Comblike Polymers with Octadecyl Side Chain and Carboxyl Functional Sites: Scope for Efficient Use in Miniemulsion Polymerization

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ABSTRACT: The scope for the efficient use of comblike polymers to synthesize polystyrene latexes with a narrow distribution of particles in a size range of 100−250 nm has been demonstrated. The polymers comprising of octadecyl side chains with a statistical distribution of carboxylic groups and in the molecular weight range of ca. 4×10^4 have been synthesized by free radical polymerization reaction. The characterization of polystyrene latexes synthesized using these comblike polymers with different acid compositions, 0.11 and 0.31 mole fraction of both acrylic and methacrylic acid in the feed, with respect to the particle size, the surface coverage of the latex surface with carboxylic groups, and the surface tension of the latex throws interesting information on the probable mechanism underlying this typical miniemulsion polymerization system. The high efficiency of the polymer in miniemulsion polymerization suggests that the polymer undergoes a typical reorganization process with octadecyl groups covering the styrene oil phase and the retaining carboxylate groups being located at the interface. The stability of the miniemulsion droplets prior to polymerization against aging is in support of the suppression of Ostwald ripening and coalescence processes and proves that the polymer acts both as a surfactant and—although located at the interface—as an osmotic agent. Preservation of the original particle size and distribution throughout polymerization underlines the predominance of droplet nucleation.

Introduction

The characteristic and significant features of miniemulsions, (a) to perform polymerization under preservation of droplet size, distribution, and composition and (b) to use surfactants in a very efficient manner, account for their growing scientific and technical interest. Miniemulsions can be described as aqueous dispersions of relatively stable oil droplets in the size range 50−500 nm.[1] They are prepared by shearing a system containing oil, water, surfactant, and a hydrophobe.[2] The stability of a miniemulsion system is basically dictated by (1) the suppression of Ostwald ripening (τ_1 process),[3] controlled by an osmotic pressure in the droplets afforded by the hydrophobe, and (2) minimizing coalescence enabled by a sufficient surface coverage by surfactants. Miniemulsion formulations, even when they are critically stabilized,[3] promote droplet nucleation mechanism[4] and thus afford an 1:1 copying of droplets to particles[5] as established by a combination of SANS, surface tension measurements, and conductometry.[6]

The functional roles of the hydrophobes and the surfactants used in miniemulsions have been well elaborated in recent literature. The formulation of a stable miniemulsion depends on the choice of the hydrophobe. Various hydrophobes exhibiting different chemical structures and satisfying the primary requirement of poor water solubility in the range 5.9×10^{-6}−4.1×10^{-5} g/dm^3 are described in the literature. To cite a few, e.g. cetyl alcohol, hexadecane,[4,7,8] dodecyl mercaptan,[9] and reactive alkyl methacrylates[10] have been employed as hydrophobes. It was shown that long chain alkanes are more effective hydrophobes than fatty alcohols of the same chain length. Recent reports on the additional influence of predissolved polystyrene[11,12] in miniemulsion system employing cetyl alcohol in comparison with those containing hexadecane substantiate the significance of the interaction between the hydrophobe and the dispersion media in controlling the Ostwald ripening process. The evaluation of reactive methacrylates with C_{12} (lauryl methacrylate, LMA) and C_{18} (stearyl methacrylate, SMA) chains as hydrophobes in miniemulsion formulations in the presence of a nonionic surfactant has shown the predominant operation of a droplet nucleation mechanism as a consequence of suppressed Ostwald ripening.[10] It was shown that SMA performs as an efficient hydrophobe equivalent to hexadecane.

A systematic study using surfactants drawn from nonionic, cationic, and anionic series has revealed the very efficient, close to ideal use of surfactant in miniemulsions.[14] Low surface coverages of the droplets afforded by a model surfactant like sodium dodecyl sulfate (SDS) have been found to effectively control the collision process. The equilibrium concentration of the surfactant required to form critically stabilized miniemulsions has been found to be well below the cmc, and this rules out the existence of micelles in the dispersion phase. A much higher surface tension of the polymerized latexes in comparison to the equilibrium surface tension values of respective surfactants further substantiate the absence of surfactant micelles in the dispersion phase and hence rules out micellar or homogeneous nucleation polymerization. It has been shown recently that miniemulsions realize the minimal droplet size for the distinct amount of surfactant, and they are critically stabilized with respect to collision processes (τ_2).[3]

