



Rapid Communication

Emulsifier-free (meth)acrylic colloids stabilized by cationic monomer containing two charged moieties

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ABSTRACT

Emulsifier-free cationic polymer colloids produced by emulsion polymerization have gained important relevance for diverse applications. However, the control of colloidal characteristics is still challenging due to the cationic monomers structure, in which the charge is placed between two hydrophobic moieties making them less efficient in providing colloidal stabilization. This challenge was confronted by employing a minor quantity of cationic monomer containing two charges, styrenic 1,4-diazabicyclo[2.2.2]octane, to provide colloidal stability to waterborne (meth)acrylic dispersions. For first time, high throughput production of cationic dispersions with controlled colloidal and film properties is achieved. High solids content stable dispersions comprising mono-dispersed particles with 170 nm average diameter and high charge density ranging 24–180 $\mu\text{C}\cdot\text{cm}^{-2}$ are produced, giving rise to films with tunable mechanical and water resistance. This work offers a novel concept for colloidal stabilization of polymer colloids and can be extended towards stabilization of challenging colloidal dispersions or design of novel surfactants.

1. Introduction

Colloidal polymer dispersions are products with a wide range of industrial applications including coatings, adhesives, additives for textile and leathers, carpet backing and paper [1,2]. Continuous demand on novel and high performance dispersions has placed a requirement for new colloidal particles with respect to chemistry, surface properties and colloidal stability.

Emulsion polymerization is a technique of choice for high-throughput synthesis of dispersed polymer particles with great industrial significance. Nevertheless, the use of surfactants in such process is a requisite, which from the other hand affects negatively the properties and performance of the resulting dispersions. While different alternatives have been investigated, the attention was turned towards surfactant free polymer colloids synthesized by emulsion polymerization using small quantity of ionic monomers.

Most of emulsifier-free waterborne dispersions have been synthesized using anionic monomers [3–7]. However, in recent years greater attention has been focused on cationically charged polymer dispersions owing to their ability to bind strongly with DNA and proteins [8].

Moreover, the antimicrobial activity of cationically charged surfaces increased additionally the interest in these dispersions [9]. This opens a way of potential use of cationic polymer dispersions in biomedical and biotechnology applications, as well as, antimicrobial coatings in large volume applications (paints and protective coatings) and niche application (protection of biomedical devices).

The control of the characteristics of the cationic emulsifier-free polymer dispersions stabilized with cationic monomer, such as the average particle size, the monodispersity and the location of cationic moieties and their content are essential but still challenging. This is a consequence of the structural characteristics of most of the cationic monomers, in which the charge is usually placed between two hydrophobic moieties that makes them less efficient in providing colloidal stabilization with respect to the most common anionic monomers [10]. The high throughput of the process along with performance of the products are compromised by this fact, resulting in rather low solids content dispersions with relatively large particles size [11–18], moreover the presence of hydrophilic species as cationic monomers increase largely the water sensitivity of the products [19]. The colloidal stability is strongly related to the incorporation of the ionic monomer onto

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polymer particle that determines the surface charge density and concentration of the soluble oligomers in the aqueous phase, both indispensable to provide the stability.

Various cationic monomers have been studied for that aim, such as 2-vinylpyridine [8] and 2-(diethylamino)ethyl methacrylate [8], which possess dependent ionic state; or permanently cationically charged monomers as (1-methyl-4-vinylpyridinium bromide [8] and [2-(methacryloyloxy)ethyl] trimethyl ammoniumchloride [8]. All of them have a common characteristic of one charge per molecule. The attempts to avoid the drawbacks of the cationic polymer dispersions by increasing the concentration of ionic monomers induced either stability issues [8,20] or lack of control of particle size [13], due to the increased ionic strength in the dispersions, causing drop in the performance.

