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Communication

Polymer nanospheres with hydrophobic surface groups as supramolecular building blocks produced by aqueous PISA

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A robust and straightforward synthesis of waterborne polymer nanospheres bearing the supramolecular association unit dialkoxynaphthalene at their surface is presented using polymerization-induced self-assembly (PISA). A RAFT agent bearing this unit is first employed to produce poly(acrylic acid) chains, which are then chain extended with styrene (S) to spontaneously form the nanoobjects via RAFT aqueous emulsion polymerization. The particular challenge posed by the dialkoxynaphthalene hydrophobicity can be overcome by the use of PISA and the deprotonation of the poly(acrylic acid). At pH = 7, very homogeneous latexes are obtained. The particle diameters can be tuned from 36 to 105 nm (with a narrow particle size distribution) by varying the molar mass of the PS block. The surface accessibility of the dialkoxynaphthalene moieties is demonstrated by complexation with the complementary

host cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺ · Cl⁻), highlighting the potential of the nanospheres to act as building blocks for responsive supramolecular structures.

1. Introduction

The incorporation of supramolecular recognition units into polymer materials enables spontaneous assembly into complex superordinate structures. The reversible non-covalent interactions make this a powerful methodology with growing importance for the development of new responsive materials.^[1] In this context, the electron-rich dialkoxynaphthalene unit and its complementary host, the electron-deficient cyclophane cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺, structures shown in Figure 1),^[2-4] constitute one of the most prominent, attractive and versatile pairs for supramolecular assembly. In both water and organic solvents, they spontaneously form a very stable pseudorotaxane host–guest complex (schematically shown in Figure 1). Its dissociation can, however, be reversibly triggered by different external stimuli, such as heat, electrochemical oxidation/reduction,^[5] or the addition of competitive guest molecules.^[2, 6]

When these units are covalently attached to polymer chains, their characteristic responsive capacities are imparted to the resulting material.^[7, 8] It was shown that the properties of polymers carrying dialkoxynaphthalene groups at the chain end are drastically, but reversibly, changed upon complexation of these units with the hydrophilic CBPQT⁴⁺ · 4 Cl⁻.^[3] If both complementary units are linked to polymer chains, their spontaneous complexation leads to the formation of block copolymers with the supramolecular link in the middle of the chain.^[9] The redissociation to the individual polymer chains can be triggered by the aforementioned external stimuli and, in addition, the phase transition of one of the polymers^[6, 10] which can in turn be actuated by temperature, solvent, pH value, or pressure.^[11]

Given the straightforwardness and flexibility of creating triggerable bonds, it is extremely promising to expand the toolbox of nanosized structures functionalized with these connector units beyond simple linear polymer chains to more advanced structures. As a useful candidate in the toolbox, we target here nanosized polymer particles bearing multiple dialkoxynaphthalene groups on the surface (Figure 1). A variety of interesting superordinate

multiresponsive structures such as crosslinked particle networks for self-healing elastomers, biohybrid materials when coupled with biological molecules, or reversible one-component coatings can be envisaged by combining these nanoparticles with different CBPQT⁴⁺-functionalized counterunits. To realize the full potential of these systems, the intrinsic hydrophilicity of CBPQT⁴⁺ demands availability of the dialkoxynaphthalene building blocks in water, which is also the essential solvent in many of the applications mentioned above.