Scope of Comblike Polymers in the Heterophase Polymerization. With the functional roles of hydrophobes and surfactants in miniemulsions being demonstrated through extensive and exhaustive studies, it becomes an open question now whether a comblike amphiphilic polymer consisting of a long hydrophobic side chain similar to hydrophobe and a polar functional

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Table 1. Synthesis of Comblike Polymers: Mole Fraction of the Comonomers in the Feed, Ionomer, and Gel Permeation Chromatography (GPC) Characteristics

sample no.	polymer	mole fraction of ODMA in the feed	mole fraction of acid monomer in the feed	mole fraction of ODMA in the ionomer	mole fraction of acid in the ionomer	mol wt (M_w) 10^4	poly-dispersity	intrinsic viscosity, [η] mL/g
1	CPAA1	0.69	0.31 AA	0.76	0.24	4.7	3.07	27.4
2	CPAA2	0.89	0.11 AA	0.91	0.09	3.4	2.06	20.5
3	CPMA1	0.69	0.31 MA	0.73	0.27	4.3	3.15	26.4
4	CPMA2	0.89	0.11 MA	0.90	0.10	4.3	1.98	22.7

site capable of adsorbing at the oil/water interface could be an alternative and ideal choice in this special heterophase polymerization system. It has been shown that monomer-soluble polymeric hydrophobes could be successfully used as osmosis controlling agents to produce kinetically stable miniemulsions.[15] The use of amphiphilic polymers in miniemulsions totally eliminating low molecular weight hydrophobes and surfactants however is not described and could have specific advantages. In the first place, the problems associated with the evaporation or film formation of the hydrophobe (smell and oily grip) could be eliminated. Second, the high water sensitivity of such films due to surfactant mobility (whitening and pinhole formation) could be suppressed. Third, the incorporation of the carboxylic polymer leads to a convenient functionalization of the particles.

In this paper, comblike polymers with octadecyl side chains and a statistical distribution of carboxylate groups synthesized by free radical polymerization were chosen to investigate whether such polymers really are able to replace the low molecular weight hydrophobe and the surfactant at the same time. The scope for the use of these polymers in miniemulsion systems would primarily require the ability of the polymer to undergo the typical organization processes through high shear monomer droplet formation. The following issues will be addressed in this paper:

1. We will investigate the scope for the effective use of the synthesized comblike polymers in miniemulsion formulations involving styrene as the monomer oil phase and subsequent polymerization. The miniemulsion of styrene in water would be formulated only with the comblike polymers, and in the absence of traditional hydrophobes or surfactants, and the reaction will be started using an oil-soluble initiator, azobis(isobutyronitrile) (AIBN). The comblike polymer therefore has to act as surfactant and as an osmotic agent at the same time.

2. The role of functional polar carboxyl sites in influencing the miniemulsion formulation and polymerization reaction will be investigated by employing comblike polymers bearing different kinds and concentrations of carboxylate groups. The difference in behavior of poly(methacrylic acid) and poly(acrylic acid) as a function of pH supports a possible effect of the distribution of carboxylic acids along the amphiphilic chain in contributing to different interfacial characteristics of the copolymers. For this reason, copolymers have been synthesized using 0.31 and 0.11 mole fractions of both acrylic and methacrylic acid in the feed. The influence of polar functional sites of the synthesized polymers in influencing the surface coverage of the droplets and the ultimate particle size distribution will be analyzed by the particle size determination and surface tension measurements.

3. The interfacial tensions of the styrene/water interface is measured after the addition of aliquots of the copolymer to the styrene phase as a function of pH in order to demonstrate the functional role of adsorption of the polymer at the oil/water interface facilitated by hydrophilic carboxylate ions.

Experimental Section

Materials. Acrylic acid and methacrylic acid (Aldrich) were purified by distillation. Octadecyl methacrylate (ODMA), azobis(isobutyronitrile) (AIBN) from Aldrich, and ethyl methyl ketone (EMK) from Fluka were used as received. Deionized water was used in all the experiments. A standard poly(octadecene)-*co*-(maleic anhydride) (Sokolan CP9, $M_w = 12\,000$) was donated by BASF and used as a reference system. Styrene from Aldrich distilled under reduced pressure and stored at −5 °C was used in the polymerization experiments.

