



Cite this: *Nanoscale*, 2017, 9, 1670

Pick up, move and release of nanoparticles utilizing co-non-solvency of PNIPAM brushes†

Yunlong Yu,^a Ricardo A. Lopez de la Cruz,^b Bernard D. Kieviet,^{‡,a} Hubert Gojzewski,^a Adeline Pons,^b G. Julius Vancso^a and Sissi de Beer^{*a}

A critical complication in handling nanoparticles is the formation of large aggregates when particles are dried e.g. when they need to be transferred from one liquid to another. The particles in these aggregates need to disperse into the destined liquid medium, which has been proven difficult due to the relatively large interfacial interaction forces between nanoparticles. We present a simple method to capture, move and release nanoparticles without the formation of large aggregates. To do so, we employ the co-non-solvency effect of poly(*N*-isopropylacrylamide) (PNIPAM) brushes in water–ethanol mixtures. In pure water or ethanol, the densely end-anchored macromolecules in the PNIPAM brush stretch and absorb the solvent. We show that under these conditions, the adherence between the PNIPAM brush and a silicon oxide, gold, polystyrene or poly(methyl methacrylate) colloid attached to an atomic force microscopy cantilever is low. In contrast, when the PNIPAM brushes are in a collapsed state in a 30–70 vol% ethanol–water mixture, the adhesion between the brush and the different counter surfaces is high. For potential application, we demonstrate that this difference in adhesion can be utilized to pick up, move and release 900 silicon oxide nanoparticles of diameter 80 nm using only 10 × 10 μm² PNIPAM brush.

Received 28th November 2016,
Accepted 4th January 2017

DOI: 10.1039/c6nr09245d

www.rsc.org/nanoscale

Introduction

Nanoparticles are nowadays broadly applied in personal hygiene products,^{1–3} catalysis,^{4,5} bioanalysis,^{6,7} drug-delivery⁸ and water-treatment.^{9,10} To prepare these nanoparticles, the most commonly employed technique^{11,12} is the sol–gel method,^{13–15} where the particles are formed in solution *via* hydrolysis and a polycondensation reaction of the precursor. After synthesis, the nanoparticles need to be transferred to another medium for storage or further processing. Generally, this is realized *via* a two-step method:^{12,15} first, the particles are precipitated from solution by, for example, ultra-centrifuge. Next, the particles in the aggregate are allowed to diffuse into the new medium for further processing. The dissolution of the nanoparticles from the aggregate is often difficult to realize,¹⁶ because of the relatively strong interfacial forces acting between these particles that have high surface-to-volume ratios. To enable the dispersion,

many techniques are employed, such as chemical or physical surface modifications,^{17,18} and sonication.¹⁹ A smart alternative to these techniques is, however, the pick-up and release of particles by employment of stimulus responsive polymer brushes,²⁰ because within this method aggregation of the particles during the extraction is less likely to occur.

Polymer brushes consist of macromolecules that are attached with one end to a surface at a density that is high enough for the polymers to stretch away from the grafting surface.²¹ The degree of stretching of the polymers depends on the solvent quality. In poor solvents the polymers form a dense layer at the surface, while the polymers stretch more strongly in good solvents. Adhesion between the brush and the counter-surface (CS) is usually low when brushes are swollen in a good solvent,^{22–24} especially when brush–solvent interactions are favored over brush–CS interactions. In poor solvents, the adhesion is generally much higher, because of the possibility of more direct interaction between the brush and the CS.^{22,25–27} When the brushes are composed of polymers for which the effective solvent quality can be altered *via* an applied stimulus, such as temperature,²⁸ pH,²⁹ solvent,³⁰ light,³¹ salts,³² electronic³³ and magnetic field,³⁴ adhesion can be reversibly switched between high and low.^{24,35–44}

Poly(*N*-isopropyl acrylamide) (PNIPAM) is a stimulus responsive polymer,^{45–47} which can change its conformation from an extended coil to a collapsed globule upon increasing the temperature above the lower critical solution temperature

^aMaterials Science and Technology of Polymers, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, the Netherlands.

E-mail: s.j.a.debeer@utwente.nl

^bPhysics of Fluids, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, the Netherlands

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c6nr09245d

‡Present address: The Hague University of Applied Sciences, Johanna Westerdijkplein 75, The Hague, 2521 EN, the Netherlands.

