

Surfactant-free artificial latexes from modified styrene–maleic anhydride (SMA) copolymers

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Abstract

We describe the preparation of surfactant-free artificial latexes on the basis of poly(styrene-*alt*-maleic anhydride) (SMA) copolymers. The SMA copolymers were first partially alkyl-imidized and then partially ammonolyzed in acetone. Upon adding to water and after the removal of acetone, the modified copolymers formed stable latexes, with a diameter of ~ 150 nm and a PDI < 0.2 . In the absence of alkyl groups the particles became completely soluble in water after a few days. The latexes from the partially alkyl-imidized polymer were found to remain stable at pH > 2 . The incorporation of alkyl groups into the copolymers significantly lowered the T_g of the polymer from 150 to 75 °C, depending on the amount of alkylamines added. It was found that the molecular weight as well as the molar mass distribution of the SMA polymers did not show major effects on the properties of the artificial latexes.

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Keywords: Surfactant-free artificial latex; SMA copolymer; Waterborne coatings

1. Introduction

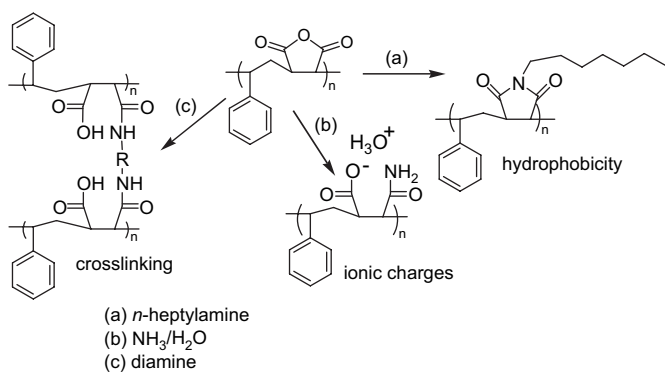
Waterborne coatings play a very important role in today's coatings industry, both in quantity and in versatility, due to more and more stringent legislations limiting the use of large amounts of volatile organic compounds (VOCs). Alkyd, acrylic, epoxy, acrylic/epoxy hybrid, polyurethane, polyester and other resins are widely used in the formulation of waterborne coatings [1,2]. Aqueous polymer dispersions can be divided into two groups: primary and secondary dispersions [3]. The primary dispersions (or synthetic latexes [4]) are formed by polymerization in the dispersed phase, whereas the secondary dispersions (or artificial latexes [4]) are formed via emulsification of a polymer solution. Synthetic latexes generally have a higher solid content than artificial latexes, but in most cases surfactants are used to produce stable latexes. In the

presence of surfactants, latexes are stabilized via steric and/or electrostatic interaction [5,6]. The use of surfactants has a drawback in that the final properties of the material after film formation may be influenced by the surfactants. Surfactant-free emulsion polymerization can be used to overcome this problem. However, the formed particles are generally larger than 500 nm in diameter and the solid content is normally less than 10 wt%. This makes the latex produced in this way not suitable for application as a coating material, since a solid content of 30–40 wt% is generally required.

Alternating copolymers of styrene and maleic anhydride (SMA) are commercially available. Hydrophobic groups can be introduced by partial imidization of the anhydride groups with hydrophobic primary amines [7–11], whereas partial ammonolysis of the anhydride with ammonia leads to an amide and a carboxylic acid group [10] (so called amic acid), which can stabilize SMA-based particles in aqueous medium by electrostatic interactions. Furthermore, the remaining anhydride can be used for crosslinking with, for instance, diamines [12,13] as is schematically represented in Scheme 1. Potentially SMA

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Scheme 1. Schematic representation of the different possible reactions in cyclic anhydride units in the SMA polymer.

can be applied as adhesion promoter for polymer and substrates such as glass and metal surfaces [14] or for enhancing the compatibility of immiscible polymers [15–17]. Although this polymer displays very interesting potential properties in relation to coating applications, the use of these polymers as a coating is still very limited [18].

The objective of this paper is to make artificial latexes by self emulsification of copolymers based on SMA which can be used as waterborne coatings. To check the possible effects of the molecular weight distribution (MWD) of SMA on the latex properties, a polymer with a narrow MWD will be compared with a polymer with a broad MWD made via free radical polymerization. One well-studied route to produce SMA polymers with a narrow MWD is reversible addition–fragmentation chain transfer (RAFT) mediated polymerization [13,19,20]. Besides control over the molecular weight (distribution), the architecture of the polymers can also be regulated to obtain, for instance, block copolymers [13] or gradient copolymers [21].