Synthesis of Ionomers with an Octadecyl Side Chain and a Carboxyl Functional Site. The statistical copolymers of ODMA and acrylic or methacrylic acid have been synthesized employing the simple solution polymerization technique. Typically, to a stirred homogeneous solution of ODMA (0.98 mol) in EMK were added acrylic acid (0.46 mol) and AIBN (1% on monomer weight basis). By this, about 65% conversion was achieved. The reaction was performed by heating the mixture for 6 h to 60 °C under continuous stirring. The ultimate polymer was isolated from the reaction medium using methanol as precipitating solvent. Repeated processes of dissolution in EMK and precipitation using methanol ensure almost complete removal of unreacted monomer. The polymer was finally dried under vacuum at room temperature and further characterized using nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) (yield, 45%). Four sets of ionomers have been prepared, where the comonomer ratio between acrylic and methacrylic acid and the respective mole fractions in the feed mixture were varied as presented in Table 1. Acrylic/methacrylic acid component in the copolymer has been estimated from pH titration using sodium methoxide as titrant, and the results are presented in Table 1.

Formulation of Miniemulsions Employing the Amphiphilic Copolymers. A 6 g sample of styrene was mixed with the respective amounts of the ionomers, 150 mg of AIBN initiator, and 24 g of water containing the required amount of sodium hydroxide to maintain the final pH of the dispersion at 8.50. After stirring for 1 h, the dispersion was sonicated for 2 min at 90% amplitude with a Branson sonifier W450 Digital. The polymerization reaction was carried out at 65 °C for a period of 6 h. For comparison, such miniemulsion formulations have been attempted also with a technical, alternating copolymer of octadecene and maleic anhydride.

Characterization of the Ionomers. NMR measurements for the characterization of the ionomers were performed on a DPX 400 (400 MHz) spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal standard. The polymer molecular weights and the intrinsic viscosities were determined by GPC analysis performed on a P1000 pump with UV1000 detector ($\lambda = 260$ nm) (both from Thermo Separation Products) with 5 μm 8 × 300 mm SDV columns with 10^6, 10^5, and 10^3 Å from Polymer Standard Service in THF with a flow rate of 1 mL min^{-1} at 30 °C. The molecular weights and the intrinsic viscosities were calculated with a calibration relative to PS standards.

Methods for the Characterization of the Polymerized Miniemulsions. The particle sizes of the miniemulsion latexes were measured using a Nicomp particle size analyzer (model 370, PSS Santa Barbara, CA) at a fixed scattering angle of 90°. The surface tension measurements were performed with the K-12 processor tensiometer from Krüss employing the DuNuöy-ring method. The radius of the Pt−Ir ring RII2 was 9.45 mm, and the wire had a radius of 0.185 mm. The values reported below are averages of several measurements.

Interfacial Tension Measurements. Interfacial tension measurements were performed for the styrene/water interface in the presence of copolymers as a function of the carboxylate content and pH at 25 ± 0.1 °C using a K-12 processor tensiometer described above. In a typical measurement, 56 mL of water was taken in a beaker, and 28 mL of styrene containing fixed concentrations of the polymer was added on top of the aqueous phase. The platinum ring was fully immersed into the styrene phase. The rising of stage with styrene water sample was enabled and controlled by a built-in microprocessor and stopped automatically as soon as the ring came into contact with water phase. The average value obtained from several measurements is reported here.