Clearly, there is a need of a new type of cationic monomers to provide colloidal stability and cationic charge on the particle's surface without compromising the properties and performance. Recently, a synthesis of new styrenic monomer based on cationic 1,4-diazabicyclo[2.2.2]octane was reported (Fig. 1) [21,22]. This monomer has few distinctive features than the common ionic monomers, such as two cations per molecule that are not sterically hindered, which might increase the charge density and colloidal stability of polymer colloids. These characteristics keep the promise to improve the colloidal properties and the control of the characteristics at low ionic monomer concentration.

Cationic monomers with two cationic moieties per molecule were incorporated into polymers using other techniques than emulsion polymerization [23–25]. Apart, there is one study reported by Zhan et al., in which cationic polymer particles were synthesized by emulsion polymerization by incorporation of an amidine monomer containing two charges per molecule to provide colloidal stability, however, the aim of the study was to achieve re-dispersible polymer dispersions not colloidal stabilization [26]. Moreover, the maximum solids content achieved is of 20% versus 40% of solids attained by incorporation of DABCO in the present study.

The production of stable cationic polymer colloids with high solids content (40 wt%), controlled particle size (about 170–180 nm) and with excellent immediate and shelf stability (up to 6 months) are the main outputs of this work. Nevertheless, the main contribution of this work is the introduction of novel concept using chemical moieties containing two ions for more efficient colloidal stabilization. The concept might be extended on designing of more efficient surfactants or polymer dispersions based on monomers coming from renewable resources.

2. Experimental section

2.1. Materials

Technical grade monomers n-butyl acrylate (BA, Quimidroga), methyl methacrylate (MMA, Quimidroga) were used, as well as 1,4-diazabicyclo[2.2.2]octane (DABCO, Sigma Aldrich), 1-bromohexane (Sigma Aldrich), ethyl acetate (C₄H₈O₂), 4-vinylbenzyl chloride (90%, Sigma Aldrich) and acetonitrile (CH₃CN, Sigma Aldrich). The 2,2'-Azobis(2-methylpropanamide) dihydrochloride cationic initiator

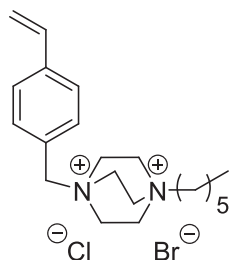


Fig. 1. Styrenic DABCO cationic monomer chemical structure.

(AIBA, Sigma Aldrich), hydroquinone (Fluka), technical grade tetrahydrofuran (THF, Scharlab), high-performance liquid chromatography grade THF (Scharlab) and silver nitrate (AgNO₃, Sigma Aldrich) were utilized. All materials were employed as received without any purification.

2.2. Monomer synthesis

DABCO cationic monomer was synthesized following the procedure of Zhang et al. [21,22], described in Supporting Information. The partitioning of DABCO between water and organic phase (BA/MMA) was examined by mixing DABCO monomer, water and BA/MMA in different ratios. After phase separation, the content of DABCO in each phase was analyzed by H¹-NMR. The procedure and results are detailed in Supporting Information.

2.3. Synthesis of emulsifier-free dispersions

The polymer dispersions were synthesized by emulsifier-free semi-continuous seeded emulsion polymerization process. Initially, a seed was synthesized following the formulation in Table 1. BA/MMA (50/50 wt%) and DABCO monomer (1 mol%) at 10% s.c. were charged into reactor and stirred for 20 min under N₂ atmosphere at 200 rpm. Then the temperature was increased to 70 °C, aqueous solution of initiator was added as a shot and left to react for 90 min.

In the second step, the reactor was loaded with appropriate amount of seed (30%). Upon achieving 70 °C, initiator aqueous solution (AIBA) was added as a shot, whereas the monomers (MMA/BA in 50/50 weight ratio) an aqueous solution of DABCO (1–5 mol%) were fed in two streams (according to formulation shown in Table 1). After 180 min feeding, the system was allowed to react for one hour. The final solids content was 40%.

