Polymeric Coatings Based on Acrylic Resin Latexes from Miniemulsion Polymerization Using Hydrocarbon Resins as Osmotic Agents

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ABSTRACT: Waterborne acrylic resins with a solid content higher than 40 wt % were obtained by miniemulsion polymerization of methyl methacrylate, butyl acrylate, and acrylic acid using a hydrocarbon coumarone–indene resin (HCR) as osmotic agent. HCR is a cheap polymer widely used for coatings and pressure-sensitive adhesives. The resin leads to a higher hydrophobicity for the acrylic latex film and acts as osmotic agent in miniemulsion polymerization preventing Ostwald ripening, leading to latexes with particle sizes, size distributions, and stability comparable to those obtained using *n*-hexadecane as osmotic agent. However, the monomer conversion and molecular weight were lower, indicating the occurrence of a chain-transfer reaction. Atomic force microscopy analysis demonstrated that a smooth film surface with phase-separated morphology was formed when using HCR. Faster film hardness development was achieved with HCR comparing with hexadecane. Compared with market standard in a paint formulation, a similar performance was achieved. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40569.

INTRODUCTION

Miniemulsion polymerization is a powerful technique that allows the formation of structured polymer and composite nanoparticles.[1] In a miniemulsion system, the typical droplet size is around 100 nm and the droplets are stabilized in a way that the droplet is the main nucleation locus of polymerization. In some publications, it is also referred as "nano-emulsion" polymerization.[2]

The fact that there is no effective mass transfer through the continuous phase during the polymerization process has important implications such as the possibility of using highly hydrophobic monomers,[3,4] conducting several polymerization techniques apart from classic free radical polymerization,[5–8] and encapsulating of a variety of materials.[9–11] These characteristics are very important for applications in biomedicine or coatings.[12–16]

Particularly for coating technology, the miniemulsion polymerization can help improving the performance of water-based paints.[17–19] For some high-performance applications, for instance anticorrosive paints, there is still a large performance gap between the solvent-based and the water-based technology.[20] For instance, waterborne coatings use latexes that are typically prepared by conventional emulsion polymerization. However, these polymers are not suitable for anticorrosive metal protection. Acrylic resins latexes normally are polymers having poor solvent and chemical resistance owing to their hydrophilic structure and poor crosslinking density. Besides, after film formation, the high amount of surfactant, typically above the critical micelle concentration (CMC) employed in conventional emulsion polymerization allows water uptake, which is not desirable for anticorrosive purposes and leads to a fast degradation of the polymeric film.[21,22]

The negative environmental aspects of volatile organic components in solvent-based coatings created the need for having alternatives to improve the performance of water-based coating systems. In this context, the miniemulsion polymerization technique has many advantages that allowed the formulation of

Additional Supporting Information may be found in the online version of this article.

resins with much lower amount of surfactant than in the conventional emulsion polymerization as it is possible to use surfactant concentrations below the CMC.[23] In addition, monomers with high hydrophobicity can be used. All these characteristics have demonstrated to improve the water resistance of the coating film.[24–27]

The high stability of the droplets in a miniemulsion is ensured by the combination of a surfactant, and the costabilizer or osmotic agent, which is soluble and homogeneously distributed in the droplet phase. The costabilizer has a lower solubility in the continuous phase than the rest of the droplet phase and therefore builds up an osmotic pressure in the droplets counteracting the Ostwald ripening effect.

Many materials have been used as costabilizers such as hydrophobic reactive monomers,[28] polymers,[29,30] and solvents.[6] One of the most common costabilizers used in miniemulsion polymerization is the model compound n-hexadecane (HD).

The hydrocarbon coumarone–indene resins (HCRs) are widely used as a vehicle for several types of solvent-borne coatings and adhesives.[31,32] Therefore, they are readily available on the market. Furthermore, the resins have the advantage of being less volatile than HD. The resins possess all the characteristics of a costabilizer as they are highly soluble in the monomer droplets and polymer matrix as well as almost completely insoluble in the continuous phase (water). In addition, their molecular weight is below 1000 g mol^{-1}. This guarantees the creation of a sufficient osmotic pressure to control Ostwald ripening.

In this study, we have used HCR as costabilizer of miniemulsions. These materials can bring many advantages concerning coating applications, such as higher surface hydrophobicity. We investigated the efficiency of HCR as osmotic agent in miniemulsion polymerization of acrylic latex compared to HD in terms of monomer emulsion, polymer latex stability, and particle size distribution.