Results and Discussion

Characteristics of the Synthesized Comblike Polymers. The ^{1}H NMR spectrum of a representative polymer, CPMA1, indicates the absence of unreacted monomers in the synthesized polymers and also the formation of copolymer through the addition across the vinyl bond. This is shown by the complete absence of vinyl peaks at δ 5.5−6.5 ppm. Peak assignments for the typical copolymer, CPMA1, are as follows. δ: 0.86−0.9 ppm, end $-CH_3$ of octadecyl side chain; 1.09 ppm, CH_3 attached to α-carbon of main chain; 2.0−2.34 ppm, $\rangle CH_2$ of backbone chain; 3.67−4.01 ppm, α-$\rangle CH_2$. Almost similar ^{1}H NMR spectra have been observed with the other polymers, CPMA2, CPAA1, and CPAA2. The weight-average molecular weight of the polymers estimated using GPC are presented in Table 1. The estimation of molecular weight and intrinsic viscosity of the investigated ionomers from GPC basically applies the Mark−Houwink−Sakurada parameters estimated for standard linear polystyrene. There is no doubt that solute−solvent interaction and size parameters play significant roles in such measurements, and there is scope for underestimation of molecular weight and intrinsic viscosity data. However, when a comparison is made among polymers with similar, but different contents of chemical components, this method serves useful, especially to control the molecular weight range and polydispersity. In the synthesis of the polymers, conditions have been standardized so as to produce low molecular weight polymers with molecular weights in the range of $(3.4-4.7) \times 10^4$ and polydispersity of about 2.0−3.2 in order to minimize the probable additional effects, in droplet formation, droplet number, and polymerization reaction. Octadecyl methacrylate has been chosen as one of comonomers in the synthesis of comblike polymers of interest, in view of its ability to control Ostwald ripening process and perform as an efficient hydrophobe equivalent to the well-established hexadecane. Acrylic and methacrylic acids are in heterophase polymerization well-known hydrophilic comonomers capable of being located at the oil/water interface contributing to the stabilization of the latexes. The compositions of the monomers in the polymer as estimated from a titration method are of course slightly different from the feed compositions (Table 1). Various factors such as reactivity of the respective monomers, composition of the feed mixtures, and propagating radicals might have contributed to such differences. The main aim of this work is to explore the scope for application of the ionomers in miniemulsion system under investigation. Studies on estimation of reactivity ratios or change in composition of the polymers with percentage of conversion are therefore beyond the scope of this work. However, in view of the significance of such parameters, works in this direction are in progress.

Table 2. Characteristics of Polystyrene Latex Produced Using Comblike Polymers

polymer	[polymer] [wt %]	particle size [nm]	std dev	surf. area per COO^- [nm^2]	σ [mN/m]
CPAA1	1.66	190	0.38	3.57	61.5
	5.00	171	0.16	1.38	57.1
	10.00	170	0.17	0.73	57.8
CPAA2	2.50	255	0.44	5.47	61.5
	5.00	241	0.15	2.98	60.8
CPMA1	2.50	189	0.42	2.11	61.5
	5.00	131	0.22	1.56	60.5
	10.00	108	0.21	1.00	59.8
CPMA2	2.50	246	0.54	5.10	62.5
	5.00	213	0.32	3.00	60.3
Sokolan CP9	5.00	182	0.55	0.18	57.8
	10.00	112	0.27	0.14	57.2

Characteristics of the Miniemulsion Latexes. a. Effect of Concentration of Polymer on the Particle Size. Table 2 presents data on particle sizes with standard deviations, surface coverage of the particles expressed as area /molecule of sodium acrylate (or methacrylate), and surface tension of the latexes produced using different kinds of synthesized polymers. The retention in surface tension characteristics and particle size distribution of miniemulsion before and after polymerization reaction confirm the formation of critically stabilized miniemulsions, indicating the droplet identity to particle. Extensive investigations on the droplet/particle identity are given elsewhere.[6] Miniemulsions of polystyrene have been formulated using different concentrations of the polymers in order to evaluate the efficiency of the polymers in controlling the droplet number and therefore the droplet size. A continuous decrease in particle size from 189 to 108 nm with a change in concentration in the range 2.5−10% of for example polymer CPMA1 could be observed. A similar trend of decrease in the particle size (190 to 170 nm, Table 2) with increasing concentration of the polymer has been observed in the case of the polymer CPAA1, although with different slope. The particle size distributions with 2.5 wt % polymer are comparably broad, and it has to be stated that this is about the minimal surfactant load where stable miniemulsions can be formulated. An attempt to formulate miniemulsions employing a lower concentration of polymer to an extent of 1.25% resulted in unstable particles with coagulum. At higher amounts of surfactant (i.e., 5% and 10%), the miniemulsions are however very stable and rather monodisperse. It is to be noted that the commercial copolymer, Sokolan CP9, is also found to stabilize miniemulsions, however with higher sample polydispersities, which might be due to the lower homogeneity of the technical product.

A quantitative picture on the surface coverage of the droplets could be obtained from the surface area per molecule of sodium acrylate (or methacrylate) from stoichiometry and particle size with the assumption that all the carboxylate groups of the copolymer are adsorbed at the interface.[3] All the miniemulsion polymerization reactions are taken to 100% conversion and result in percent yield of the product. Negligible weight losses occur under the conditions of these reactions.