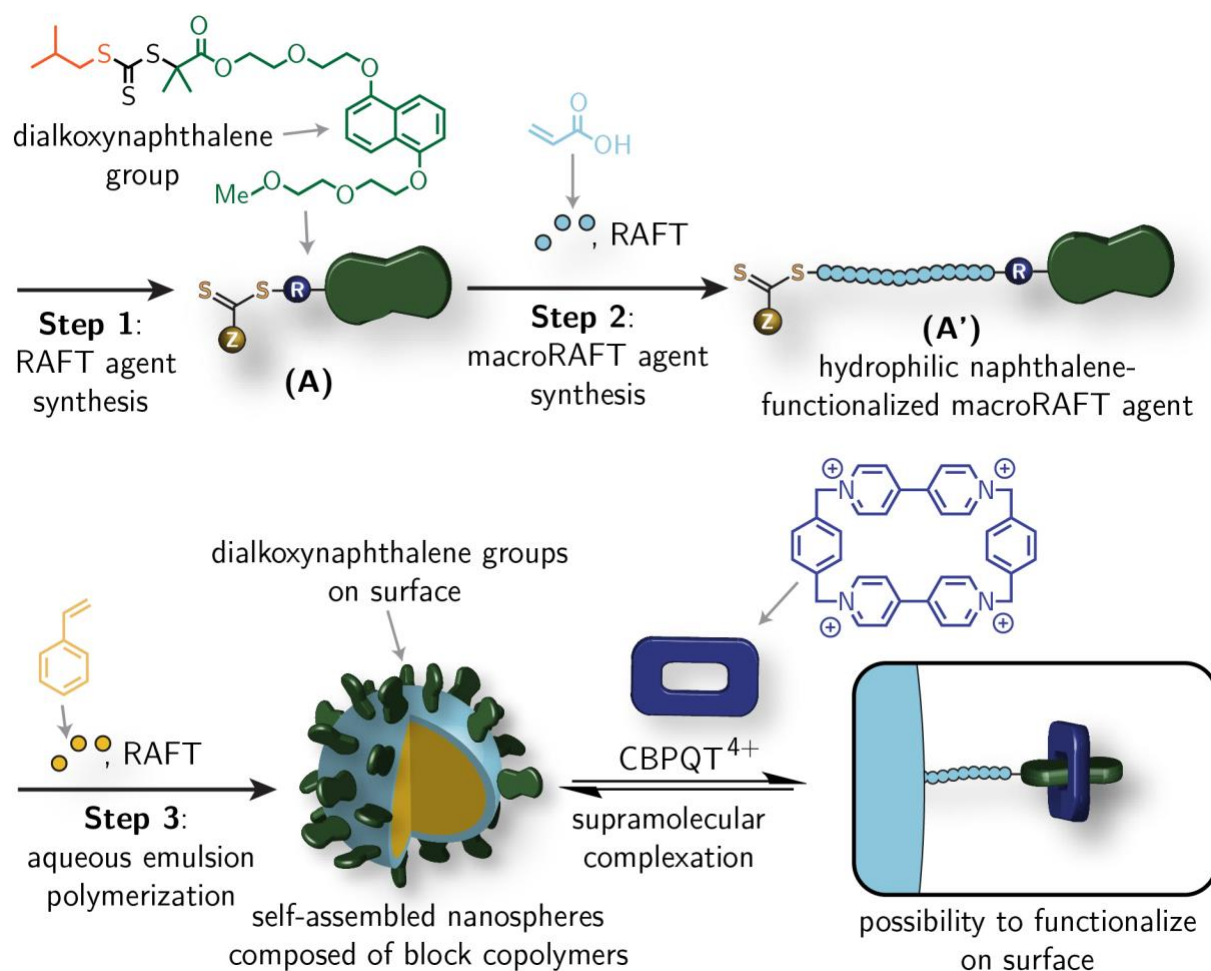


Figure 1. Overview of synthesis strategy.

In the realm of emulsion polymerization,^[12] an efficient and potent tool for the tailored and straightforward synthesis of polymer colloids (latexes) is the polymerization-induced self-assembly (PISA) process.^[13-16] In PISA, water soluble polymer chains are extended with an insoluble block using reversible-deactivation radical polymerization (RDRP). In this way, colloiddally stable self-assembled nanoparticles are spontaneously formed after the hydrophobic

block reaches a critical length and becomes water insoluble. Particles, in which the polymerization takes place until all hydrophobic monomer is consumed, are thereby formed without the need of surfactant. The final latex particles are composed of amphiphilic block copolymers with predefined and narrowly distributed molar masses. When reversible addition-fragmentation chain transfer (RAFT) polymerization is used as the RDRP technique, surface functionalization can be introduced via the design of the initial RAFT agent (thiocarbonylthio compound $Z-C(=S)-SR$).^[17, 18] Any chemical function connected to the R-group will be retained at the hydrophilic chain end and form the particle surface. In principle this presents an opportunity for making hydrophobic units such as dialkoxynaphthalene available in water, but also entails the challenge of retaining them at the water interface without disrupting the self-assembly process.

This study presents a robust synthesis of water-dispersed polymer nanoparticles decorated with dialkoxynaphthalene groups on the surface via PISA, based on RAFT aqueous emulsion polymerization. The aforementioned challenge of bringing very hydrophobic groups on the surface of particles is overcome by using a poly(acrylic acid) (PAA)-based macroRAFT agent. The parameters of the PISA process are optimized in emulsion polymerizations of styrene (S) to obtain uniform dialkoxynaphthalene-decorated latexes with tailored particle size. Their ability to associate with CBPQT⁴⁺ is also demonstrated.

