Emulsion polymerization of styrene using a new series of rigid rod-like cationic surfactants

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SUMMARY: A series of pyridinium salts (PCX) *N*-substituted with an ω-(4′-methoxy-4-biphenylyloxy)alkyl group has been synthesized and used as surfactants in the emulsion polymerization of styrene. These molecules have an alkyl chain with an even number (X = 6, 8, 10, or 12) of methylene groups and bromine as counterion. For these molecules a typical behavior of colloidal electrolytes has been observed by conductivity measurements on water solutions and the critical micelle concentrations (CMC) determined by this technique are 2.14, 1.47, 0.214, and 0.0097 mmol for PC6, PC8, PC10, and PC12, respectively. Latices prepared with three components (water/styrene/PCX) were fairly stable showing in all experiments a monodisperse particle size distribution (1.01 to 1.1) with particle diameters from 70 to 160 nm. These results are compared with those obtained using dodecylpyridinium bromide (DPB) as the surfactant.

Introduction

The most important class of cationic surfactants is the quaternary ammonium salt substituted with at least one long organic radical, which is normally a long alkyl chain[1, 2] or an alkylaryl group[3]. Another important type of cationic surfactant is based on one or more heterocyclic ionic moieties, among which pyridinium salts are the most representative[4]. The emulsification properties of these amphiphiles depend strongly on the ionic part, and in some extent on the nature and size of the non-ionic radical, which can modify the performance of the surfactant. In most cases, the hydrophobic radical of the surfactants is a flexible group, typically a hydrocarbon chain. Relatively few works concerning stabilized colloidal dispersions (oil/water/surfactant) report the use of surfactants having a rigid hydrophobic group incorporated into the long organic radical. In this respect, Finkelmann et al.[5,6] have reported some amphiphiles combining an oligo-oxyethylenic chain with a rigid rod-like hydrophobic moiety. For these molecules they have observed the development of mesophases at well defined intervals of temperature and concentration. Molecular aggregations were all lamellar, regardless of the hydrophile-lipophile balance of the amphiphiles. The molecular packing of these amphiphiles was different compared with that formed with non-ionic amphiphiles having a flexible hydrophobic group. On the other hand, Kunitake and Okahata[7] have reported the synthesis of a series of quaternary ammonium salts having a biphenyl azomethine group in the hydrophobic radical and bromine as counterion. In dilute aqueous solution these amphiphiles form lamellar and vesicular structures, which were reported to form a bilayer assembly. In another work, Kunitake et al.[8] have reported 62 single-chain amphiphiles having a flexible tail, a rigid moiety (biphenyl, biphenyl azomethine, azobenzene, etc.) and a hydrophilic head group (quaternary ammonium group) as structural elements. They have found some relation between the morphology of the molecular aggregates and the polarity and geometry of the rigid group. In a similar context, Menger and Littau[9, 10] have synthesized and studied a series of non-conventional surfactants called “gemini surfactants”. These surfactants combine in the same molecule the following sequence of chemical groups: a long alkyl chain, an ionic group, a rigid segment, a second ionic group, and a second hydrocarbon tail. The two hydrophobic tails make these surfactants to show an abnormal CMC-hydrocarbon tail length dependence. Molecular aggregation for these surfactants is different to that observed with conventional single tail surfactants. It seems that gemini aggregates fall into the lamellar range, but structural details were not fully described. Other amphiphiles having rigid elements in their chemical structure and showing unusual molecular aggregation have been reported by Stein and Gellman[11] and Menger and Whitesell[12].

Hundreds of surfactants combining in the same molecule ionic or non-ionic hydrophilic groups with long organic radicals have been tested in emulsion polymerization in order to improve both the stabilization and the polymerization process. However, in this method of polymerization the use of surfactants containing a rigid group in the organic radical is almost nonexistent. In this respect we can cite the use of alkylphenyldisulfonic acid salts as surfactant in the emulsion polymerization of vinyl acetate[13].

In the present work, we investigate a new class of surfactants (Scheme 1) having in their chemical structure three distinct parts in the following sequence: a positively

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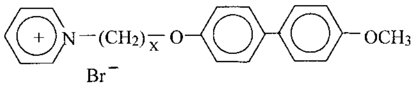
Scheme 1:



charged pyridinium ring associated with its negatively charged counterion, a flexible aliphatic chain and a rigid methoxybiphenyl group. We report the use of these surfactants in the emulsion polymerization of styrene. Results are discussed in terms of the length of the alkyl chain and the concentration of surfactants. In order to compare with the use of a classical surfactant we also report some results obtained with dodecylpyridinium bromide.