EXPERIMENTAL

Materials
Acrylic acid (AA), butyl acrylate (BA), methyl methacrylate (MMA), sodium dodecyl sulfate (SDS), azobisisobutyronitrile (AIBN), and n-HD were purchased from Sigma-Aldrich and were used as received without further purification. MilliQ water was used to prepare the water-based coatings.

The hydrocarbon resin (HCR) was purchased from Quattor and used as received. The resin is referred as coumarone–indene resin although some other monomers can be used (e.g., styrene). An IR spectrum is shown in Supporting Information Figure A. The main characteristics of the hydrocarbon resin were as follows: molecular weight (M_n) = 590 g mol^{-1}; polydispersity (M_w/M_n) = 2.7; softening point (ASTM E-28) = 127°C; glass transition temperature (T_G) = 56°C; Gardner Color (ASTM D-1544) = 5–6; acid number, <0.10 g KOH g^{-1}.

Preparation of BA/MMA/AA Miniemulsions
The proportion of BA/MMA was 50/50 w/w. The amounts of AA and SDS used were 2 and 0.4 wt %, respectively, in relation to BA+MMA+HCR mass. The organic components (BA+M-

MA+HCR+AA) were maintained at 40 wt % upon the total latex. The HD concentration was 3.8 wt % of the organic phase. The total weight of the components was around 30 g.

In an 80-mL beaker, 50 mg of SDS and 240 mg of AA were dissolved in 17.8 g of water. In another beaker, the osmotic agent (HD or HCR) was dissolved in the total amount of the monomers BA and MMA. After total dissolution, the monomers and the osmotic agent solution were mixed with the water+surfactant+AA solution forming an initial emulsion. This emulsion was mixed with a magnetic stirrer for 50 min at 1000 min^{-1}. Subsequently, the emulsion was ultrasonicated for 120 s (5 s on/off pulse regime) at 90% of intensity (Branson sonifier W450 digital 0.5 in. tip) under water bath.

Preparation of Poly(BA-*co*-MMA-*co*-AA) Latex Through Radical Polymerization in Miniemulsion
The proportions of all components were maintained the same as described in the preparation of miniemulsions. AIBN was used as the initiator (2 wt %, based on monomers).

Standard Procedure

After ultrasonication, the emulsion was transferred into a round-bottomed flask with a solution of 360 mg of SDS in 3.6 g of water and a magnetic stirrer. The flask was then closed with a rubber stopper followed by a purge with argon for 5 min. The polymerization was carried out at 72°C for 2 h under magnetic agitation (200 min^{-1}).

Surfactant Postaddition Procedure

In some experiments, additional surfactant (3.0 wt % of the BA+MMA+HCR content) was added after ultrasonication to increase the latex stability. In this case, the amount of water initially added was 14.2 g. The remaining water was used to solubilize the additional surfactant.

Preparation of Paints
Paints were prepared by adding the latex to an aqueous dispersion composed of fillers, pigments and anticorrosive pigments, and additives under continuous agitation. The dispersion was kindly provided by *Killing S/A Tintas e Adesivos* (Novo Hamburgo, Rio Grande do Sul, Brazil). The formulation was derived from a standard anticorrosive primer recipe. Except for the commercial latex used, the latexes were neutralized with triethylamine prior to the addition. The final paint had a solid content of around 45 wt % and pigment volume concentration of 25%.

Characterization of the Miniemulsion, Latex, Film, and Paint
The viscosity of the monomers and the osmotic agents was measured with a capillary viscometer (Schott Instruments) at 20°C. The results were reported relatively to the pure monomers (BA and MMA) mixture.

The particle size and its distribution were measured with a Nano-ZS particle sizer (Malvern Instruments, United Kingdom) at a fixed scattering angle of 173°. The samples were diluted in deionized water (five drops of the emulsion or latex per milliliter of water) just prior to the analysis. The intensity mean of the particle diameter (*Z*-average or cumulant mean) was given by dynamic light scattering (DLS) measurements.

The molecular weight of the polymer was measured by gel permeation chromatography (GPC). The equipment used was a Viscotek VE2001 equipped with TODA 302 detector equipped with crosslinked polystyrene columns with pore sizes of 500, 10^3, 10^4, and 10^5 Å. Tetrahydrofuran high-performance liquid chromatography (HPLC) grade was the eluent (1 mL min^{-1}). Polystyrene of different molecular weights was used as standard for the calibration curve.