3. Results and Discussion

3.1. Choice of the starting hydrophilic macroRAFT agent

While the design of a synthesis strategy for functionalized polymer nanoparticles could be built on a solid groundwork of studies exploring the PISA process in emulsion using RAFT,^[19-22] the introduction of the dialkoxynaphthalene group imparts a particular challenge to the system. With the use of a suitable RAFT agent having the dialkoxynaphthalene group as part of the

reinitiating R group, the corresponding hydrophilic macroRAFT agent can indeed be created in a relatively straightforward way by radical polymerization of a water-soluble monomer. RAFT agent **A** (see Figure 1) – a trithiocarbonate bearing a dialkoxynaphthalene group – was used. Its synthesis was carried out by Steglich esterification of the acid-functionalized RAFT fragment and the hydroxyl-terminated dialkoxynaphthalene precursor as previously published.^[10]

Our first trials were based on the use of neutral hydrophilic poly(*N*-acryloylmorpholine) (PNAM) macroRAFT agents as they had been successfully employed to mediate styrene emulsion polymerization under PISA conditions in emulsion previous studies.^[23, 24] First, well-defined hydrophilic PNAM chains bearing the dialkoxynaphthalene group were obtained using **A** in dioxane (see SI). The products were then used for emulsion polymerization of styrene (S). However, our attempts to obtain stable PS latexes failed and styrene conversion levelled off at below 35 % regardless of the molar ratio of styrene and PNAM (from 200 to 1600) and the initiator concentration. We suspect that this resulted from the low hydrophilicity of the dialkoxynaphthalene group which tends to face away from the water phase and impedes efficient self-assembly, and thus particle nucleation. This shows the impact of the chemical nature of the R group installed on the α -chain end of the hydrophilic macroRAFT on the self-assembly during PISA. A crucial impact of the R group in RAFT-PISA on the morphology of the resulting latex has rarely been observed before.^{[25],[26]} To tackle the challenge imposed by the very hydrophobic end group, acrylic acid (AA) was chosen as the monomer for the hydrophilic starting block. Its very high hydrophilicity can be amplified by deprotonation, to give better chance of overcoming the dialkoxynaphthalene's hydrophobicity. Functionalized PAA macroRAFT agents **A'** were synthesized using **A** in dioxane at 70 °C targeting a molar mass of 4000 g mol⁻¹, corresponding to 47 AA units. The polymerization was run to full conversion and the product was purified by repeated precipitation in diethyl ether. In the ¹H-NMR spectrum (Figure S1), the intensities of the signals corresponding to the PAA backbone, the aromatic naphthalene group, and the protons adjacent to the trithiocarbonate group proved

the expected degree of polymerization and full retention of end groups. SEC using dimethyl formamide as eluent ($M_n = 5900 \text{ g mol}^{-1}$, $D = 1.08$, PMMA standards) also confirmed the structure.

3.2. Emulsion polymerizations of styrene with **A'**

The prepared macroRAFT agent **A'** was employed in aqueous emulsion polymerizations of styrene using conditions found to work well in our previous study.^[27] Nine emulsion polymerizations are presented here for which critical parameters were systematically varied to optimize the system: the molar ratio of macroRAFT agent and radical initiator $r_{A'/ini}$, the starting pH value of the system, and the molar ratio of styrene and macroRAFT agent $r_{S/A'}$. All parameters and results for the discussed polymerizations are listed in Table 1.

Table 1. Emulsion polymerizations of styrene in the presence of macroRAFT agent **A'** (80 °C, $c_S = 2.4 \text{ mol L}^{-1}$).

Sam ple	$r_{S/A'}$ ^a	$r_{A'/i}$ ^b	pH value ^c	Conver sion ^d	Time [h] ^d	Coagul ate ^e	Z_{av} ^f [nm]	PDI ^f	Partic les ^g	Diameter ^g [nm]
1	800	2.5	3.4	0.89	6	10.1 %	—	—	—	—
2	800	1.5	3.5	1	2.0	12.8 %	106	0.49	1475	33 ± 7
3	800	2.0	3.3	1	2.5	9.8 %	84	0.35	2162	36 ± 10
4	400	2.0	2.9	1	2.5	8.6 %	96	0.55	2104	30 ± 7
5	1200	2.0	3.3	1	2.5	11.0 %	67	0.27	870	37 ± 8
6	800	2.0	5.0	1	3.0	5.5 %	54	0.28	500	27 ± 8
7	400	2.0	7.0	1	3.0	3.0 %	66	0.04	6351	36 ± 10
8	800	2.0	7.0	1	2.5	0.3 %	86	0.05	6705	53 ± 11
9	1200	2.0	7.0	1	2.5	1.6 %	138	0.02	5838	105 ± 15