Experimental part

Materials

Pyridinium bromide salts *N*-substituted with an *ω*-(4′-methoxy-4-biphenylyloxy)alkyl group were synthesized by a similar method reported in a previous paper[14]. 4,4′-Biphenyldiol, dimethyl sulfate and *α*,*ω*-dibromoalkanes (even numbers from 6 to 12 of methylene groups) from Aldrich were used as received. Dodecylpyridinium bromide (DPB) was obtained by reacting dodecyl bromide (Aldrich) with pyridine (in excess). Pyridine was distilled under vacuum in the presence of KOH. All solvents and styrene (St) were distilled before use. Polymerizations were initiated with 2,2′-azo(2-amidinopropane) dihydrochloride from Wako (V-50), previously recrystallized in methanol.

Instruments

All intermediates and final products (PCX) were analyzed by the coupled technique gas chromatography-mass spectroscopy (GC-MS) using a Hewlett Packard instrument (model 5890), by infrared spectroscopy using an FTIR from Nicolet (Magna-IR 550) and by ^{1}H NMR using an Varian spectrometer (Gemini 200 MHz). Conductivity measurements for the CMC determination were performed with a conductimeter from Jenway (cell constant 0.95 and 1 KHz of frequency) at 25 °C ± 0.1 and using purified water (conductivity 0.5 µS) obtained from a combination of ion exchanger filter cartridges from Cole-Parmer (universal and research grades). Particle size (D_p) and particle size distribution (PSD) of latices were determined using a light scattering Malvern instrument (Series 4700). Micrographies were obtained by the secondary ion technique using a scanning electronic microscope (SEM) from Topcon (SM-510). Molecular weights ($\overline{M}_n$ and $\overline{M}_w$) of the polymers were obtained by size exclusion chromatography (SEC) using a Waters instrument (150-C).

Polymerizations

All emulsion polymerizations were carried out in a 250 mL three neck round bottom flask using in all experiments the same concentration of water (80 g), styrene (20 g) and initiator (0.2 g). Styrene and water were bubbled with argon during 30 min before use. Surfactant concentration [PCX] was varied from 12 to 72 mmol. Experiments were carried out at 60 °C under argon atmosphere using mechanical stirring (600 rpm). In all experiments, materials were introduced into the reactor in the following sequence: water, surfactant, monomer, and initiator. Aliquots of 3 mL of the reaction mixture were removed with a syringe at specified intervals and the polymers were recuperated by the freeze drying method. Two polymerizations were carried out for each concentration of surfactant in order to check the reproducibility of the reaction. Similar experiments were carried out using DPB as surfactant.

Results and discussion

Critical micelle concentration of PCX surfactants

An important parameter to measure before starting a study related to the use of new surfactants is the critical micelle concentration (CMC). This property was determined by electric conductivity measurements of a series of water-surfactant solutions of different concentration. This method was chosen because of the ionic character of the synthesized molecules. The CMC for each PCX surfactant was determined graphically as shown in Fig. 1 for the PC6 surfactant. Results were as follows: 2.14, 1.47, 0.214, and 0.0097 mmol for PC6, PC8, PC10, and PC12, respectively. The CMC of DPB at 40 °C has been reported at 10.0 mmol[15]. By comparing the CMC values between PC12 and DBP (both molecules containing a dodecyl chain), it can be concluded that the CMC value decreases drastically due to the presence of the methoxybiphenyl rigid segment. Also, it can be observed that the amphiphiles with the longest chain (PC10 and PC12) show very low CMC values. This result is certainly related to the length of the amphiphile but it is also related to the hydrophile-lipophile balance of the molecules which decreases at longer alkyl chain lengths. Low CMC values (10^{-2} – 10^{-1} mmol) for rigid rod-like molecules were also reported by Lühmann and Finkelmann[5] and Kunitake and Okahata[7].