2. Experimental

2.1. Chemicals

Solvents used for the synthesis of polymers, such as methyl ethyl ketone (MEK) and *i*-propanol, as well as for the preparation of the dispersions (acetone), were purchased from Biosolve and were used without further purification. Styrene (St) was obtained from Merck and disposed of inhibitor (4-*tert*-butylcatechol) by using an aluminum oxide (basic, activated, obtained from Acros) column prior to use. α,α' -Azobisisobutyronitrile (AIBN) was purchased from Merck and used as received. Maleic anhydride (MAN) (Aldrich, 99%, briquettes) was ground and used without any further purification. *n*-Heptylamine (99%) was purchased from Aldrich and used without purification. Ammonia solution (25 wt% in water) was purchased from Merck, and titrated to determine the NH_3 concentration prior to use. Deuterated DMSO was obtained from Cambridge Isotope Laboratories, Inc. 1,2-Cyclohexyldicarboxylic anhydride (CDA) was purchased from Acros, and dried at 120 °C prior to use. A polymer synthesized with

standard free radical techniques (SMA-FR, St/MAN molar ratio: 1:1) was kindly provided by Sartomer (SMA 1000F) and used as received.

2.2. Synthesis of poly(styrene-*alt*-maleic anhydride), SMA-RAFT

First, the RAFT agent 2-phenylprop-2-yl dithiobenzoate was synthesized as described in literature [22], and purified by liquid chromatography on a silica column using a mixture of equal volumes of pentane and heptane; 30.0 g (0.288 mol) St, 29.80 g (0.300 mol) MAN, 3.15 g (12 mmol) 2-phenylprop-2-yl dithiobenzoate and 0.189 g (1.2 mmol) AIBN were dissolved in 300 ml MEK and degassed by performing three freeze–pump–thaw cycles. The reaction mixture was then put in a 90 °C oil bath and left stirring overnight under an argon atmosphere. Precipitation in 1 l *i*-propanol yielded 48.2 g of polymer after drying in a vacuum oven at 70 °C for 20 h.

2.3. Imidization of anhydride

A two-step reaction was performed to convert some of the anhydride groups into imides. The first step was the addition of an amine to obtain amic acid. The second step led to ring closure of the amic acid to form the imide. A 40 ml acetone solution containing 3.4 g *n*-heptylamine was dropwise added to a solution of 20 g polymer in acetone at room temperature. This was left to stir for 30 min at room temperature, followed by removal of solvent at 40 °C on a rotary evaporator. The dry material was then put in a vacuum oven at 150 °C for 20 h to convert the amic acid to a maleimide residue, yielding 23.0 g of partially imidized polymer.

This imidization reaction was also performed by using a model compound, CDA in $\text{DMSO-}d_6$; 0.115 g (1 mmol) *n*-heptylamine was dissolved in 3 ml $\text{DMSO-}d_6$ and added dropwise to 0.154 g (1 mmol) CDA dissolved in 3 ml $\text{DMSO-}d_6$ at 150 °C. Samples for NMR analysis were taken every 30 min.

2.4. Self-emulsification

First 4 g ammonia (25 wt% in water) was added to 100 ml acetone at room temperature. The ammonia solution was then added dropwise to a solution of 30 g partially imidized polymer in 500 ml acetone and left stirring for half an hour. This mixture was then dropwise added to 270 ml water under vigorous stirring and application of a nitrogen flow to evaporate the acetone. This resulted in dispersions with a solid content of 10 wt%. Higher solid contents (30%) could easily be reached by evaporation of water, without changing the properties of the latex.

2.5. Characterization

^1H NMR and ^{13}C NMR measurements were performed at room temperature on a Varian Mercury 400 or Varian Gemini 300 spectrometer in $\text{DMSO-}d_6$.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was performed on a Bio-Rad Excalibur FTS3000MX infrared spectrometer (four scans per spectrum, resolution: 4 cm^{-1}) with an ATR diamond unit (Golden Gate). The measurement was performed by applying a DMSO solution of the material on the ATR diamond. A full spectrum was taken every 5, 10 or 20 s (depending on the rate of the reaction). Heights of the carbonyl peak at 1710 cm^{-1} were taken as a measure of the extent of the reaction. The signal arising from the aromatic ring of the styrene unit at 700 cm^{-1} was used as internal standard for the polymer systems, whereas the peak at 2937 cm^{-1} , originating from the C–H stretching of CDA, was taken as reference for the model compound measurements.