The dispersions nomenclature is DABCO1 containing 1 mol%, DABCO3 with 3 mol% and DABCO5 with 5 mol% DABCO.

2.4. Characterization

Monomer conversion was studied gravimetrically and coagulum amount was calculated based on the total monomer. The average particle size and the particle size distribution (PSD) were determined by Capillary Hydrodynamic Fractionation (CHDF) chromatography. The morphology of latex particles was studied by means of Transmission Electron Microscopy (TEM). Zeta potential was measured in a Zetasizer Nano Z (Malvern instruments). Incorporation and surface charge density were determined by titration. The insoluble fraction of polymer in THF was determined by Soxhlet extraction. The molar masses of the THF-soluble fraction were analyzed by Size Exclusion Chromatography. These characterizations are described in details in the Supporting Information.

The film morphology was examined by TEM, the thermal characterization by differential scanning calorimetry (DSC), the mechanical properties were measured by tensile tests and the water resistance was

Table 1
Formulations employed for synthesis of 10% seed and 40% cationic dispersion.

Compound (wt%)	First step (Seed)		Second step (Seeded-semibatch)			
	Initial charge	Shot	Initial charge	Stream 1	Stream 2	Shot
Seed	–	–	30	–	–	–
BA	5	–	–	18.5	–	–
MMA	5	–	–	18.5	–	–
DABCO	1 ^a	–	–	–	1.5 ^a	–
AIBA	–	0.25 ^a	–	–	–	0.25 ^a
H ₂ O	80	10	–	–	28	5

^a mol based on main monomers (BA/MMA) (mol%).

examined by water uptake test after immersion of the film in water (see Supporting Information for further details).

3. Results and discussion

Emulsion polymerization is a heterogeneous process, in which hydrophobic monomers are dispersed and polymerized in aqueous phase, for which it is essential to have slightly water soluble monomers to diffuse through the aqueous phase [27]. However, if the hydrophilicity is high, the monomers can undergo polymerization in the water phase rather than in the monomer droplets that are the main reaction loci. To check this, the partitioning of DABCO monomer between the aqueous and organic phase (BA/MMA) was studied by H^1 -NMR. It was determined that the cationic monomer's nature is hydrophilic, as >95% of it was placed in aqueous phase (see Supporting Information). This makes the emulsion copolymerization of the hydrophobic BA/MMA with hydrophilic DABCO challenging. On the other hand, the creation of the amphiphilic units by DABCO incorporation in the hydrophobic (meth)acrylic chains is an instrument that ensures the colloidal stability of the dispersions in emulsifier-free polymerization.

Reaction engineering tool was used to overcome the challenges. Emulsion polymerization was performed in semicontinuous mode, which ensures low monomer concentration in reactor and elimination of the effect of reactivity ratios on co-polymer compositions. On the other hand, use of water-soluble initiator creating radicals in aqueous phase, where most of DABCO is, assures its copolymerization with the main monomers, which ensures the copolymerization and on-site creation of the stabilizing units. The colloidal stability attained is a demonstration that the cationic moieties were incorporated onto the particle surface. In order to control the PSD, a seed dispersion was prepared batchwise producing latexes with 10% s.c., to pre-create polymer particles that were grown in the second step. By changing the quantity of DABCO in 1–5 mol% range, stable emulsifier-free cationic dispersions were produced with solids content of 40%.

3.1. Characteristics of the cationic dispersions

The main characteristics of the colloidal dispersions are summarized in Table 2.

Table 2 shows that full monomer conversion was achieved in the seed, giving rise to a particle diameter of 100 nm and narrow PSD as shown in Fig. 2a. However, a shoulder at around 50 nm was observed, which indicates presence of smaller particles. As creation of new particles (secondary nucleation) was not expected, due to initial lack of colloidal stabilizer (it was created in situ), the dispersions were analyzed by TEM to check whether the shoulder was another population of particles or an artefact. In the TEM image in Fig. 2b, monodispersed seed particles can be observed, indicating that the shoulder observed in Fig. 2a is an artefact. As summarized in Table 2, 28% of the DABCO was incorporated onto the particles surface, providing a surface charge density of $7 \mu\text{C cm}^{-2}$. Low DABCO incorporation indicates that water-soluble oligomers rich in DABCO were formed that suffer aqueous phase termination instead of radical entry into particles, likely due to high monomer concentration in reactor (batch-reaction), behavior previously observed for NaSS ionic monomer copolymerization with MMA/

BA [28].