The thermal behavior was studied with a differential scanning calorimeter (DSC 7, Perkin Elmer). The T_Gs were determined with heating rates of 10°C min^{-1} (temperature range, −140 to +160°C).

The residual monomer was measured by HPLC using methanol as diluent and commercial grade monomers as external standards. The method was described elsewhere.[33]

The atomic force microscopy (AFM) images were obtained by scanning the dry-casted films of each experiment with a Dimension 3100 CL instrument equipped with an Olympus OMCL-AC160TS-W2 cantilever operating in noncontact mode at room temperature. The elastic constant (K) was 42 N m^{-1} and the resonance frequency (F_0) was 300 kHz. The samples were prepared by drop-casting the latex without dilution on glass plates. The films were left to dry for 7 days prior to analysis.

The latexes shelf lives were estimated by accelerated stability analysis using the Dispersion Analyzer LUMiSizer. The latex samples (2 mL) were transferred to a glass cuvette and placed in the equipment without dilution. The analysis consists of optical detection of local transmission changes of near infrared light trough the samples while it is centrifuging at a given speed.

The hardness of the latex and paints films was measured according to ASTM D4366 test method. The values reported were in number of oscillations. The paint films were applied with a 150-μm drawdown bar over glass panels.

For the gloss and adhesion measurements, the paints were applied in the original viscosity with a 150-μm drawdown bar over cold rolled steel panels (grade, 1020). After 10 min, the panels were put in an oven (30 min at 60°C). The final thickness was measured using Byko-test equipment, model 4200 (BYK).

The gloss measurements were made according to ASTM D523 using a glossmeter micro-TRI-gloss (BYK). The adhesion was measured according to ASTM D3359.

RESULTS AND DISCUSSION

Stability of Monomer Miniemulsions

In miniemulsion polymerization, high stability of the monomer droplets is desirable to ensure that the composition does not change during the polymerization process. This behavior can be achieved by the suppression of the coalescence and Ostwald ripening during the polymerization.[34] The monomer emulsion stability can be easily assessed by testing the tendency to form two phases owing to creaming and phase separation of the monomers.[29]

The monomer miniemulsions of BA/MMA/AA with different amounts of hydrocarbon resin (HCR) as the osmotic agent (0, 4, 6.5, 9, and 12 wt % of the sum of monomers and HCR) were prepared. Only the miniemulsions with 9 and 12 wt % were stable after 72 h, as observed by visual inspection. A photograph of the miniemulsions is shown in Supporting Information Figure C.

For comparison, a miniemulsion using n-HD was prepared at the same conditions. The amount of hexadecane used was 4 wt % of the dispersed phase according to the literature.[35] The results were compared with the miniemulsion prepared with 12 wt % of hydrocarbon resin to guarantee stability for the system. The droplet size of a nonpolymerized monomer miniemulsion was measured after 2 weeks.

The droplet size in the monomer miniemulsion using HCR increased from 216 to 247 nm, which is slightly lower than the increase in size observed for the droplets prepared with HD (236–304 nm). This suggests slightly higher droplet stability in the HCR-stabilized miniemulsion. This difference can be explained by the higher hydrophobicity of HCR. It is important to observe that part of the difference in the particle size has to be addressed by the difference of the amount of the dispersed phase (organic phase). For all experiments, the sum of weight concentrations of monomers and HCR was kept constant at 40 wt % (final solid content).

The compound HD was typically used in the literature as an osmotic agent in miniemulsions because of its high hydrophobicity, convenient use, and inertness in the polymerization.[36] Usually, it was used in concentrations of about 4 wt % or 0.169 mmol·g^{-1} of the dispersed phase. It has been demonstrated that the stability of a miniemulsion is proportional to the molar concentration of the osmotic agent in the dispersed phase.[36–39] For this concentration (0.169 mmol g^{-1}) and considering that the HCR has a molecular weight (M_n) of approximately 590 g mol^{-1}, the equivalent weight concentration of HCR would be 10.4 wt % of the dispersed phase which is among the values found to have stabilized the miniemulsion (9 and 12 wt %). These results showed that HCR can be used efficiently as osmotic agent in miniemulsion polymerization preventing Ostwald ripening.

