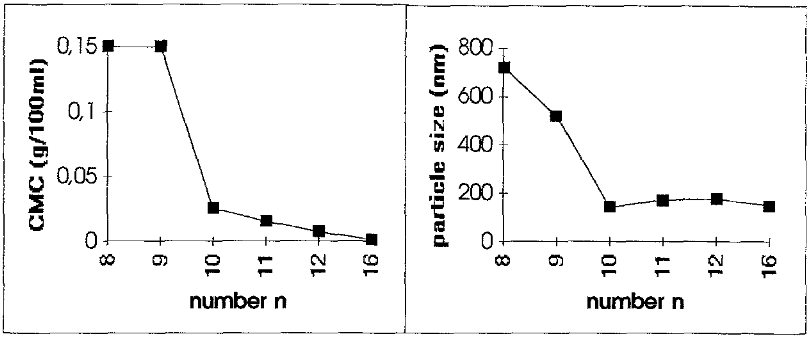

Fig.2 Influence of C_nH_{2n+1} chain length on particle size (left) and CMC (right)

Table 1 Styrene emulsion polymerization in the presence of carbohydrate amphiphiles[a]

type	conc.[b] (wt.-%)	X	n	S	CMC[c] (g/100ml)	size[d] PCS (nm)	size[e] TEM (nm)	Δ[f] (%)
C8	1.33	H	8	maltose	0.150	720	645	11
C9	"	"	9	"	0.150	520	400	7
"	0.67	"	"	"	"	600	540	14
"	2.67	"	"	"	"	110	85	25
C10	1.33	"	10	"	0.025	140	120	7
C11	"	"	11	"	0.015	170	133	8
C12	1.33	"	12	"	0.007	175	150	8
"	0.67	"	"	"	"	130	n.d.[g]	15
"	0.11	"	"	"	"	155	n.d.[g]	30
C16	1.33	"	16	"	<0.001	150	134	7
C9M	"	Me	9	"	0.170	235	209	2
C11M	"	Me	11	"	0.017	110	75	20
C10UM[h]	"	Me	10	"	0.070	320	273	5
C11MT	0.67	Me	11	maltotriose	0.410	195	155	7
C12MT	0.67	H	12	"	0.041	156	133	5
AUG[a]	1.33	Me	10	glucamine	n.d.[g]	280	240	15

a) C_nH_{2n+1}NH-CO-N(X)-N=CH-S and **AUG** N-methyl-N-[11-(acryloylamino)-undecanoyl]-glucamine, b) weight- % with respect to styrene, c) CMC: critical micelle concentration, d) measured with photon correlation spectroscopy, e) measured with transmission electron microscopy, f) standard deviation of particle sizes, g) n.d.: not determined, h) decenyl substituent.

Critical micelle concentrations (CMC), average latex particle sizes and particle size distributions, reflected by particle size measurement standard deviation Δ, are summarized in Table 1 for various amphiphiles and concentration ranges (cf. C9 and C12). Semicarbazone amphiphiles as well as amphiphile monomer **AUG**, added in 1,33wt.-% concentration with respect to styrene, gave stable dispersions with narrow particle size distributions. As illustrated in Fig.2, both average particle size of the polystyrene latex and amphiphile CMC decrease with increasing chain length of the n-alkyl substituent. Above n=10, the alkyl chain length appeared to be much more important than the presence of maltose or maltotriose head groups. Below n=10 water solubility increases and the hydrophobic alkyl chain is too short to afford adequate latex stability. At amphiphile concentration three-times CMC similar average particle sizes, varying between 120 and 160nm regardless of the amphiphile type, were observed. When amphiphile concentration was lowered to approach CMC, amphiphile concentrations started to influence particles sizes and also particle size distributions which was broadened markedly. Also the amphiphilic carbohydrate comonomer **AUG** afforded stable dispersions of polystyrene particles of 280nm average diameter, which exhibit glucamide-functional particle surfaces.