In the second step, the seed was grown by feeding BA/MMA and DABCO (1, 3 and 5 mol%) until 40% s.c. was reached, with high monomer conversion (> 95%) for all DABCO concentration. The kinetic curves of the polymerization processes (Fig. 3, full dots) show similar trends indicating that the DABCO quantity did not affect the polymerization rate.

The instantaneous monomer conversion curves (Fig. 3, continuous lines) revealed that for DABCO1 a monomer accumulation can be observed during the process, whereas in case of DABCO3 and DABCO5 it was observed only at around 100 min, likely occurring because the polymerization rate was lower than the monomer feeding rate. According to Table 2, similar average particle size (d_p) was obtained for the three DABCO concentrations. Nevertheless, if PSDs shown in Fig. 2a are compared, there is a tendency of d_p decreasing with increasing of DABCO content in the formulation, as there is a slight shift of the distribution curves towards smaller sized for higher DABCO contents. Likely, this is a result on two contradictory effects caused by the increasing DABCO concentration. According our previous experience in emulsifier-free MMA/BA emulsion polymerization using ionic monomers, at higher ionic monomer concentration there is more creation of colloidal stabilizing species that stabilize smaller particle sizes [29]. Simultaneously, due to promoted water-phase polymerization there is increased production of water-soluble oligomers that enhance the ionic strength of the dispersions and decreases the colloidal stability of the system. These two phenomena contradictory affected the colloidal properties of the system.

The advantage of the particle size control of this approach is clear from the comparison with recent report on cationic BA/MMA polymer colloids obtained with ionic monomer 2-dimethyl amino ethyl methacrylate charged with a single cation per molecule [34]. Particle sizes in a range of 240–250 nm were achieved only in case when non-ionic surfactant was added and are still higher than these from this work (169–180 nm). The amount of coagulum (< 5%) was slightly increased with the DABCO content because beside highest DABCO incorporation, the concentration of DABCO-rich soluble oligomers caused elevated ionic strength. Nevertheless, according to the Derjaguin–Landau–Verwey–Overbeek theory, a balance between attractive Van der Waals forces and the electrostatic repulsion governs the stability of the colloidal systems [30,31]. The magnitude of the zeta potential as a key indicator of the stability of the colloidal systems of about 50 mV (Table 2) indicates a great stability of the systems [32]. However, the increase in surface charge density did not affect the obtained zeta potential values because of the same effect of increased ionic strength at higher DABCO content that contradictory affected the z-potential.

In Fig. 2c the TEM image of DABCO1 dispersion is shown, whereas the TEM images of DABCO3 and DABCO5 are shown in Fig. S2, Supporting information due to the similar results. Smooth and spherical particles were observed showing augmentation of the particle size from seed to final dispersions. Nevertheless, the particle sizes determined by TEM are higher than those obtained by CHDF, probably due to the flattening of the particles during sample preparation for the TEM imaging.

Table 2 summarizes the incorporation and the surface charge density values for each of the dispersions. It is worth mentioning that the cationic initiator was not taken into account in incorporation

Table 2
Characteristics of cationic polymer dispersions.