A comparison of particle sizes of the latexes produced using the same concentration, e.g. 5% copolymer, CPAA (1 and 2), suggests that the polymer CPAA1 comprised of 0.24 mole fraction of carboxylate group produces smaller particles (171 nm) compared to CPAA2 with 0.09 mole fraction acid (241 nm). This observation is also true with respect to the polymers (CPMA) bearing a methacrylic acid group; the polymer with 0.27 mole fraction MAA leads to 131 nm particles, whereas the polymer with 0.10 mole fraction MAA results in particles of 213 nm. It is observed that latexes with smaller particle sizes are obtained in the presence of methacrylic acid polymers, in comparison to acrylic acid polymers. For example, formation of polystyrene latex with mean diameter of 107 nm has been afforded from 10% CPMA1 ionomer, in contrast to CPAA1. Such a difference in the performance of ionomers probably arises from the higher methacrylic acid component of the ionomer as compared to acrylic acid (Table 1).

It has been found that higher concentrations of SDS result in latexes with smaller particle size and the similarity in the trend on influence of SDS and carboxylate group of the polymer on the particle size could be observed. Looking at the area per polar headgroup, it is found that for the polymer with 0.24 mol of acrylic acid an area of 1.38 nm^2 per carboxylate group and for the polymer with 0.09 mol of acrylic acid an area of 2.92 nm^2 is stabilized. For the polymer with MAA the areas per carboxylate group are larger; i.e., with 0.27 mol of methacrylic acid the area per carboxylic group is 1.56 nm^2 and with 0.10 mol of methacrylic acid it is 3.00 nm^2. The larger value for the methacrylate polymers leads to the interpretation that the carboxylate groups of MAA can be better distributed on the surface which is presumably due to copolymerization statistics probably contributing to blockiness of carboxyl groups promoting better adsorption characteristics at the interface. Latexes of similar size prepared with SDS, the most efficient surfactant for miniemulsions we know, show a lower surface coverage (for the 180 nm latex, the area per ionic headgroup is 7.12 nm^2; for 134 nm, the area per SDS molecule is 4.80 nm^2). Note that for SDS the headgroups can adopt any distance, whereas for the blocks, the headgroups are interconnected along the chain ("patches") which means that each polymer just allow one minimal surface coverage. Furthermore, one of the interesting effects of ionomers contributes to a decrease in polydispersity as a function of concentration of ionomer which substantiate the surfactant–cosurfactant effects of ionomers in this miniemulsion polymerization system.

The main driving force for droplet formation involving comblike polymer arises from the adsorption of carboxylate ions at the styrene/water interface. The surface coverage provided by the polymer through the hydrophilic groups protects the droplets against coalescence due to collision and thus afford stable particles.

It is well-known that stable miniemulsion latexes cannot be achieved just by using sodium salts of acrylic or methacrylic acid polymers due to their high hydrophilicity. Octadecyl methacrylate in its monomer form has been established to provide stability to droplets against Ostwald ripening process equivalent to hexadecane. These facts suggest the scope of the octadecyl methacrylate group present in the polymer in regulating the osmotic pressure and therefore controlling the Ostwald ripening process of the droplets, although they are presumably located close to the droplet interface; i.e., the droplets can deal with an osmotic pressure gradient and nevertheless establish a stable situation.

It is inferred that the comblike polymer is capable of undergoing a typical organization process under the conditions of the formation of miniemulsions. Such an organization process probably involves the orientation of hydrophobic octadecyl methacrylate segments toward the styrene oil phase with the adsorption of polar carboxylate group at the oil/water interface. Further experimental evidence is of course required to explore the organization process of the polymers, and this is not covered under the scope of this paper. However, it will be more significant to note that a similar comblike polymer dissolved in cyclohexane is able to contribute to increase in I_3/I_1 intensity ratios of emission peaks of pyrene fluorescence probe, suggesting the scope for the polymer to exhibit a typical organization process contributing to decrease the micropolarity of the system.[17] Also, such an organization process as established from the fluorescence technique has been reported in the case of an alternating copolymer similar to the commercial product.[18]