^{a)} Ratio of styrene and macroRAFT agent **A'** corresponding to the number of styrene units per chain at full conversion; ^{b)} ratio of macroRAFT agent **A'** and ACPA; ^{c)} starting pH value; ^{d)} conversion determined by gravimetry and the time to reach it; ^{e)} amount of coagulate (gravimetry); ^{f)} Z_{av} and PDI values measured by DLS; ^{g)} number of evaluated particles, mean diameter, standard deviation determined by TEM.

Polymerizations **1–3** were carried out to identify the necessary initiator concentration. A value of 2 (polymerization **3**) was chosen for $r_{A'/ini}$ in the subsequent experiments since it was the

minimum amount of initiator necessary to reach full conversion. Degrees of polymerization of the PS block ranging from 400 to 1200 (corresponding to the ratio of styrene and **A'**, $r_{S/A'}$, samples **3–5**) were targeted under the same conditions. Although particles formed, the particle sizes (> 66 nm) and the particle size distributions obtained by DLS ($PDI > 0.27$) revealed that the stability provided by **A'** at natural pH was low. This was indeed confirmed by the rather high amount of coagulum obtained (around 10%), which is in sharp contrast to comparable experiments successfully performed in our group using the equivalent dialkoxynaphthalene-free RAFT agent^[27] and underlines again the impact of the α -chain end on the self-assembly process. Subsequently, polymerizations **6** and **8** were performed under conditions identical to polymerization **3**, but with increased pH values (pH = 5 and 7) of the starting system, set by addition of sodium hydroxide. Basic pH values were not targeted as this could lead to hydrolysis of the trithiocarbonate groups. In our earlier work on the dialkoxynaphthalene-free system,^[27] it had been found that the latex quality could not be improved by raising the pH to higher values. This was rationalized by the mutual repulsion of the ionized polymer chains, especially during the very first addition steps which are impeded in non-acidic environment.^[27]

In the systems presented here, elevating the pH value had a different effect. While the system performed only slightly better at pH = 5 (sample **6**), a drastic improvement of the stability of the final objects was observed from polymerization **6** to **8** (pH from 5 to 7), mostly evidenced by the extremely low PDI (< 0.05 by DLS, efficient nucleation) and strongly reduced amounts of coagulum (down to 0.3 %). Going from natural pH via pH = 5 through to pH = 7, the mean particle sizes declined from (36 ± 10) nm to (27 ± 8) nm and then rose to (53 ± 11) nm. In contrast to the non-functionalized system, the mutual electrostatic repulsion of the charged chains does not exert a negative effect on the latex homogeneity.

The final two polymerizations **7** and **9** were carried out under the same conditions at pH = 7 with variation of the concentration of **A'**. Very well-defined and stable dispersions were obtained for $r_{S/A'} = 400, 800$ and 1200. Figure 2 shows representative TEM images of latexes

7, **8**, and **9** with particle diameter histograms (obtained from multiple close-up micrographs) as inlays. Latex particles with three distinct sizes of (36 ± 10) nm, (53 ± 11) nm, and (105 ± 15) nm were obtained. DLS values were in excellent agreement (Table 1) given that DLS gives the hydrated diameter, while TEM is measured in the dry (non-hydrated) state. The final particle diameter can therefore be easily fine-tuned in the remarkable range from 36 nm up to 105 nm by varying the length of the hydrophobic block in this versatile system, depending on the target application.

The whole process (starting from the RAFT agent **A**) was repeated twice using the conditions of polymerization **8** for the last step, but increasing the reaction volume from 6 mL to 40 mL and then to 100 mL. Very similar results (Z_{av} : 91.6 nm and 92.9 nm; TEM: (57 ± 14) nm and (57 ± 16) nm) were obtained, indicative of the robustness and reproducibility of the method.