Latex	s.c. (%)	Conversion (%)	d_{pCHDF} (nm)	d_{pCHDF} (after 6 months) (nm)	Zeta potential (mV)	Coagulum (%)	Surface incorporation (DABCO %) ^a	Surface charge density ($\mu\text{C cm}^{-2}$)
Seed	9.5	99	100 ± 2	–	–	–	28 ± 2	7 ± 1
DABCO1	39	95	180 ± 3	181 ± 4	52 ± 1	3	25 ± 1	24 ± 1
DABCO3	38	97	171 ± 1	171 ± 3	53 ± 1	4	42 ± 1	77 ± 2
DABCO5	38	97	169 ± 1	165 ± 2	52 ± 1	5	62 ± 1	180 ± 5

^a Incorporation was calculated based on DABCO monomer.

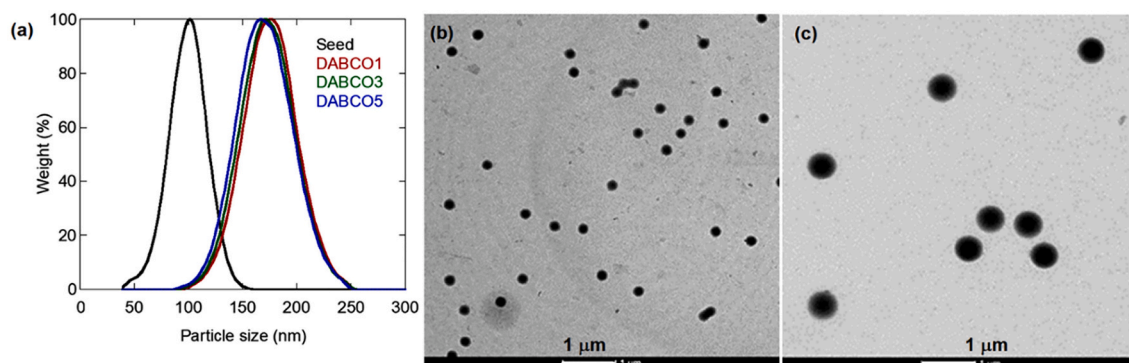


Fig. 2. (a) PSD of all dispersions; (b) TEM image of the seed and (c) TEM image of DABCO1 dispersion.

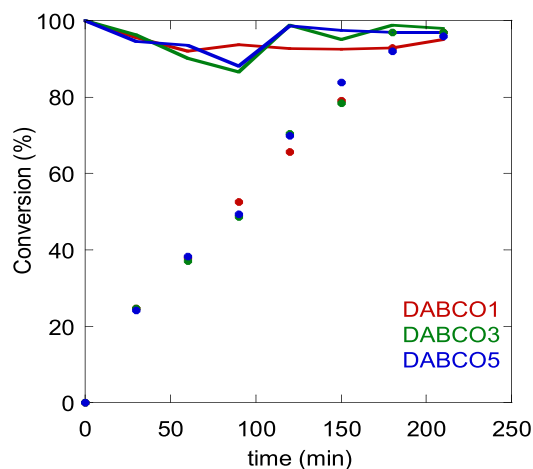


Fig. 3. Conversion evolution in polymer dispersions containing different DABCO cationic monomer concentration. Continuous line represents the instantaneous monomer conversion, while the dots the overall conversion.

calculation, owing to the much lower amount. The DABCO incorporation increased with its concentration from 25% to 62% likely because at higher ionic strength in the dispersions, the adsorption of the ionic species shifted towards the polymer particles, effect already observed for ionic monomers [29] and conventional surfactants [33]. Accordingly, the surface charge density increased with DABCO content, from $24 \mu\text{C cm}^{-2}$ to $180 \mu\text{C cm}^{-2}$. Compared to our previous work in which cationic particles were synthesized using 2-(dimethylamino)ethyl methacrylate (DMAEMA) using non-ionic surfactant, maximum incorporation achieved was of 33% (for 1% DMAEMA), giving rise to a surface charge density of $9 \mu\text{C cm}^{-2}$ [34]. The higher charge density achieved here, even at lower incorporation (25% incorporation with charge density of $24 \mu\text{C cm}^{-2}$) is a clear benefit of the two DABCO charges. Nevertheless, the charge density was higher than expected when compared to DMAEMA, which probably is related to the steric hindrance effect of DMAEMA that makes less available the cations during the titration process used to determine the charge density. The effect of both, the double charge per molecule and the higher availability of the charges in DABCO are likely responsible for the small d_p and increased stability of the cationic dispersions obtained in this work.