Coagulum Formation During Polymerization

The miniemulsion polymerization was carried out using the standard procedure described before using HCR as osmotic agent. A NMR spectrum of the polymer formed is shown in Supporting Information Figure B. Therefore, considerable amount of coagulum was formed. Similar amounts of coagulum were observed when using HD as well. The coagulum formation can be attributed to comparatively high dispersed phase content (>40 wt %).[40]

The reaction yield was 87 wt % (gravimetric) and the residual monomer determined by HPLC was 1%. Consequently, the calculated coagulum was 12 wt % (related to the theoretical solid content), which is not suitable for coating applications. The coagulum had a similar molecular weight distribution as the latex. This means that both polymer and HCR were present in the coagulum at similar concentrations as in the latex, which allows assuming that the coagulum formation is caused by the
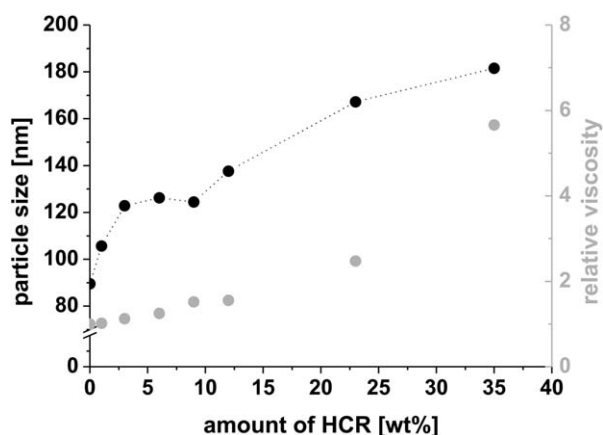
Figure 1. Effect of HCR content on particle size and relative monomer's viscosity. Addition of 4 wt % of HD results in a relative viscosity of 1. The dotted line is a guide for the eyes only.

coalescence of the particles already polymerized as Ostwald ripening and homogeneous nucleation are unlikely to happen owing to the mass transfer limitations of the HCR.

Chern et al.[41] demonstrated that, among other factors, the concentration of surfactant plays a significant role in the coagulum formation of the conventional emulsion copolymerization of BA and MMA. To test this hypothesis, higher amounts of surfactant were tested.

The different amounts of surfactant (0.4, 0.9, and 1.7 wt %) used for the preparation did not affect the amount of coagulum. Using higher amounts of surfactant (3.5 and 7.0 wt%), gel formation before and after polymerization was observed. These results are in accordance with the work of Hecht et al.[42] These authors demonstrated that using high concentrations of surfactant, more droplets are generated with smaller particle sizes, leading to an increase in the collision rate. After a critical point, the collision rate is so high that the surfactant barrier is not enough to prevent coalescence, leading to gelification or phase separation. In other words, the barrier increase owing to higher surfactant concentration competes with the increase in the collision rate.

To increase the surfactant concentration without decreasing the droplet size, therefore maintaining the collision rate, addition of surfactant after ultrasonication (postaddition) was proposed. Landfester et al.[43] demonstrated that more stable latexes can be achieved by adding additional surfactant after ultrasonication. In this study, the authors used a relatively low solid content latex (25 wt %) and the formation of coagulum was not

observed. Here, additional surfactant was added (3.0 wt % upon the BA+MMA+HCR content) after ultrasonication. The coagulum could be reduced by >50% (<5 wt %) by adding surfactant to the miniemulsion after sonication although increasing the surfactant concentration.

Latex Characterization

Miniemulsion polymerization using the postaddition procedure was carried out with different HCR contents investigating the effect on the particle size (Figure 1), keeping the surfactant concentration at the abovementioned 0.4 + 3.0 wt %. The concentrations used were up to 35 wt %. Higher amounts were not accessible because of the limited solubility of HCR in the monomers. It is clear that a continuous increase is found in the droplet size, increasing the amount of HCR.

As shown in Figure 1, higher concentrations of HCR increased the viscosity of the dispersed phase, most pronounced starting from 24 wt % of HCR. The higher the viscosity of the organic phase, the less effective is the droplet break up during ultrasonication, eventually leading to a higher droplet size.[44] These findings are in agreement with the work of Lopez et al.[45] where different contents of an alkyd resin were tested in the miniemulsion terpolymerization of BA, MMA, and AA. A similar behavior was found for high amounts of alkyd resin. These authors used a conventional osmotic agent together in the tests and they have not tested small amounts of the alkyd resin.

The results of the experiments conducted with the osmotic agents HD and HCR are summarized in Table I. The concentration in the organic phase used was 3.8 wt % (0.17 mmol g^{-1}) and 12 wt % (0.20 mmol g^{-1}) of HD and HCR, respectively. Although the particle size was almost the same, there were differences in the shelf life, the ζ-potential, and the molecular weight of the polymer.