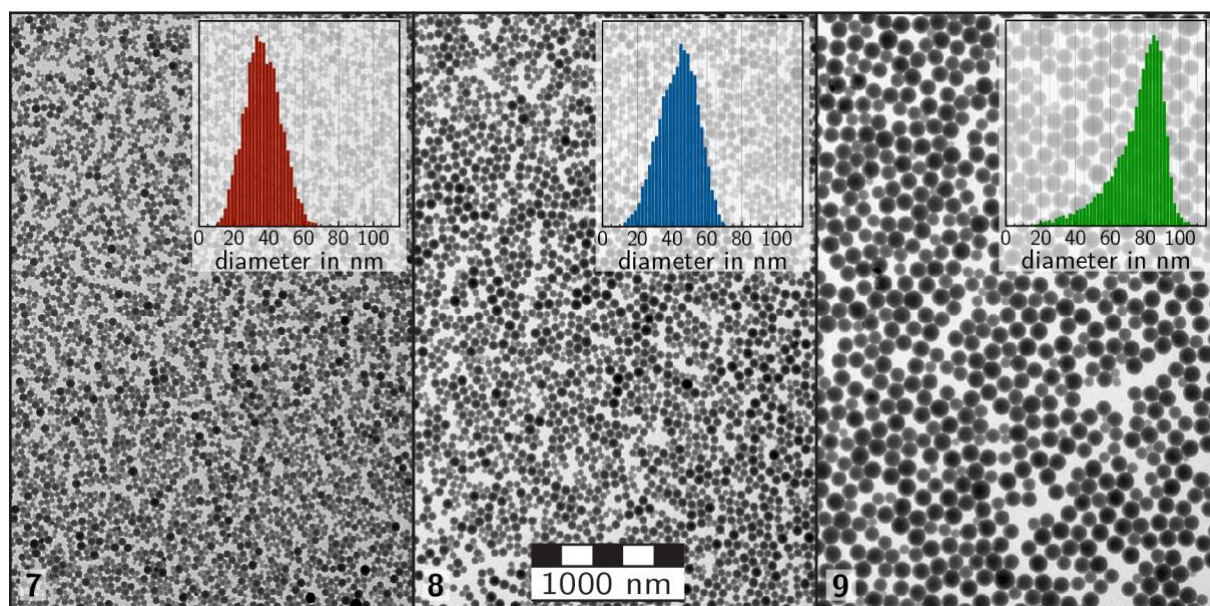


Figure 2. TEM images of latexes **7**, **8**, and **9** with particle diameter histograms (obtained from different more zoomed-in images) as inlays. The scale bar applies to all three micrographs.

3.3. Complexation tests

A basic complexation test was performed in order to make sure that the dialkoxynaphthalene groups on the surface were accessible to complexation and that the defined particles were retained in the process. An aqueous solution of one equivalent of $\text{CBPQT}^{4+} \cdot 4 \text{Cl}^-$ with respect to the number of dialkoxynaphthalene moieties was added to latexes **7**, **8**, and **9**. The formation

of the supramolecular complexes was observed immediately through the colour change (pink) caused by the characteristic charge–transfer transition of the naphthalene–CBPQT⁴⁺ complex at 522 nm. Side complexation can in principle also take place on the deprotonated carboxylate moieties of the PAA backbone at pH = 7. However, the distinct absorption band can only be observed if CBPQT⁴⁺ is complexed with the dialkoxynaphthalene group. This proves the targeted complexation. After spinning down the latex in a centrifuge, a colorless supernatant was obtained, proving that the complexation had taken place exclusively on the surface of the nanoparticles. The complexed latexes were also analyzed again using DLS and TEM. It was found that the integrity of the very narrow particle size distributions was perfectly retained after complexation (Figure 3 for latex **8**).

