Synthesis and characterization of poly(methylmethacrylate) microlatexes and microgels

Annie Mura-Kuentz* and Gérard Riess

Ecole Nationale Supérieure de Chimie de Mulhouse
Institut de Chimie des Surfaces et Interfaces
3 rue Alfred Werner, 68093 Mulhouse Cedex, France

*Present address : Parfums Christian Dior, 45804 Saint Jean de Braye Cedex, France

Dedicated to the memory of J. Guillot

SUMMARY : PMMA microlatexes were prepared by batch emulsion polymerization in the presence of ω dicarboxy functionalized polyesters as surfactants and butanediol dimethacrylate (BDMA) as crosslinking agent. The size of the particles was determined by dynamic light scattering in the aqueous phase and as microgels after their transfer in organic medium such as butylacetate. These characteristics leading to the swelling index of the microgels were examined as a function of the polyester and the monomer concentrations. The efficiency of microgel formation was determined by size exclusion chromatography.

INTRODUCTION

Microgels, which are small network particles sterically stabilized in aqueous or organic solvents, were extensively studied by FUNKE (1) and by ANTONIETTI (2). In his pioneering work, FUNKE has for instance developed microgels by polymerization of styrene and divinylbenzene in the presence of "water soluble" polyesters which have found interesting applications as coatings.

In connection to this problem, the aim of our work was to develop PMMA microlatexes leading to microgels with different crosslink densities. As a difference with respect to FUNKE's work, we have used ω dicarboxy functionalized polyesters as surfactants with well defined micellar characteristics. This polymeric surfactant, necessary as a colloid stabilizer during the emulsion polymerization, becomes after drying of the microlatex or the microgel, such as in paint or cosmetic applications, a valuable constituant of the final film.

 CCC 1022-1360/00/$ 17.50+.50/0

EXPERIMENTAL

PES surfactant (3, 4)

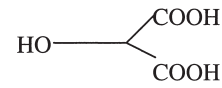
The ω dicarboxy polyester, supplied by AKZO COATINGS, has the schematic structure given below.

The main chain is a condensation product of isophtalic anhydride with a slight excess of 1,5-pentanediol. The end-standing hydroxy groups thus obtained are reacted with one mole of trimelletic anhydride. The characteristics of this polyester are given in Table 1.

The polyester becomes a stable water dispersable micellar system by neutralization with stoechiometric amounts of N, N' dimethylethanolamine (DMEA). The average micelle size is given in Table 1.

Table 1. Characteristics and schematic structure of the polyester surfactant (MD 90)

PES	Acide index	M_n	M_w	Micelle size* nm	CMC** g/L
MD 90	90	1330	4060	15.3 ± 0.8	~ 1



* micelle size : D_w after neutralization with DMEA ; ** critical micellar concentration at 20°C as determined by surface tension measurements

Emulsion polymerization

The microlatexes are prepared by batch emulsion polymerization, following the classical procedure, e.g. purified monomers (MMA) and crosslinking agents (BDMA = n butanediol dimethacrylate), degassed distilled water, nitrogen blanket,..., with a typical receipe as follows :

1000 g distilled water ; 1.5 – 32.5 g neutralized PES ; 0.67 g $NaHCO_3$
30 – 250 g monomer (MMA + crosslinking agent) ; 1.64 g AIBN
Temperature : 70°C ; Reaction time : 24 h
Conversion : 85 – 95 % of microlatex with respect to the monomers.

Microlatex characterization

The size of the particles is determined by dynamic light scattering (DLS). From the particle size and the solid content, additional information can be obtained, such as the number of particles (N_p/L), the specific surface area (S) of the microlatex. The surface covered by the surfactant can also be calculated knowing that 1 molecule of neutralized MD 90 occupies a surface of 0.63 ± 0.03 nm^2 (3).

Preparation and characterization of the microgel

If the microlatexes are crosslinked by using a difunctional monomer, they can be transfered after polymerization from the aqueous medium in an organic solvent. The transfer from the aqueous in the organic phase can be operated, either by drying the microlatex followed by its dispersion in the organic medium, or preferably by distillation of the water in the presence of a suitable organic solvent such as butyl acetate (BuAc). A stable microgel is thus formed in the organic solvent.

The particle size of the microgel in the organic phase are determined by DLS. The *swelling index* of the microgel, which is mainly a function of its crosslink density, is defined as SI = particle volume in the organic phase / particle volume in the aqueous phase, e.g.

$$SI = [D_w \text{ (organic)} / D_w \text{ (aqueous)}]^3$$

The fraction of non-crosslinked polymer, including the polyester used as surfactant, is determined directly by GPC either in BuAc or in THF. The difference in elution volume between the microgel (molecular weights > 10^6) and the soluble polymers (molecular weights in the range of 10^3 to 10^5) are usually quite sufficient to estimate the weight fractions, and thus the yield, of microgel.

RESULTS AND DISCUSSION

Characterization of the microlatexes

As a first parameter, it was of interest to check the influence of PES concentration on the particle size of the microlatex. As expected one can notice from Table 2 that the particle size decreases with increasing surfactant concentration. Furthermore Table 2 shows that the number of latex particles par L (Np/L) and the specific surface increase with increasing concentrations of polyester MD 90.