Gel permeation chromatography (GPC) was used to determine both molecular weight and molecular weight distribution of the polymers. A Waters GPC with a Waters model 510 pump and a model 410 differential refractometer were used at room temperature with THF, containing 5 wt% of acetic acid, as eluent. Two mixed bed columns (Mixed-C, Polymer Laboratories) which were calibrated with polystyrene standards ranging from 600 to $7 \times 10^6\text{ g/mol}$ were used to perform the chromatography.

Differential scanning calorimetry (DSC) was carried out on a TA Instruments Advanced Q1000 calorimeter. Samples were heated from 20 to $180\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C/min}$ followed by an isothermal step for 5 min. A cooling cycle to $25\text{ }^\circ\text{C}$ with $10\text{ }^\circ\text{C/min}$ was performed prior to a second heating run to $180\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C/min}$. T_g was determined from the second heating run.

Dynamic light scattering (DLS) experiments as well as ζ -potential measurements were performed on a Malvern Zeta-Sizer Nano ZS at $20\text{ }^\circ\text{C}$. The particle size and the distribution thereof were determined according to ISO 13321 (1996). The concentration of the samples was $\sim 0.1\text{ wt\%}$, unless stated otherwise. All samples were measured three times to obtain an average value. The pH dependence measurements of size and ζ -potential were performed by adding a 0.071 M HNO_3 aqueous solution with a Malvern MPT-2 Autotitrator to the latex, starting at the pH of the dispersions as prepared. The pH value was lowered by 0.5 prior to the next ζ -potential and particle size determination until $\text{pH} = 2$.

Cryogenic-transmission electron microscopy (cryo-TEM) was performed on a FEI Tecnai G2 Sphera microscope at $-170\text{ }^\circ\text{C}$, operated at 200 kV; $3\text{ }\mu\text{l}$ samples were applied to a glow discharged Lacy grid in a Vitrobot™ (PC controlled vitrification robot, FEI) instrument at $22\text{ }^\circ\text{C}$ and 100% relative humidity. The excess of dispersion was removed by blotting with a filter paper, followed by vitrification of the film by insertion into liquid ethane at $-172\text{ }^\circ\text{C}$. Photos were obtained with a Gatan $1\text{ k} \times 1\text{ k}$ CCD camera.

3. Results and discussion

3.1. Polymer synthesis

SMA copolymers with relatively narrow MWD were obtained by RAFT-mediated polymerization, using 2-phenylprop-2-yl dithiobenzoate as RAFT agent. The M_n of the synthesized

Table 1

Molecular weights (relative to PS standards) of the used polymers as determined with GPC

	M_w (g/mol)	M_n (g/mol)	M_w/M_n
SMA-FR	4000	2650	1.95
SMA-RAFT	5200	4200	1.23

polymer was determined by GPC to be 4200 g/mol with $M_w/M_n = 1.23$ (Table 1). To compare the possible influence of the MWD on the artificial latex properties, a polymer synthesized by free radical polymerization, SMA-FR, was also studied, which has an $M_n = 2650\text{ g/mol}$ with $M_w/M_n = 1.95$.

3.2. Preparation of artificial latexes

3.2.1. Latexes from SMA without imidization

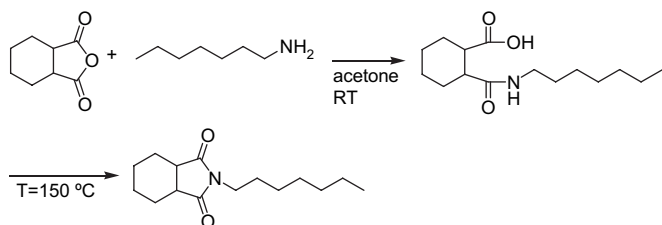
Both SMA-RAFT and SMA-FR were used to create artificial latexes. The polymer was first ammonolyzed by adding NH_3 (aq) to the polymer solution in acetone to increase the hydrophilicity of the polymer, followed by the dropwise addition of the partially ammonolyzed polymer solution to water under vigorous stirring, leading to the formation of latex. The amount of ammonia added played a crucial role in the preparation of a stable dispersion. When more than 70 mol% of all anhydride was ring-opened with ammonia, the polymer became fully water soluble within 24 h. When less than 30% of the anhydride was ammonolyzed it was found that the particles formed aggregates and precipitated upon addition to water. When 30–70 mol% anhydride was ammonolyzed, initially stable latexes were obtained.