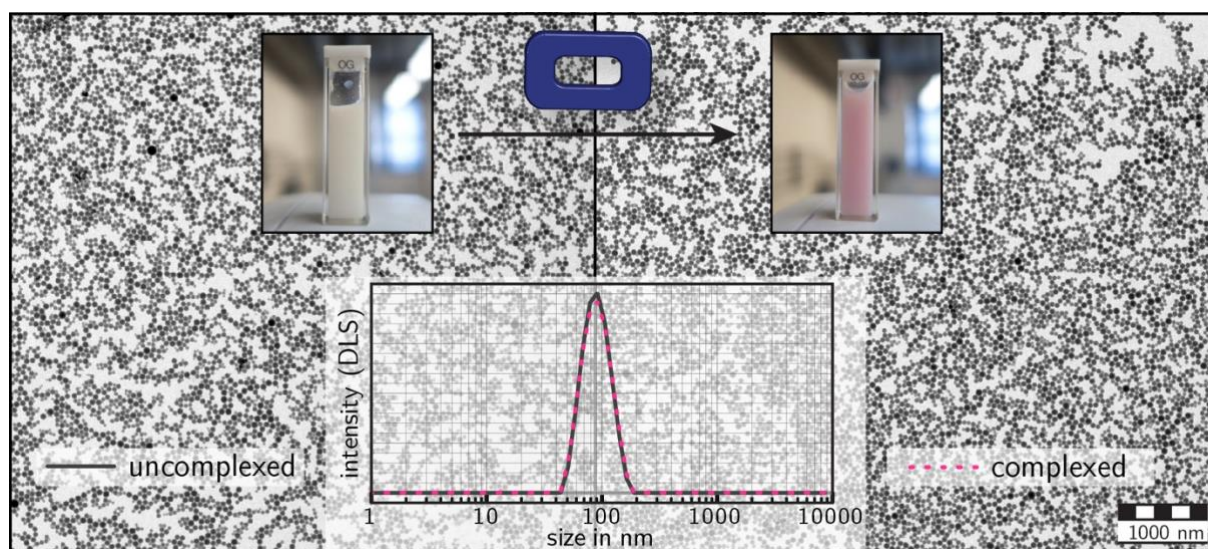


Figure 3. Complexation of latex **8** with CBPQT⁴⁺. Photos of latex and corresponding TEM images before (left) and after (right) complexation. The center diagram shows the size distribution obtained from DLS.

4. Conclusions

Producing latex particles decorated with surface-hydrophobic moieties by emulsion polymerization in water is a real challenge. Employing the PISA process using RAFT polymerization for the synthesis in water of nanoparticles with very hydrophobic groups on the surface is a major step ahead from established systems with non-functionalized or typically

hydrophilic surfaces. Using a PAA starting block at $\text{pH} = 7$, a process was designed which not only allows for the robust and straightforward synthesis of very well-defined aqueous nanoparticle dispersions with dialkoxynaphthalene groups at the surface, but also for the finetuning of the nanoparticle diameter from 36 nm to 105 nm, which corresponds to a factor of 25 in volume. Since the whole process was shown to be very robust and reproducible, it is expected that the principle can easily be transferred to other hydrophobic end groups.

While synthetically more challenging, the resulting latexes allow the introduction of supramolecular chemistry to this field of nanomaterial science. It was demonstrated that complexation between CBPQT^{4+} and dialkoxynaphthalene takes place on the nanoparticle surface without changing the integrity of the system. The developed systems will be used as universal building blocks for a variety of sophisticated systems by being coupled with different CBPQT^{4+} -containing partners in upcoming studies, one promising next step being the combination with bifunctional CBPQT^{4+} linkers. Since the presented process allows for the synthesis of polymer nanoparticles with different sizes, the same strategy can be used to provide different components to be mixed in special systems. Future studies will also focus on the multiresponsive properties of the formed systems and resulting material properties.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Keywords: polymerization-induced self-assembly, emulsion polymerization, RAFT polymerization, polymeric nanoparticles, supramolecular assembly.