Effect of PCX concentration

In emulsion polymerization, the rate of polymerization (R_p) depends on the number of particles (polymerization sites) and this in turn on the surfactant concentration[16]. The number of particles per milliliter of water (N_p) can be obtained by theoretical[17] and experimental[18] methods. Tab. 1 shows the experimental N_p values for several latices of polystyrene prepared using two different concentrations of PCX and DPB surfactants. The theoretical N_p value has been calculated considering the head group

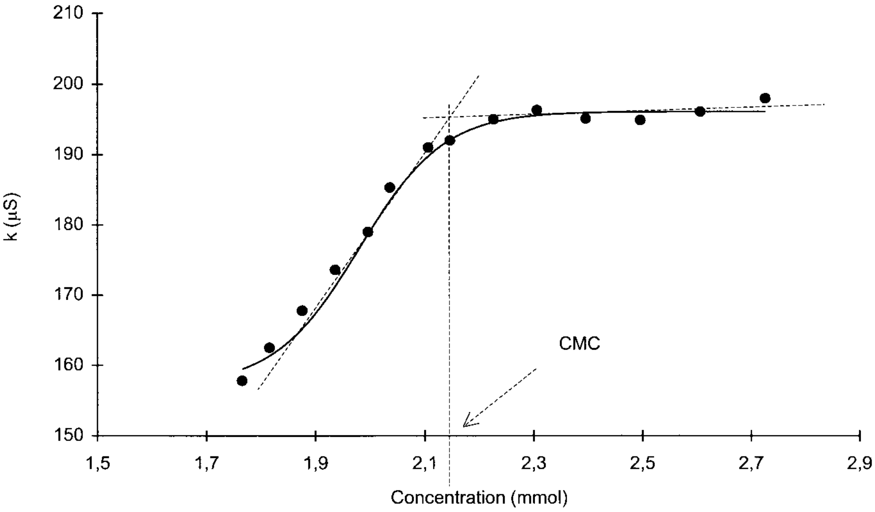


Fig. 1. Electric conductivity (*k* in µS) vs. surfactant concentration for the PC6 surfactant, temperature: 25 °C ± 0.1

Tab. 1. Experimental and calculated number of particles per water milliliter (N_p) and rate of polymerization (R_p) for emulsions stabilized with indicated amounts of PCX surfactants and DPB

Surfactant	$N_p \times 10^{-14}$ 12 mmol	$N_p \times 10^{-14}$ 36 mmol	R_p in mol/(L · min) 12 mmol	R_p in mol/(L · min) 36 mmol
PC6	2.11	5.19	0.0208	0.0493
PC8	2.55	5.37	0.0261	0.0475
PC10	2.31	5.32	0.0273	0.0500
PC12	3.00	4.46	0.0273	0.0444
DPB	–	5.39	–	0.0175
Theoretical	19.0	38.3		

surface area of the pyridinium ring[14]. It can be noticed that the theoretical N_p value is higher than the experimental one obtained for all pyridinium salts. Such disagreement between theoretical and experimental N_p values is common and it could be due to the fact that theoretical calculations do not consider the monomer concentration and other molecular factors. On the other hand, it can be seen that the N_p value for latices prepared with PCX surfactants is quite similar to that obtained for those prepared with DPB. The latter result merely indicates that the number of particles depends on the polar head surface area and not on the hydrophobic group. In spite of the similar N_p values between PCX and DPB amphiphiles, it has been observed that latices prepared with DPB were considerably less stable at similar concentration. It can be pointed out that it was almost impossible to carry out an emulsion polymerization experiment at 12 mmol of DPB, whereas the polymerization with PCX at such concentration was fairly stable even for the longest surfactant (PC12) used in this work. The molecular aggregation of rigid rod-like PCX amphiphiles on the water/monomer interface is not yet well understood, but it is possible that the rigid group enhances the stability of latices by means of a mechanism of lateral molecular interactions, as it occurs in lamellar lyotropic[19] and smectic thermotropic[20] liquid crystals with similar chemical structure. For instance, in liquid crystals containing in the same molecule a flexible alkyl chain and one polar head group or one elongated aromatic core, the observed smectic ordering (molecules arranged in layers) is related to the lateral interaction of molecular moieties segregated in distinct layers periodically arranged in space[14].

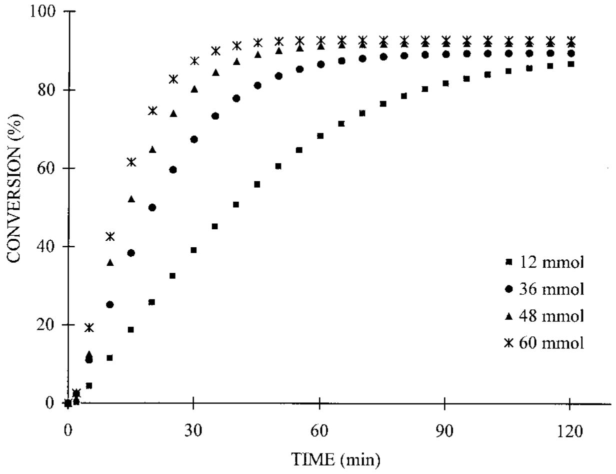


Fig. 2. Conversion vs. time for emulsion polymerizations stabilized with PC10 at various concentrations