However, none of these initially stable latexes retained their colloidal stability longer than a week. Unreacted anhydride groups were apparently hydrolyzed during storage, to form carboxylic acids and render the polymer more hydrophilic. This was inferred from a drop in pH of the dispersions. Initial dispersions showed a pH value of 7, whereas the solutions showed pH values of 3–4, which is in accordance with values reported for fully dissolved SMA [23].

3.2.2. Latexes from partially imidized SMA

To prevent the complete hydrolysis of the anhydride, the polymer was partially imidized by reacting some anhydride groups with *n*-heptylamine. The produced imides are hydrophobic and much more stable against hydrolysis and will therefore form the core of the particles upon addition to water. Grundke et al. [7] and Appelhans et al. [8] have described reactions between amines and anhydrides to obtain imides. A similar approach was used in this paper (Scheme 2). To study this reaction by NMR a model compound CDA was chosen. The main problem with NMR studies of SMA polymer was the overlapping of peaks in both ^1H and ^{13}C NMR spectra, preventing quantitative analysis [24].

NMR revealed the mechanism of the imide formation, which was found to consist of two steps. At room temperature the addition of the amine to the anhydride unit led to the formation of amic acid, which was then converted to imide



Scheme 2. Reaction between CDA and *n*-heptylamine, as a model reaction for the imidization of SMA. Addition of a primary amine at room temperature leads to the formation of amic acid and heating to 150 °C leads to the ring-closed imide.

after being heated to 150 °C. The formation of the amic acid was indicated by ^{13}C NMR in the carbonyl region by the decrease of the peak at 174.0 ppm and the formation of peaks at 176.1 ppm and 185.9 ppm, as shown in Fig. 1a. The ring-closed imide shows only one peak at 179.2 ppm. With ^1H NMR the presence of the ring-opened amide was indicated by the peak at 7.6 ppm (Fig. 1b). The ring closure was apparent from the CH_2 -signal adjacent to the imide nitrogen, which was found at 3.3 ppm. After completion of the reaction only the peaks arising from the imide were observed in both ^{13}C and ^1H NMR (as shown in the insets of Fig. 1).

Besides NMR the imidization of the anhydride groups was further verified with ATR-FTIR. CDA was again used as the model compound. The ring opening of the anhydride at room temperature led to the disappearance of the anhydride signals at 1780 and 1855 cm^{-1} (Fig. 2a and b). Furthermore, two new peaks emerged (Fig. 2b), one belonging to the carbonyl stretching of the carboxamide (1661 cm^{-1}) and the other to carbonyl stretching of the carboxylic acid (1715 cm^{-1}) [25]. Increasing the temperature to 180 °C led to the formation of one peak at 1705 cm^{-1} originating from the two identical carbonyl groups from the imide (Fig. 2c). In this model study, the conversion of the anhydride into imide was complete, since no more anhydride or amic acid signals were observed, which is in agreement with the results obtained by NMR. The imidization of the anhydride in the polymeric samples was investigated