The molecular weight and the polydispersity of the polymer prepared in the presence of HD differ from the values of the polymer prepared in the presence of HCR. The increased polydispersity and the reduced M_w, as well as the higher residual monomer content suggest the occurrence of chain-transfer reactions to the hydrocarbon resin owing to the presence of allylic hydrogens. Similar behavior was found by Wang et al.[46] using a chain-transfer agent as costabilizer and supports the hypothesis. Assuming that chain transfer occurs when using HCR as osmotic agent gives one more evidence that the droplet plays a significant role in the polymerization nucleation as it would not be possible for the HCR to influence the micellar or homogeneous nucleation because of limited mass transfer owing to low solubility of the resin.

Table I. Characterization of Copolymer Dispersion of BA/MMA/AA Prepared by Miniemulsion Polymerization Using Two Different Osmotic Agents

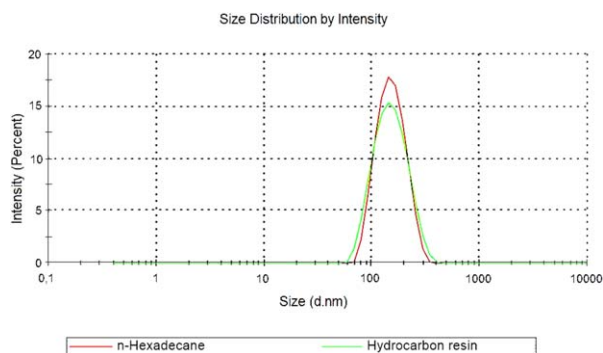| Osmotic agent	M_w (10^{-3} g mol^{-1})	Polydispersity (M_w/M_n)	Solids content (wt %)	T_G (°C)	Residual monomer (wt %)	Zeta ζ-Potential (mV)	Estimated shelf life (LUMiSizer) (months)	Average particle diameter (nm)
HD	404	2.0	38.9	13	0.1	−54	4 months	137
HCR	332	2.7	38.7	18	1.0	−45	6 months	141

Figure 2. Particle size distribution of the latexes prepared with *n*-HD and hydrocarbon resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The measured T_G of the polymers showed an expected behavior. The T_G using HCR is higher because of the HCR T_G (56°C) contribution. The HD showed little influence on T_G as it was close to the theoretical value (14°C), considering the contributions of the respective monomer homopolymers.

The ζ-potentials are both negative, as expected, owing to the use of the anionic surfactant SDS and the presence of carboxy functions on the particle's surfaces. The prediction of shelf life in the LumiSizer demonstrated that the latex with HCR exhibits higher stability. Typical commercial samples have also shelf lives of approximately 6 months.

In Figure 2, the particle size distributions of the latexes prepared with both osmotic agents are shown. The distribution was very similar.