Table 2. Microlatex characteristics as a function of surfactant concentration (MD 90)

Experiment	PES conc. g/L	D_w nm	Np/L x 10^{17}	S x 10^{21} nm^2	N_m/N_p
AK 180	1.5	43.4	4.7	2.8	1.6
AK 181	3.0	41.7	6.0	3.3	2.5
AK 183	4.5	36.8	8.7	3.7	2.5
AK 184	6.0	33.8	12.6	4.5	2.3
AK 185	32.5	20.6 ± 2	115	15.3	1.4

Reaction conditions : standard recipe with 30 g/L MMA, 3 g/L BDMA

From the initial number of micelles of surfactant present in the system N_m, estimated from their size and specific volume, one can calculate in a first approximation the number of micelles necessary to generate 1 latex particle. From the ratio N_m/N_p given in table 2 it appears that on the average 2 to 3 micelles are necessary to form 1 latex particle. Under the same experimental conditions it could be shown that with a low molecular weight surfactant

(SDS = sodium dodecylsulfate) between 50-100 SDS micelles are used up for the formation of 1 microlatex particle (4).

In these experiments given in Table 2, the solid content of the microlatex was between 3 and 6%. For the industrial practice however, it was of interest to increase as much as possible the solid content of the microlatex by keeping small particle sizes. These results are shown in Table 3.

Table 3. Characteristics of the microlatexes obtained by increasing the monomer and the surfactant concentration at a constant weight ratio monomer / PES = 5.4

Experiment	[M] g/l*	D_w nm	N_p/L x 10^{18}	N_m/N_p
AK 184	33	33.8	1.3	2.3
AK 221	57	42.7	1.2	4.3
AK 222	91	43.6	1.8	4.7
AK 223	107	44.6	1.9	5.1
AK 224	131	48.8	1.7	6.9
AK 248	167	56.4	1.4	11
AK 250	250	40 } ** 93 }	/	/

* Monomer concentration ; ** Bimodal distribution

Standard recipe with 10 wt % BDMA with respect to MMA

At this constant weight ratio monomer/PES = 5.4, one can notice that the particle size of the microlatex increases from about 35 to 55 nm by increasing the solid content, with formation of a bimodal distribution and partial coagulation at a solid content of around 20 %. Even if the number of particles N_p/L remains almost constant within the experimental error limits, it appears that more surfactant micelles are necessary for the formation of 1 latex particle when the solid content is increasing. One can therefore assume that at higher monomer / PES ratios a part of the PES is occluded in the microlatex particles.

Characterization of the microgels

The microlatexes described in the previous section were transfered in an organic solvent, such as n-butylacetate (BuAc), in order to form the microgels. From the particle size of this microgel determined by DLS one has access to the swelling index SI as defined in the experimental section. In addition, by SEC in BuAc it becomes possible to evaluate the weight fraction of microgel and that of soluble products corresponding to the non-crosslinked polymer and to the PES.

In Table 4 the main characteristics of the microgels are listed.

Table 4. Characteristics of the microgels derived from the microlatexes given in Table 2

Experiment	PES conc. g/L	D_w water nm	D_w BuAc nm	SI	Microgel* %	Soluble fraction %**
AK 180	1.5	43.4 ± 0.3	74.7 ± 3.5	5.1 ± 0.8	77	18
AK 181	3.0	41.7 ± 0.3	57.4 ± 4.4	2.6 ± 0.5	75	23
AK 183	4.5	38.6 ± 1.3	46.6 ± 2.7	2.0 ± 0.3	97	0
AK 184	6.0	33.8 ± 1.7	43.5 ± 0.9	2.1 ± 0.5	98	0
AK 185	32.5	20.6 ± 2.1	33.7 ± 0.9	4.4 ± 1.4	100	0

SI = swelling index MMA = 30 g/L BDMA = 3 g/L

* weight percent of microgel estimated by GPC with respect to the acrylic polymer

** weight fraction of soluble non-crosslinked acrylic polymer

In the intermediate range of PES concentration (3 to 6 g/L) it can be noticed that the swelling index is almost constant, with SI around 2. It deviated from this value at high concentration in PES which might interfere in the size determination, as the system contains similar amounts of PES and methacrylic microgel. Although all PES might not be adsorbed in this case on the microlatex particles, such compositions with high PES content could be of interest for coating applications. At very low concentration in PES, e.g. 1.5 g/L which is in the range of the CMC of this surfactant, we can assume that the polymerization deviates from a typical micellar system. Concerning the efficiency in microgel formation it appears that the weight percent of microgel as determined by SEC and expressed with respect to the methacrylic polymer reaches almost 100 % for concentrations in PES from 4.5 to 32.5 g/L. The soluble fraction of acrylic polymer is around 20 % at low PES concentration with the presence of 3 to 6 %

"aggregates", e.g. microgels of very high molecular weights (estimated M_{peak} from SEC measurements of 20 to 30.10^6).

CONCLUSION

It has been shown that microlatexes with particle sizes in the range of 20 to 50 nm and a solid content of approximately 20 % could be obtained by using a ω-dicarboxy polyester as surfactant. The conditions could also be defined where these crosslinked microlatexes lead to microgels with an efficiency of nearby 100 %. As an extension of this work it was possible to synthesize "hairy microgels" consisting in a PMMA crosslinked core and a fringe of grafted PMMA chains, as well as "core-shell PMMA microgels" having a PMMA core and PMMA shell of different crosslink densities (5).

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