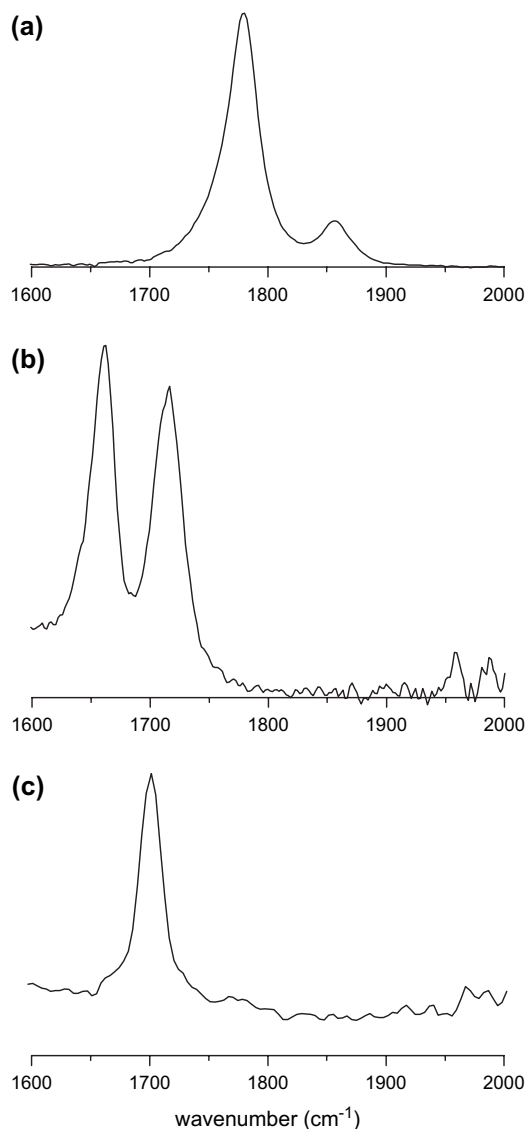


Fig. 2. ATR-FTIR spectra of: (a) CDA, (b) the formation of the ring-opened amic acid at room temperature, and (c) the ring-closed imide after heating at 180 °C.

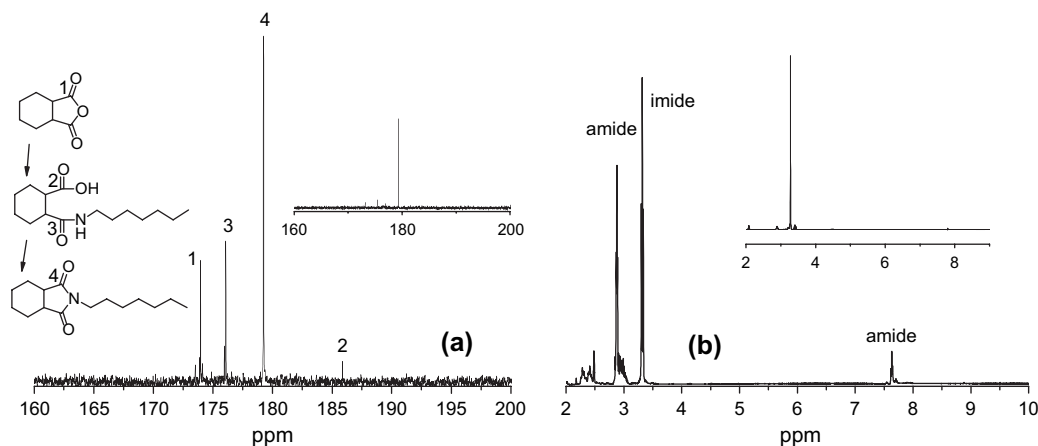


Fig. 1. (a) ^{13}C and (b) ^1H NMR spectra of an equimolar mixture of CDA and *n*-heptylamine in $\text{DMSO}-d_6$ after 10 min at 150 °C. The insets show the spectra after completion of the reaction.

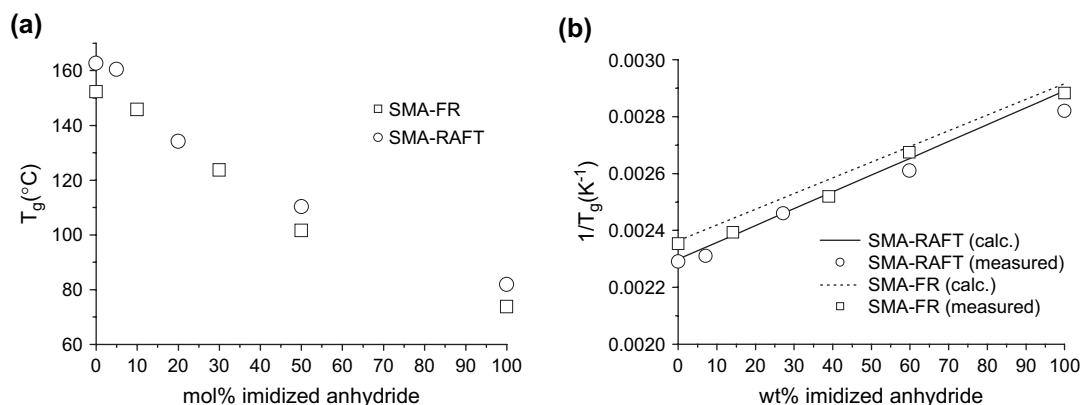


Fig. 3. (a) T_g values of SMA-FR and SMA-RAFT as a function of the degree of imidization, and (b) measured $1/T_g$ values and calculated values by Fox-equation for SMA-FR and SMA-RAFT as a function of the degree of imidization.