Surface Tension Measurements. Surface tension measurements on latexes throw useful information on the surface coverage. The tendency of the investigated copolymers to alter the surface tension of water was investigated by measuring the surface tension of solutions containing a maximum soluble concentration of the polymer. The polymer exhibits a very low solubility in water even after altering the pH to 9.0, which was so low that we were not able to determine that by classical means. At these saturation concentrations, CPMA1 and CPAA1 at pH 9 are able to lower the surface tension of water to 48.5 and 49.6 mN/m, respectively. It is shown in Table 2 that all the latexes formed using the copolymers exhibit surface tensions in the range 57.1–62.5 mN/m, which is well above the surface tension of the polymer solutions. This shows that the polymer is preferentially located at the droplet interface and that the concentration in both the water phase and the air–water phase is not saturated. The coverage of the particles is therefore not complete which is an important criterion for the presence of a true miniemulsion. The lower the surface coverage as indicated by higher surface tension results in higher particle size. In the case of CPAA1 polymer, the surface tension slightly decreases from 61.5 to 57.1 mN/m with increasing concentration of the polymer from 2.5% to 5%, ultimately resulting in a decrease in the particle size from 190 to 171 nm. This correlates well with the trend in the change of the calculated area per carboxylate group which changed from 3.57 to 1.38 nm^2. The absence of free or micellar polymer in the water phase also promoted polymerization by droplet nucleation and excludes secondary nucleation, as can be seen from the narrow particle size distribution of the particles as shown by low standard deviations in range of 0.15. It is also important to have a quantitative picture on the styrene/water interface as controlled by the polymer. Thus, interface tension measurements have been performed for the styrene/water interface in the presence of polymer as a function of the pH and the concentration of the polymer. The polymer CPMA1 is able to reduce the interfacial tension of styrene–water (pH 9.0) down to 10.38 and 3.20 mN/m when used in concentrations of 50 mg and 100 mg in 28 mL of styrene (1.78 and 3.56

mmol/L acid units, respectively), as compared to the interface tension of styrene–pure water of about 35 mN/m at 25 °C. A considerable reduction in interfacial tension value in the presence of polymer indicates the efficient adsorption of the polymer at the styrene/water interface. The influence of carboxylate group concentration on such an adsorption process could be seen from the difference in interfacial tension values obtained using same concentrations (50 mg in 28 mL of styrene; this represents 1.78 mmol/L acid units for CPMA1 and 0.57 mmol/L acid units for CPMA2) of the polymers CPMA1 and CPMA2. Thus, the interfacial tension of styrene/CPMA2–water (pH 9.0) is higher (13.52 mN/m) in comparison to that of styrene/CPMA1–water (10.38 mN/m).

A slightly higher surface tension of the latexes containing CPMA1 polymers than those with CPAA1 further suggests the possible difference in adsorption characteristics of these polymers at the interface. This effect is also reflected in the surface coverage characteristics of the latexes. These results suggest a higher efficiency of the methacrylic acid polymer in providing a more efficient lower surface coverage for the droplets there by resulting in formation of smaller droplets.

Conclusion

In this paper, the efficient use of comblike polymers with molecular weights of about 4×10^4 for the formation of polystyrene miniemulsion latexes has been demonstrated. The polymers are comprised of octadecyl acrylate and acrylic or methacrylic acid groups. A typical organization of the comblike polymer is anticipated at the oil–water interface, in view of the different polarities of the comonomer components. It has been shown that it is possible to formulate stable styrene miniemulsion latexes in a size range of 107–190 nm depending on the concentration and the nature of the carboxylic acid groups of the polymer. The increase in the polymer content from 2.5% to 10% contributes to a significant reduction in particle size, especially in the case of methacrylic acid polymers.

Some of the significant observations are that (1) the particle size decreases with increasing concentration of the carboxylate groups, (2) the particle size depends on the area of surface coverage, (3) the surface coverage depends on the nature of the acid component as observed from the increased efficiency of methacrylic acid polymers, and (4) the interfacial tension of styrene/water interface is considerably reduced by the polymer as a function of carboxylate content and pH, which supports the conclusion that the surface coverage provided by the carboxylate group serves as the main driving force for droplet formation mechanism involving these polymers. The higher surface tension values of the latexes in comparison to those of aqueous solutions of polymer show a low concentration of the polymer in the water phase and at the same time incomplete coverage of the particles by the polymer. The formation of latexes with a narrow polydispersity index supports the occurrence of droplet nucleation mechanism during polymerization. This mechanism opens up the possibility for effective use of comblike polymers in the generation of functional miniemulsion latexes where the polymer acts as a surfactant and a hydrophobe at the same time, which is of large industrial significance.

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