The stability of the dispersions was checked after storage of the dispersions for 6 months under standard atmospheric conditions ($23 \pm 3 \text{ }^\circ\text{C}$ and $60 \pm 5\%$ relative humidity) by measuring the particle size and distributions by CHDF. The results are presented in Table 2 and Fig. S3. The average particle size after 6 months did not changed significantly indicating proper dispersion stability. Moreover, as seen in Fig. S3 in the Supporting Information, three latexes kept the monomodal distribution

after 6 months, as there was no additional mode of particle sizes observed nor widening of the distribution curves.

The polymers' microstructure is presented in Table 3. A gel content of above 74% was achieved, higher than expected, owed to the lower reactivity of MMA terminated chains for H-abstraction, the absence of abstractable hydrogens in MMA and the fact that MMA radicals terminated by disproportionation, which in conventionally stabilized MMA/BA systems resulted in gel fraction lower than 10% [35]. Likely, the presence of cationic species onto particles in the present case contributes to the chains insolubility in THF. The insoluble fraction increased with the DABCO content, confirming its higher incorporation and denser charges onto BA/MMA particles. The molar masses of the soluble polymer fraction also increased with DABCO concentration. This is oppositely than in conventionally stabilized BA/MMA particles, in which the gel fraction represents crosslinked and branched chains. In such case, when the gel fraction in the polymer is raised, the molar mass of the soluble polymer decreased due to the incorporation of high-molar mass polymers into the gel. This is another indication that the gel fraction observed here is not an intrinsic crosslink/branch structure content.

3.2. Polymer films performance. When the glass transition temperature (T_g) of the aqueous polymer dispersions is lower than room temperature and the dispersion is dried under standard atmospheric conditions, a continuous polymer film is obtained. Even though DABCO homopolymer is stiff and its presence in polymer chains usually decreases their mobility and increases the T_g [22,39], the T_g of the DABCO containing polymer films was not affected by DABCO content as the values were between 16 and $17 \text{ }^\circ\text{C}$, likely because MMA/BA fraction in all the films is large and determining.

When conventional surfactants are used for the dispersion synthesis, during film formation the adsorbed surfactant migrates towards the film-air or the film-substrate interfaces, or it can be trapped at the particle/particle boundaries creating hydrophilic pathways and small aggregates in the film [36]. The mobility of the surfactant negatively affects the film performance [37]. This is why, the presence of DABCO cationic monomer on final film performance was investigated.

Continuous films were obtained for the three systems using different DABCO content and the photos of the polymer films are shown in Fig. S4. By increasing DABCO concentration, the transparency of the films decreased, which indicated that there was no complete coalescence of polymer particles within a continuous film. In order to get a deeper insight of the morphology, these films were analyzed by TEM.

Table 3
Polymers microstructure.

Latex	Gel content (%)	Mw (kDa)	\bar{D}
DABCO1	74 ± 1	310 ± 30	2.4
DABCO3	78 ± 1	430 ± 20	2.3
DABCO5	83 ± 3	466 ± 40	2.7

Fig. 4 shows the TEM images of the films' cross-section, where a honeycomb structure of deformed polymer particles was observed, more evidenced at increased DABCO content. Taking into consideration that DABCO rich chains are distributed onto the surface of polymer particles to provide colloidal stability, during film formation they form the network, which hinder the polymer chains interpenetration, acting as a barrier against particle coalescence that is essential to form continuous and transparent film. In TEM images of DABCO3 and DABCO5 films (Fig. 4a and b, respectively) the network is much more apparent, which means that, by increasing DABCO content in the film, this network is made of thicker DABCO containing polymer layers, decreasing the film transparency. This is in line with the retardation effect produced by functional groups on polymer diffusion reported for carboxylic acid [38] or NaSS containing species [29].