in a similar way, and comparable results were obtained under similar conditions.

The amount of *n*-heptylamine incorporated in the polymer backbone had a strong effect on the T_g of the polymers, as can be seen in Fig. 3a. The T_g of the initial polymer decreased with increasing heptylamine incorporation. The T_g of the pure SMA-FR was ~ 150 °C, whereas the T_g of the polymer with 50% of anhydride groups imidized decreased to ~ 100 °C. For the fully imidized SMA a T_g of 75 °C was observed. The SMA-RAFT was found to have a higher T_g , as was expected due to its higher M_n , but showed the same trend as the SMA-FR when the degree of imidization increased (Fig. 3a).

The Fox-equation [26] approximates the T_g of a copolymer ($T_{g,co}$) consisting of comonomers a and b as follows:

$$\frac{1}{T_{g,co}} = \frac{w_a}{T_{g,a}} + \frac{w_b}{T_{g,b}}$$

where w_a and w_b are defined as the weight fraction of units of a and b, and $T_{g,a}$ and $T_{g,b}$ as the T_g of the respective homopolymers. In this study, both $T_{g,a}$ for non-imidized SMA and $T_{g,b}$ for fully imidized SMA were determined experimentally. It was found that the T_g of the partly imidized copolymer followed the Fox-equation quite well, as can be seen in Fig. 3b.

The amount of *n*-heptylamine attached to the polymer backbone can therefore be used as a tool to tune the T_g of the copolymer.

3.3. Properties of artificial latexes

3.3.1. Non-imidized SMA latexes

The particle sizes of the obtained latexes were studied with dynamic light scattering directly after preparation. The latexes from non-imidized SMA were found to have a particle diameter in the order of 100–150 nm, depending on the amount of NH_3 added (Fig. 4a). It should be noted that the particles that had less than 30 mol% of the anhydride ammonolyzed showed aggregation and needed to be filtered prior to the measurement. As was already mentioned, the particles of non-imidized SMA were found to dissolve in water. For the samples with more than 70% ammonolyzed the complete dissolution was observed within 24 h, whereas the particles with lower degrees of ammonolysis gradually dissolved in ~ 4 days.

3.3.2. Imidized SMA latexes

SMA copolymers with different degrees of imidization were used to prepare latexes. It was found that at least

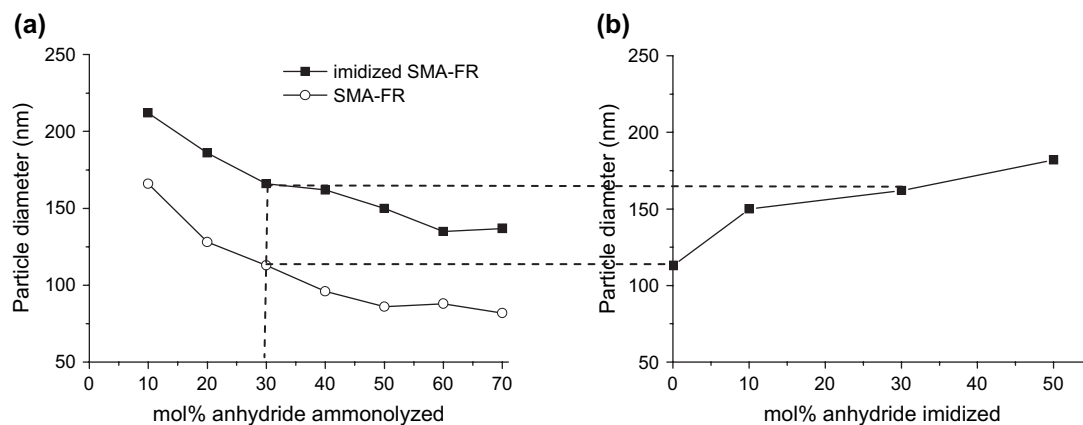


Fig. 4. (a) Particle size dependence on the degree of ammonolysis for latexes from non-imidized and 30 mol%-anhydride-imidized SMA-FR, as determined by DLS. (b) Particle size of SMA-FR latexes as a function of the degree of imidization, with the amount of ammonolyzed anhydride fixed at 30 mol%.