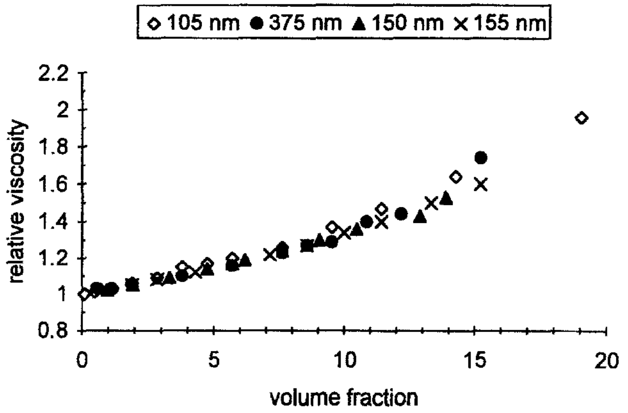

Fig.4a Relative viscosity of diluted dispersions (Ostwald viscosimeter)

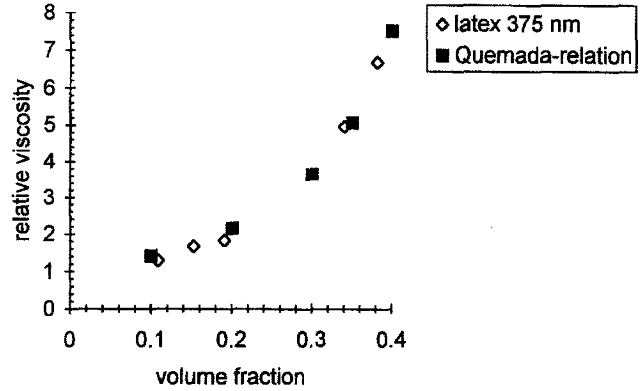

Fig. 4b Relative viscosity of concentrated dispersions (Bohlin rheometer)

Surface tension measurements were carried out to determine the amount of surfactant which is adsorbed on the particle surface. In fact, surface tensions of both latex and aqueous phase, separated by removing particles by means of centrifugation, were always >0.066 N/m. Therefore no free surfactant was present in the aqueous phase. Some latexes were further characterized with respect to their shear viscosity. In Fig. 4a the relative viscosity $\eta_r = \eta_o/\eta_s$, with η_0 and η_s being the zero shear viscosity of the dispersion and the solvent respectively, is plotted against particle volume fraction φ. Einstein behavior was found at concentrations below 8%. At intermediate concentrations, η_r can be described by Batchelor's equation [10]:

$$\eta_r = 1 + 2.5\varphi + 6.2\varphi^2$$

The viscosity behavior of highly concentrated hard sphere systems can be described by the Quemada equation [11] which relates the reduced viscosity to of the reduced concentration φ/φ_m. Here φ_m denotes the volume fraction at maximum packing density:

$$\eta_r = (1 - \varphi/\varphi_m)^{-2}$$

In Fig. 4b the experimental data is in excellent agreement with theoretical data calculated by the Quemada equation using de Kruif's value of $\varphi_m = 0.63$.This provides strong evidence that semicarbazone-based carbohydrate amphiphiles are excellent non-ionic emulsifiers, forming hard sterically stabilized spherical particles.

Conclusion

A novel range of carbohydrate amphiphiles was derived from aldehyde-functional maltose and maltotriose and N-alkyl- and N-alkyl-N'-methyl semicarbazides. This reaction is versatile and holds attractive potential for other aldehyde-functional carbohydrates. According to rheological investigations, such carbohydrate-based semicarbazone amphiphiles are efficient non-ionic emulsifiers useful in styrene emulsion polymerization. Both CMC and average latex particle sizes reflect the molecular architecture of the carbohydrate amphiphiles, especially with respect to the n-alkyl chain length. With semicarbazone amphiphiles and acrylamide-functional amphiphilic glucamide a family of carbohydrate-modified latexes is available. Steric stabilization with carbohydrate-based amphiphiles and especially copolymerization of acrylamide-functional amphiphiles represent an interesting route to latex containing saccharide-functional surfaces which may be of interest in biomedical applications, e.g., diagnostics and drug targeting.

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