To determine the performance of these films in coating application, it is important to study their mechanical and water resistance, as they affect the durability and protection function of the coating. The mechanical resistance was studied by means of tensile measurements, whereas the water sensitivity was evaluated by water uptake of immersed film in water.

The stress-strain behavior of the polymer films containing different content of DABCO is shown in Fig. 5a and the data of the mechanical properties withdrawn from the stress-strain curves are summarized in Table S2, Supporting Information. By increasing DABCO concentration, films with higher Young's modulus were produced, likely due to the reinforcing network formed by the DABCO rich polymer chains observed in Fig. 4, which became thicker for higher DABCO content, producing mechanical percolation and much stiffer films. It has been already reported that the honeycomb structure formed from stiffer ionic moieties-containing polymer chains within a softer polymer matrix is responsible for the drastic differences observed in the elastic modulus [29,40]. Furthermore, Table S2 reveal an increase in the ultimate strength and toughness with increasing DABCO amount from 1 to 5 mol %, resulting in stiffer and tougher materials without any drop in the elongation at break.

Waterborne coatings containing ionic functional groups are strongly susceptible to durability issues pertaining to poor water resistance. It was demonstrated that water absorption of a cationic film containing methacrylate ethyl trimethyl ammonium chloride (DMC) increased with DMC concentration [19]. The water uptake results obtained are presented in Fig. 5b. During the initial period, the water absorption increased sharply from 5 to 45 wt% when the concentration of DABCO increased from 1 to 5 mol%, likely due to the higher concentration of water-soluble species. However, after two days, all the films present the saturation behavior, indicating that there is no formation of hydrophilic pockets by migration of the stabilizing species during film formation,

which acted as a sink. The high water uptake occurred due to two reasons. The hydrophilic DABCO containing network, observed in TEM image (Fig. 4), creates a hydrophilic path for water diffusion. Taking into account the incorporation of DABCO onto particles (Table 2) likely there is a high quantity of water-soluble oligomers present in the dispersions that are likely distributed within the polymer films and increase its hydrophilicity. Both effects are larger for higher DABCO content, thus, these films are less water resistant. The small weight drop observed is probably a consequence of the solubilization of some of the water-soluble oligomers and their desorption towards the water phase.

4. Conclusion

High solids content (meth)acrylic waterborne dispersions stabilized by DABCO cationic monomer that contain two charges were synthesized by emulsifier-free seeded semibatch emulsion polymerization. Using 1–5 mol% DABCO, cationic dispersions with narrow PSD and d_p of around 170 nm were obtained. Despite modest incorporation of DABCO onto particles that implies high concentration of water-soluble oligomers in the dispersions, a high charge density in a range of 24–180 $\mu\text{C cm}^{-2}$ was achieved. Likely, this was the main reason for the excellent colloidal stability and control of particle diameter. The incorporation of DABCO increased with its concentration indicating that the increasing ionic strength in the dispersions shifted the adsorption of the ionic species towards the polymer particles. The polymers contain high THF insoluble fraction (gel content), probably due to the presence of cationic species in the polymer chains that make them insoluble in THF. Therefore, the higher gel content at elevated concentrations of DABCO was attributed to the higher DABCO incorporation onto the particles. Stiff but still flexible polymer films were produced, attributed to the presence of the stiff cationic network made of polymer chains rich in DABCO units within the (meth)acrylic matrix, as observed in TEM images. The network was denser for higher DABCO contents. Even though the water resistant of the films was very good for low DABCO content, it was affected by the content of DABCO monomer within the polymer, likely due to denser ionic network.

This work offers a practical route for cationically charged nanoparticles synthesis in absence of emulsifier using cationic monomer with double charge. The control of the colloidal characteristics such as surface charge density and particle size might be highly interesting for biotechnological and industrial applications, especially for antimicrobial coatings.