30 mol% of the anhydride should be imidized to obtain latexes that do not become water soluble upon storage. As can be seen in Fig. 4a, for a fixed degree of ammonolysis, the partial imidization of anhydride led to an increase of particle size. The size of the particles from SMA-FR with 30% of the anhydride imidized was ~ 50 nm larger than that of the non-imidized counterpart (Fig. 4a). The size dependence on the degree of imidization was studied in more detail for a polymer with 30 mol% of anhydride ammonolyzed (Fig. 4b). Increasing the amount of hydrophobic groups increased the size of the particles from 110 nm for unsubstituted polymer to 180 nm for a polymer that had 50 mol% of the anhydride imidized.

Furthermore, for both non-imidized polymer and polymer with 30% of the anhydride imidized, it was found that with an increasing degree of ammonolysis (added NH_3) the size of the latex particle decreased, as can be seen in Fig. 4a. This was expected because a higher amount of hydrophilic groups, forming the shell of the particles, was present, as the degree of ammonolysis increased.

Latexes from SMA-FR, with 30 mol% anhydride ammonolyzed and another 30 mol% imidized, were also examined by cryo-TEM (Fig. 5). It was found that the particle diameter was in the range of 20–250 nm, with most of the particles in the range of 60–150 nm, which is in agreement with the results obtained from light scattering experiments.

3.3.3. Influence of molecular weight distribution

To study the possible influence of the MWD of the polymer on latex properties, SMA-FR ($M_w = 4000$, $M_w/M_n \sim 2$) was compared with SMA-RAFT ($M_w = 5200$, $M_w/M_n = 1.2$). The particle size and the distribution thereof (130 nm and $\text{PDI} = 0.13$) for the latex from SMA-RAFT were very similar to those from SMA-FR (130 nm and $\text{PDI} = 0.1$). Apparently,

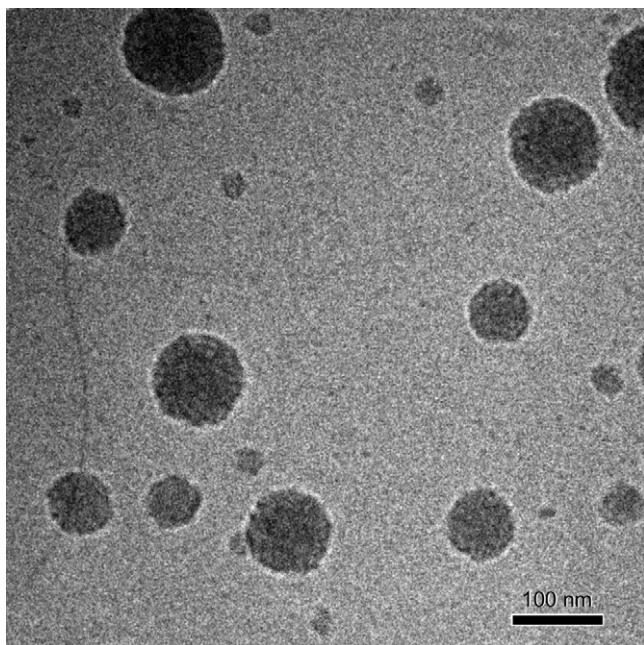


Fig. 5. Cryo-TEM picture of a latex based on SMA-FR, with 30 mol% of the anhydride reacted with NH_3 and another 30 mol% imidized by heptylamine.

the particle size does not depend on the MWD of the two polymers; this is reasonable since the total weight of a particle with a diameter of about 100 nm is a few orders of magnitude larger than the MW of individual polymer chains obtained from either free radical or RAFT-mediated polymerization.

Although the latexes from SMA obtained by RAFT-mediated polymerization did not show any advantages over the polymer obtained by normal free radical polymerization, this technique will be used in future work to control the molecular architecture of the polymers.