Film Characterization by AFM

AFM has been used as a powerful technique for studying polymer surfaces. With this technique, the assessment of morphology and phase separation is possible with a resolution comparable to scanning or transmission electron microscopy with no special surface treatment.[47] Latexes have been extensively studied by AFM. It is possible, for example, to evaluate surfactant phase separation and migration,[48] the extent of coalescence of the latex particles during film formation,[49] and the film degradation during aging time.[50]
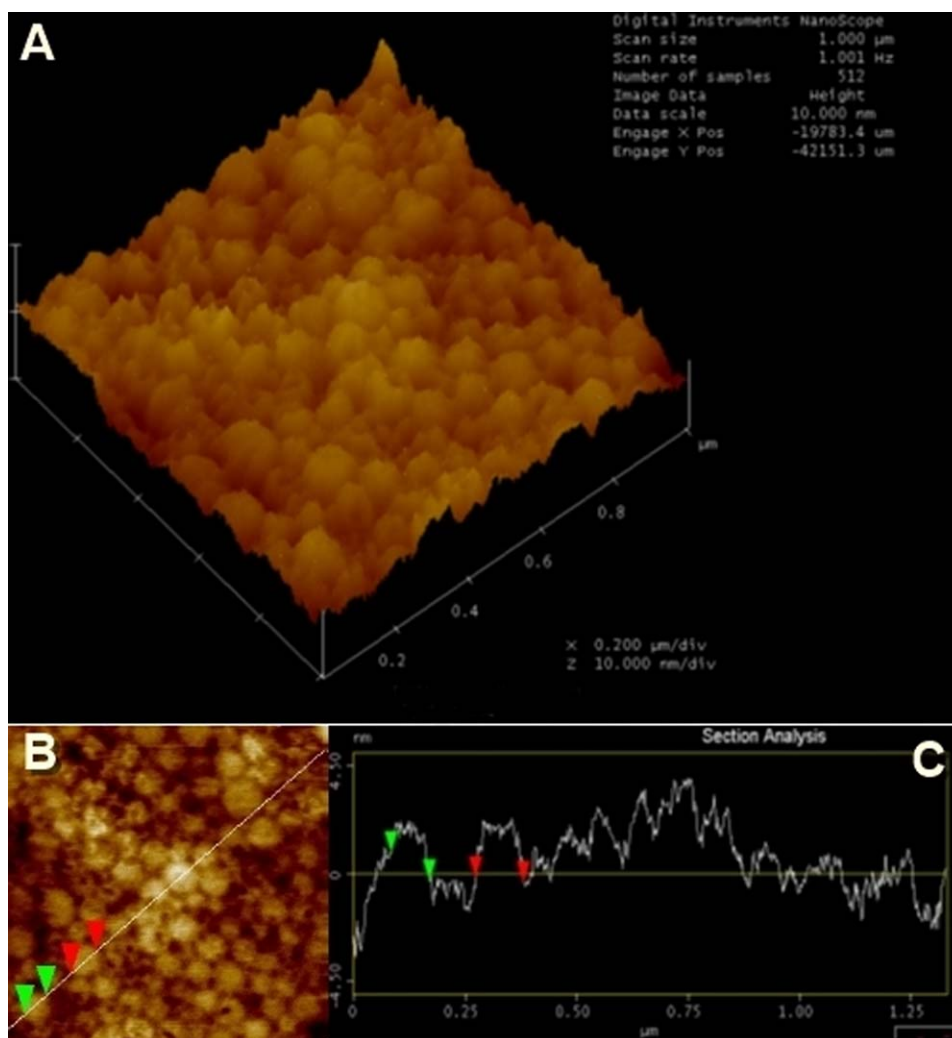

Figure 3. AFM image of the casted film of the poly(BA-*co*-MMA-*co*-AA) using HD as osmotic agent. The green and red arrows indicate the same reference point in the bottom images. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
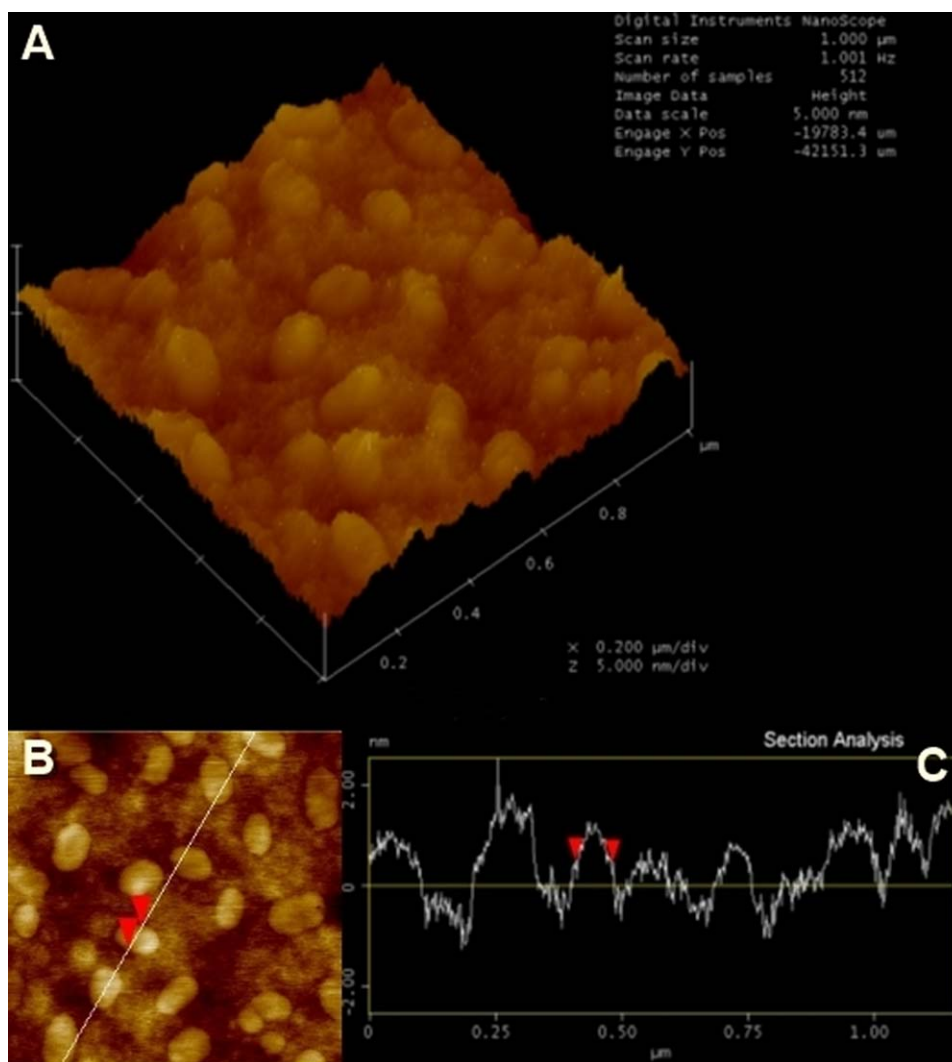
Figure 4. AFM morphology images of the casted film of the poly(BA-*co*-MMA-*co*-AA) using HCR resin as osmotic agent. The red arrows indicate the same reference point in the bottom images. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The films of the latexes prepared with HD and HCR as osmotic agents were characterized by AFM. Different morphologies were found as shown in Figures 3–5.