The kinetics of emulsion polymerizations carried out using PCX surfactants have shown the normally observed pattern in this method of polymer synthesis. Fig. 2 shows the curves of conversion vs. time for polymerizations stabilized with PC10 at different concentration. As expected,

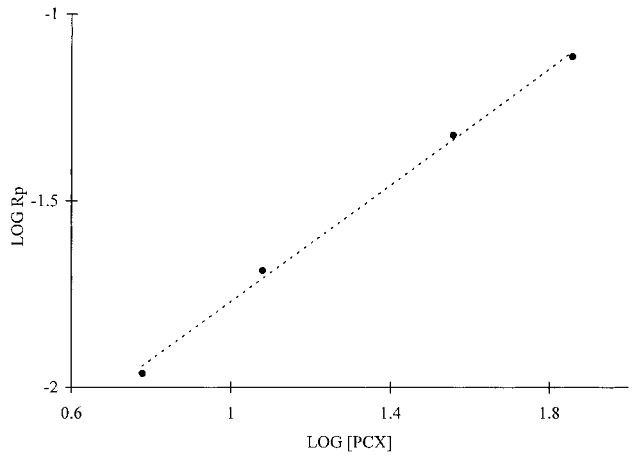


Fig. 3. log R_p vs. log [PCX] for polymerizations performed with PC8 as surfactant

the slope of the initial part of the curves increases with increasing surfactant concentration. Of course, higher conversions at similar intervals of polymerization are due to the increase in the number of polymerization sites[21]. Emulsion polymerizations with PC6, PC8, and PC12 surfactants have shown a similar behavior.

In the same context, the relation between log R_p vs. log [PCX] for polymerizations carried out using PC8 is presented in Fig. 3. According to this figure, $R_p \propto [PCX]^{\approx 0.7}$, which is not so different from predictions of the Smith-Ewart[16] and Gardon[17] theories.

Effect of chain length

The relation between conversion and time for all pyridinium surfactants at the same concentration (36 mmol) is presented in Fig. 4. It is important to note that the four PCX surfactants show similar curves, which is quite normal considering the similar N_p values for all of them. However, in spite of the N_p value for DPB (Tab. 1), which is similar to that of the PCX surfactants, the slope of the initial part of the curve for this surfactant is considerable less pronounced than the one observed in experiments using PCX surfactants. The rate of polymerization of experiments carried out using 12 mmol and 36 mmol of PCX are also summarized in Tab. 1. The difference between polymerization rates obtained using PCX and DPB could be associated to the presence of the methoxybiphenyl group in the non-polar part of the PCX molecules. At this moment we do not have an explanation for the observed enhancement of the rate of polymerization when PCX surfactants are used, but it could be associated to the lateral molecular interactions of surfactants segregated at the interface, which could perturb in some way the entrance of free radicals to the growing particle, thereby modifying the kinetics of polymer formation.

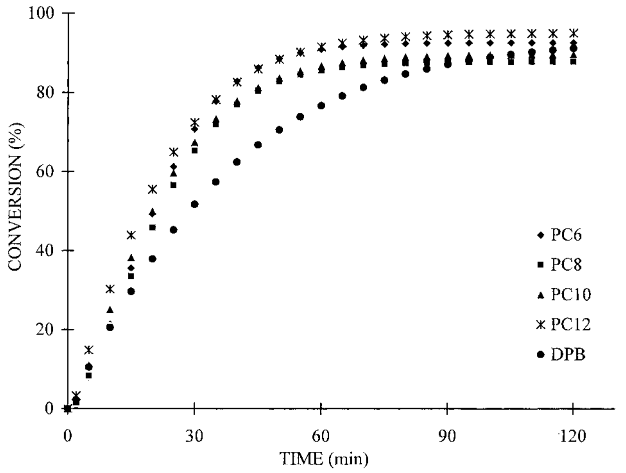


Fig. 4. Conversion vs. time for emulsion polymerization experiments using DPB and PCX surfactants at a concentration of 36 mmol

As mentioned, the R_p in emulsion polymerization is related to N_p, which in turn depends on the surface area of the surfactant polar head group and not on the length of the radical substitution. Hence, for reactions stabilized with an homologous series of linear molecules containing one polar head group and one alkyl chain of different length, the R_p must show similar values, as it occurs approximately in emulsions stabilized by the PCX series. Nevertheless, it has been reported[22] that R_p could increase several orders when the number of methylene groups of an alkyl chain of an homologous series of surfactants varies from 8 to 18. In spite of the difference of the length among the PCX surfactants, the molecular packing of surfactants of each chain length must be similar because all of them have similar chemical structures.