3.3.4. Electrostatic stabilization of artificial latexes

To study the stabilization of SMA-based latex particles, ζ -potential measurements were performed. The particles were found to be stabilized by electrostatic interactions, caused by the ring opening of the anhydride units in the polymer by NH_3 . The formed amic acid led to negatively charged carboxylic groups when the polymer was added to water. The ζ -potential of the as-prepared latex ($\text{pH} = 7$) was determined to be -70 ± 2 mV, indicating a strong electrostatic stabilization at this pH. The ζ -potential was found to remain constant during a period of over four months, as can be seen in Table 2. Also, the particle size did not change during this period. This leads to the conclusion that the particles were sufficiently stabilized by electrostatic interactions, and no additional surfactants or stabilizers need to be added to obtain stable latexes.

Another important parameter affecting the latex stability is the pH value. At low pH values the anionic groups are neutralized, leading to less electrostatic stabilization. Therefore, the pH dependence of the particle size and ζ -potential of the SMA-based latexes were investigated by lowering the pH with a 0.071 M HNO_3 solution, as shown in Fig. 6. The latexes from SMA-FR and SMA-RAFT demonstrated similar behavior. For both polymer latexes, the initial pH was just above 7. The initial ζ -potential at pH 7 for both latexes was about -60 mV, and slightly decreased to -65 mV in the pH range of 4–7. This change in ζ -potential is an indication that the remaining anhydride was hydrolyzed, catalyzed by the acid. Furthermore, it was observed that the ζ -potential for both latexes increased sharply (the absolute value decreasing sharply) upon lowering the pH below 4. This indicates that below $\text{pH} = 4$ a significant amount of carboxylic anions was neutralized, leading to decreased electrostatic repulsions. For use as a coating however, the behavior of the system at pH values above 4 is most relevant.

Table 2

Properties of a latex from SMA-FR, with 30 mol% of the anhydride reacted with NH_3 and another 30 mol% imidized by heptylamine, as a function of time at $\text{pH} = 7$

Time	Diameter (nm)	PDI	ζ -potential (mV)
Initially	143	0.16	-74 ± 2
After one week	140	0.13	N.D.
After one month	141	0.12	-69 ± 2
After four months	139	0.12	-71 ± 2

N.D. = not determined.

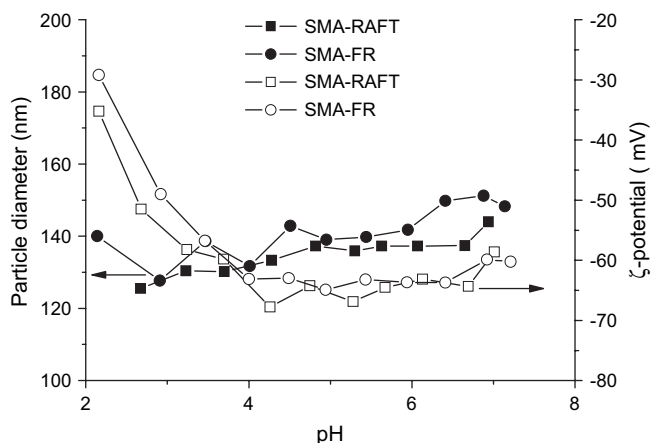


Fig. 6. pH dependence of particle size and ζ -potential for latexes from SMA-FR and SMA-RAFT; for both polymers, 30 mol% anhydride was ammonolyzed and another 30 mol% was imidized.

As the pH was lowered from 7 to 2, the particle size was found to remain in the range of 130–140 nm despite the sharp ζ -potential change in the pH range of 2–4. Apparently, the electrostatic repulsion at a ζ -potential of -30 mV was still sufficient to stabilize the particles.

4. Conclusions

Self-emulsifying latexes with an average particle diameter of 150 nm were successfully prepared by partial ammonolysis of partially imidized SMA without using any surfactant. Without the partial imidization the particles became fully water soluble. The stabilization of the latex particles was found to be due to strong electrostatic interactions, as indicated by a ζ -potential of -70 mV. The latexes were stable in the pH range of 2–7. The molecular weight distribution of the polymers was not a determining factor in the properties of the obtained latexes. Efforts to use these SMA-based latexes to prepare environmentally-friendly coatings are currently under way in our laboratories.

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