The images of the films (Figures 3 and 4) using HD as osmotic agent showed a pattern of noncoalesced particles with diameters in the range of 80–120 nm corresponding to the values obtained from DLS measurements. However, no cracking was found and furthermore the mean surface roughness calculated was 4.0 nm, suggesting a good film formation. Despite the low roughness, the appearance of the films resembled that, which was described in the literature for high T_G resin latexes.[48,51] The phase contrast image of the HD films [Figure 5(A)] showed a particle-like phase difference pattern. It is quite reasonable and according to the literature that the interstices of the particles are surfactant domains.[48]

On the other hand, the films using HCR as osmotic agent showed quite a different morphology. Some protruded ellipsoid domains with sizes from 85 to 110 nm (short axis) and from 150 to 190 nm (long axis) were found. Using the phase contrast

images [Figure 5(B)], it is possible to see that these domains are actually distributed along a homogeneous different phase medium and barely some particle interstices (surfactant domains) are seen. These domains can be attributed to the low compatibility of the HCR in the polyacrylic matrix owing to differences in polarity.

Application as Coating

Coating is an important application of the miniemulsion latex especially for anticorrosive paints as it is possible to incorporate highly hydrophobic film-forming agents, such as the HCR used in this study.

The hardness of the applied latex film with the osmotic agents HD and HCR was measured. Hardness is an essential characteristic that influences the paint behavior such as mar, scratch, and blocking resistance, as well as drying time and dirty pick-up of the film.[52] Figure 6 shows the König hardness in dependence of the time after the coating was applied to the standard test surfaces. The data show that the initial hardness of the film with HCR is higher than
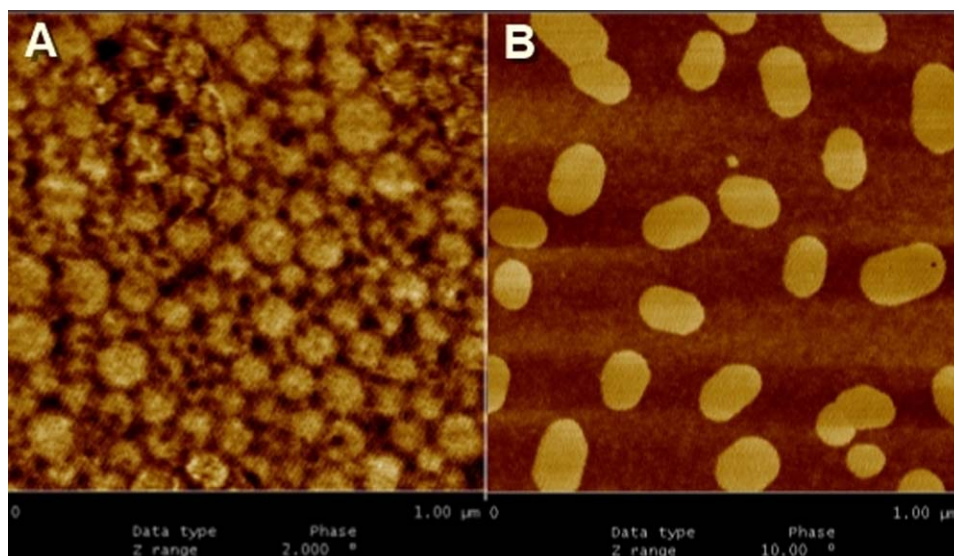
Figure 5. AFM phase contrast dry film images of the poly(BA-*co*-MMA-*co*-AA). (A) HD and (B) HCR as osmotic agents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that of with HD. This result was expected as the HD acts as a plasticizer in the first drying hours. As soon as it had evaporated from the film the hardness increased and after 120 h of application, both films (HD and HCR) have similar hardness. This result indicates that the HD slows down the drying rate.