Particle size and particle size distribution

Taking into account that N_p is quite similar for all PCX and DPB, we would expect also a similar particle diameter (D_p) for all of them. It can be seen in Tab. 2 that the measured D_p values for experiments carried out with PCX and DBP at a surfactant concentration of 36 mmol are between 72.0 and 85.0 nm and those with 12 mmol are between 100 and 108 nm, respectively. As expected, D_p decreases when [PCX] increases (see the D_p value for the PC8 series). It is important to note that all latices show a narrow particle size distribution (monodisperse). This result has been corroborated by electronic microscopy. Fig. 5 shows a SEM micrography for a polystyrene latex obtained using PC8 as surfactant. It can be noticed that the particles are quite spherical with very similar diameter (monodisperse). According to this result the rigid rod-like group in the pyridinium surfactants does not affect the monodispersity of latices because the PSD is quite similar to DPB and PCX surfactants.

Tab. 2. Particle diameters (D_p) and particle size distribution (PSD) for polystyrene latices. Data from light scattering measurements

PCX	$\frac{[PCX]}{mmol}$	$\frac{D_p}{nm}$	PSD
PC6	12	106.1	0.024
PC6	36	72.7	0.080
PC8	6	155.8	0.002
PC8	12	107.9	0.023
PC8	36	74.1	0.034
PC8	72	63.8	0.059
PC10	12	101.7	0.059
PC10	36	75.6	0.060
PC12	12	102.7	0.024
PC12	36	84.5	0.041
DPB	36	76.4	0.032

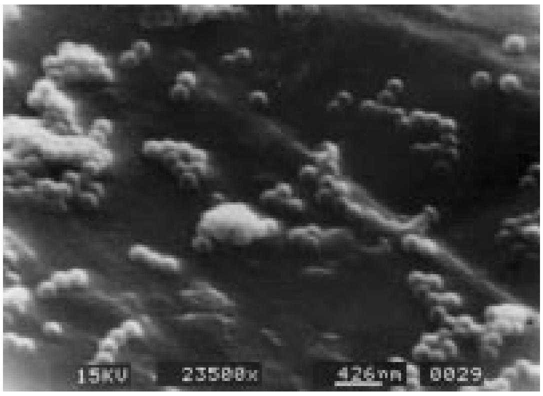


Fig. 5. SEM micrography for a polystyrene latex obtained using PC8 as surfactant, [PCX] = 6 mmol

Molecular weight

The molecular weights for polymers obtained using different concentrations of PC8 as surfactant is presented in Tab. 3. As expected the molecular weight increases with increasing PCX concentration. This result is again related to the N_p value, but it could be also related to the probability for a second free radical to enter into the growing particle in which the polymerization reaction was already initiated.

Tab. 3. Weight average ($\overline{M}_w$) and number average ($\overline{M}_n$) molecular weights and polydispersity index (I) for polystyrene obtained using PC8 as surfactant

$\frac{PC8}{mmol}$	$\overline{M}_w$	$\overline{M}_n$	I
6	700 000	160 000	4.37
12	830 000	240 000	3.46
36	925 000	246 000	3.76
72	1 500 000	350 000	4.29

Conclusions

This work is the first attempt to polymerize styrene with a surfactant having a rigid rod-like methoxybiphenyl group (PCX), and results indicate good stability during and after polymerization. The CMC values for these amphiphiles are very low when compared with similar amphiphiles with non-rigid moieties. As expected, the stability of the latices depends on the number of particles/mL of water (N_p). At N_p values higher than 5×10^{14} or surfactant concentration higher than 36 mmol, the latices were fairly stable. It has been found for the PCX surfactants that the N_p value is not affected by the presence of the methoxybiphenyl group; the N_p value depends only on the surface area of the polar head group. In spite of the similar N_p values between PCX and dodecylpyridinium bromide (DPB), it has been observed that emulsions prepared with DPB were considerably less stable at similar concentrations. This difference in stability could be related to lateral molecular interactions between molecular moieties of the rigid rod-like group of amphiphiles segregated at the water/monomer interface. It seems that the methoxybiphenyl group also affects the polymerization rate (R_p) because the polymerizations carried out with PCX surfactants show a higher R_p than the one carried out with DPB at the same concentration. Finally, latices prepared with PCX surfactant have shown particle diameters from 60 to 160 nm with a very narrow particle size distribution (monodisperse).

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