Declaration of Competing Interest

The authors declare that they have no known competing financial

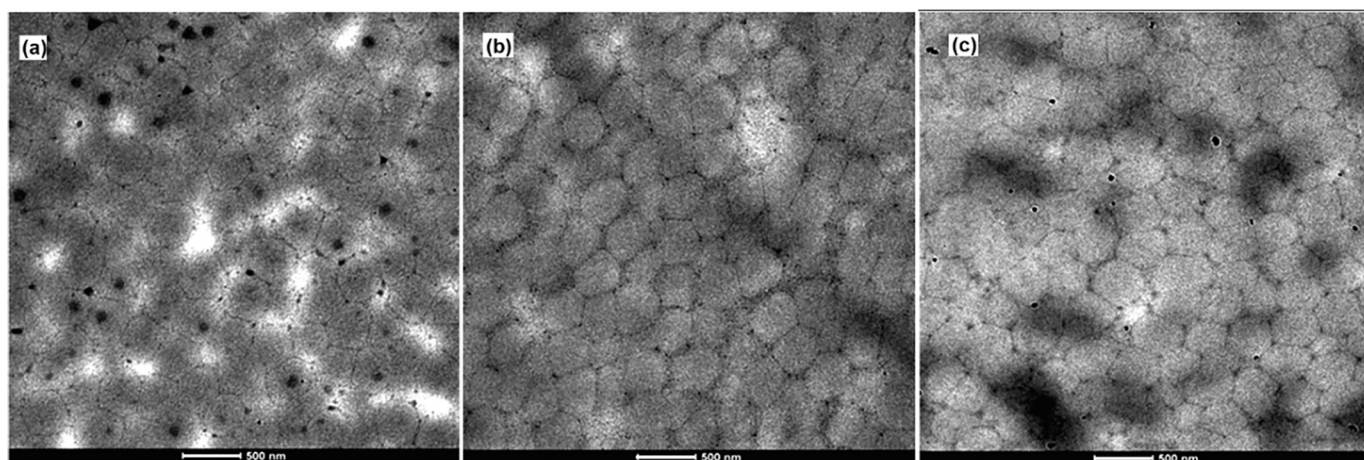


Fig. 4. TEM images of film cross-section: (a) DABCO1, (b) DABCO3 and (c) DABCO5. Scale bar in all images is 500 nm.

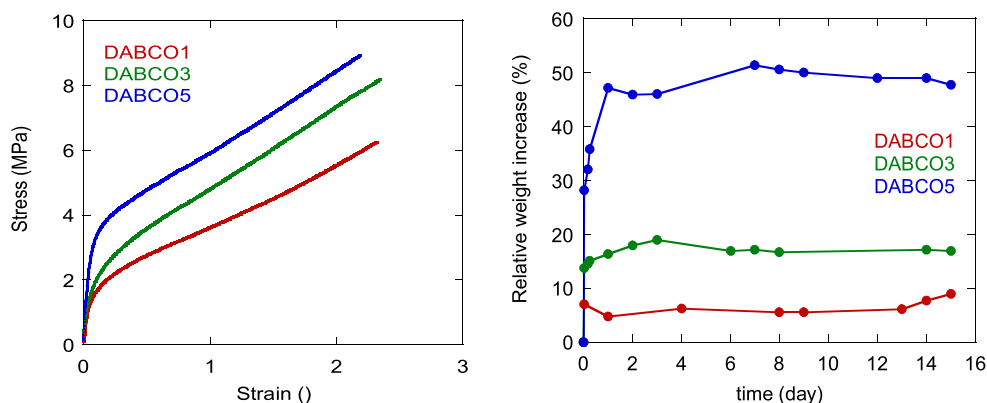


Fig. 5. (a) The stress-strain curves and (b) water uptake of films containing different DABCO concentration.

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.colcom.2022.100659>.

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