References

- [1] J. Bigot, B. Charleux, G. Cooke, F. Delattre, D. Fournier, J. Lyskawa, L. Sambe, F. Stoffelbach, P. Woisel, *J. Am. Chem. Soc.* **2010**, *132*, 10796.
- [2] M. Bria, J. Bigot, G. Cooke, J. Lyskawa, G. Rabani, V. M. Rotello, P. Woisel, *Tetrahedron* **2009**, *65*, 400.
- [3] M. Bria, G. Cooke, A. Cooper, J. F. Garety, S. G. Hewage, M. Nutley, G. Rabani, P. Woisel, *Tetrahedron Lett.* **2007**, *48*, 301.
- [4] J. Louisy, F. Delattre, J. Lyskawa, A. Malfait, C. E. Maclean, L. Sambe, N. Zhu, G. Cooke, P. Woisel, *Chem. Commun.* **2011**, *47*, 6819.
- [5] F. Barka-Bouaifel, J. Niedziolka-Jonsson, X. Castel, O. Saison, A. Akjouj, Y. Pennec, B. Djafari-Rouhani, P. Woisel, J. Lyskawa, L. Sambe, G. Cooke, N. Bezzi, R. Boukherroub, S. Szunerits, *J. Mat. Chem.* **2011**, *21*, 3006.
- [6] L. Sambe, F. Stoffelbach, K. Poltorak, J. Lyskawa, A. Malfait, M. Bria, G. Cooke, P. Woisel, *Macromol. Rapid Commun.* **2014**, *35*, 498.
- [7] J. Bigot, D. Fournier, J. Lyskawa, T. Marmin, F. Cazaux, G. Cooke, P. Woisel, *Polym. Chem.* **2010**, *1*, 1024.
- [8] L. Sambe, V. R. de La Rosa, K. Belal, F. Stoffelbach, J. Lyskawa, F. Delattre, M. Bria, G. Cooke, R. Hoogenboom, P. Woisel, *Angew. Chem. Int. Ed.* **2014**, *53*, 5044.
- [9] L. Sambe, K. Belal, F. Stoffelbach, J. Lyskawa, F. Delattre, M. Bria, F. X. Sauvage, M. Sliwa, V. Humblot, B. Charleux, G. Cooke, P. Woisel, *Polym. Chem.* **2014**, *5*, 1031.
- [10] J. Bigot, M. Bria, S. T. Caldwell, F. Cazaux, A. Cooper, B. Charleux, G. Cooke, B. Fitzpatrick, D. Fournier, J. Lyskawa, M. Nutley, F. Stoffelbach, P. Woisel, *Chem. Commun.* **2009**, 5266.
- [11] B. Ebeling, S. Eggers, M. Hendrich, A. Nitschke, P. Vana, *Macromolecules* **2014**, *47*, 1462.
- [12] P. A. Lovell, M. S. El-Aasser, Editors, "Emulsion Polymerization and Emulsion Polymers", John Wiley and Sons, 1997.
- [13] B. Charleux, G. Delattre, J. Rieger, F. D'Agosto, *Macromolecules* **2012**, *45*, 6753.
- [14] S. L. Canning, G. N. Smith, S. P. Armes, *Macromolecules* **2016**, *49*, 1985.
- [15] M. Lansalot, J. Rieger, F. D'Agosto, in *Macromolecular Self-Assembly*, L. Billon and O. Bourisov, Eds., John Wiley & Sons, Inc., Hoboken, New Jersey, 2016, p. 33.
- [16] J. Zhou, H. Yao, J. Ma, *Polym. Chem.* **2018**, *9*, 2532.
- [17] C. St Thomas, R. Guerrero-Santos, F. D'Agosto, *Polym. Chem.* **2015**, *6*, 5405.
- [18] M. Bathfield, F. D'Agosto, R. Spitz, M.-T. Charreyre, C. Pichot, T. Delair, *Macromol. Rapid Commun.* **2007**, *28*, 1540.
- [19] I. Chaduc, M. Girod, R. Antoine, B. Charleux, F. D'Agosto, M. Lansalot, *Macromolecules* **2012**, *45*, 5881.

- [20] I. Chaduc, W. Zhang, J. Rieger, M. Lansalot, F. D'Agosto, B. Charleux, *Macromol. Rapid Commun.* **2011**, *32*, 1270.
- [21] W. Zhang, F. D'Agosto, O. Boyron, J. Rieger, B. Charleux, *Macromolecules* **2011**, *44*, 7584.
- [22] W. Zhang, F. D'Agosto, O. Boyron, J. Rieger, B. Charleux, *Macromolecules* **2012**, *45*, 4075.
- [23] I. Chaduc, E. Reynaud, L. Dumas, L. Albertin, F. D'Agosto, M. Lansalot, *Polymer* **2016**, *106*, 218.
- [24] J. Lesage de la Haye, X. Zhang, I. Chaduc, F. Brunel, M. Lansalot, F. D'Agosto, *Angew. Chem. Int. Ed.* **2016**, *55*, 3739.
- [25] J. R. Lovett, N. J. Warren, L. P. D. Ratcliffe, M. K. Kocik, S. P. Armes, *Angew. Chem. Int. Ed.* **2015**, *54*, 1279.
- [26] S. Y. Khor, N. P. Truong, J. F. Quinn, M. R. Whittaker, T. P. Davis, *ACS Macro Lett.* **2017**, *6*, 1013.
- [27] I. Chaduc, A. Crepet, O. Boyron, B. Charleux, F. D'Agosto, M. Lansalot, *Macromolecules* **2013**, *46*, 6013.