The prepared latexes were used in an anticorrosive paint formulation and applied in a cold-rolled steel panel to evaluate basic properties such as adhesion, appearance, and gloss. The results were compared with a commercial latex sample and can be seen on Table II. The paints were applied with a 150-μm drawdown bar and dried in an oven for 30 min at 60°C. All the tests were made after leaving the panels 7 days at room temperature.

All the paint films had a smooth and homogeneous appearance. The thicknesses obtained in the panels were similar, allowing direct comparison of the different latexes. Very good values of adhesion were obtained which is very important for

anticorrosive purposes. A photograph of the adhesion test is shown in Supporting Information Figure D. Therefore, some differences in gloss were observed. The higher gloss of the commercial latex can be attributed to the lower hardness of the polymer. Furthermore, no differences in the film hardness were observed comparing the osmotic agents. However, lower gloss was observed when using HCR, which is probably caused by the phase separation, as shown by AFM.[53]

CONCLUSIONS

In this study, we demonstrated the use of a HCR as osmotic agent in the miniemulsion polymerization of MMA, BA, and AA. It was found that HCR is needed in a minimum amount of 9 wt % to produce (long time) stable monomer emulsions which is equivalent to the molar amount of HD typically used for the preparation of monomer miniemulsions. Using HCR as osmotic agent, an acrylic latex with particle size, size distribution, and coagulum formation similar to the use of HD was obtained. Lower molecular weight and a slightly higher free monomer content was found when using the HCR. This can be considered as an evidence of chain-transfer reactions occurring with HCR. AFM analysis of the dry films showed a smoother
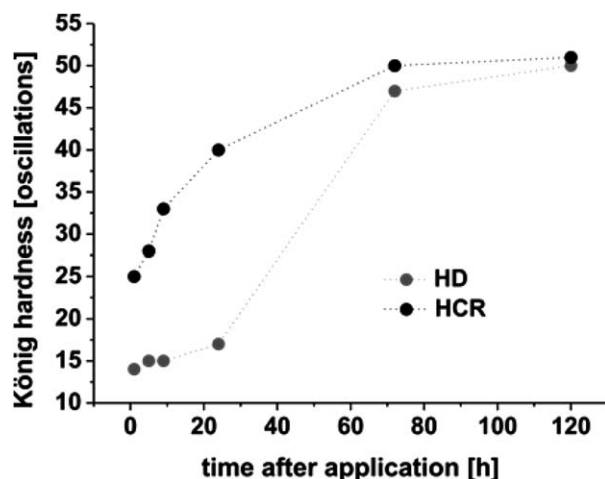

Figure 6. Comparison of the pure latex film hardness (ASTM D4366) with different osmotic agents. Application on glass panels with a 150-μm wet thickness drawdown bar.

Table II. Characterization of Paint Films with Latexes Prepared by Miniemulsion Polymerization with Different Osmotic Agents Compared to a Commercial Acrylic Dispersion

Osmotic agent	Thickness (μm)	Adhesion (ASTM D3359)	Gloss (ASTM D523 —60°/85°)	Hardness (ASTM D4360)
HD	30–35	GR0	9/32	21
HCR	35–45	GR0	9/25	19
Commercial latex	30–34	GR0	14/38	14

surface and phase separation when using the HCR compared to HD. The hardness of the latex films showed that the film containing HCR has faster drying time. In comparison to paints based on a commercial latex, paints containing the miniemulsion-based latex exhibited higher hardness, and comparable adhesion to the samples surface. The HCR is very cheap and widely available and its utilization in latex can bring many advantages for the application in waterborne coatings and paints like high-film hydrophobicity, which can improve scrub and corrosion resistance.

ACKNOWLEDGMENTS

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