(LCST) of 32 °C in pure water.^{48–50} This effect can be employed to switch the adherence between PNIPAM brushes³⁸ or PNIPAM and different CSs.^{24,35,51} Reversible adherence changes by heating and cooling PNIPAM have been applied to capture and release polymer particles,⁵² cells⁴⁰ and dye.⁵³ However, considering the energy cost, it might not be practical to change the temperature repeatedly and it could be more efficient to alter the adherence by adjusting the solvent composition.

Besides being temperature-responsive, PNIPAM can also be responsive to changes in the solvents composition.^{54–57} The LCST of PNIPAM shifts to lower temperatures in certain mixtures of two good solvents. For example, for methanol–water mixtures between 30 and 65 vol%,⁵⁸ the LCST is lower than 20 °C and PNIPAM precipitates at room temperature. This effect is called co-non-solvency and has been observed for PNIPAM in methanol–water,^{57,59} tetrahydrofuran (THF)–water^{56,60} and dimethyl formamide (DMF)–water⁶¹ mixtures, too. Though the mechanism of co-non-solvency of PNIPAM is still under debate,^{54,57,62–65} the effect is already regularly employed in fermentation gating,⁶⁶ regulating channel permeability,⁶⁷ and force actuation.⁶⁸

In this article, we show that co-non-solvency of PNIPAM can be utilized to capture nanoparticles from their aqueous solution and re-disperse them into another solution. By systematically varying the solvent composition, we find that the change in adhesion between PNIPAM and different CSs is maximum upon changing the composition between pure ethanol (low) and 30–70 vol% ethanol–water (high). The magnitude of the adherence-change depends on the CS, but is in all cases larger than a factor of 100. Using this method, we can pick up 900 silicon nanoparticles with a diameter of 80 nm at $10 \times 10 \mu\text{m}^2$ of PNIPAM brush in a 30–70 vol% ethanol–water mixture and redistribute them into a fresh solution of pure solvent. This can be achieved by simple dipping of the PNIPAM covered surface in the ethanol–water mixture, removing it and then dipping it into the pure solvent. We show that the percentage of aggregates is less than 2% and increases by less than 4% after several release and pick-up cycles. The number of the aggregates we observed in the brushes is always less than 20 particles. This shows that the presented method holds great potential for application in nanoparticle transfer between solutions without the formation of large aggregates.

Results and discussion

Fig. 1 shows the adhesive force and brush swelling for a PNIPAM brush (dry height 75 nm) measured by a silicon colloid probe using atomic force microscopy (AFM) in different ethanol–water mixtures between 0 and 100 vol% ethanol. More information on the materials and experimental procedures can be found in ESI.† The variation in swelling ratio with the ethanol content in the solvent mixture shows qualitatively the same trend as in our recent publication, where we compared different measurement techniques to extract brush swelling.²³

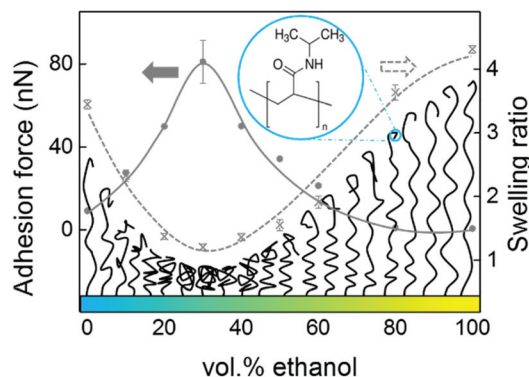


Fig. 1 The PNIPAM swelling ratio and adhesion force between PNIPAM and a SiO₂ colloid (diameter 7.75 μm) in various compositions of ethanol–water mixtures. The swelling ratio is calculated from the swollen height of brushes (measured by AFM imaging under a load of 1.5 nN over a scan size of 30 μm using a scan rate of 1 Hz), which is normalized by the dry height of the brush. The adhesion force is obtained from the AFM force separation curves measured for a retraction velocity of 0.8 μm s⁻¹ after the colloid has been pushed into the brush with a normal force of 70 ± 6 nN. The error bar of adhesion force at 30% represents the uncertainty in measurement data and denotes the standard error with a 95% confidence interval.

The swelling ratio of the PNIPAM brush in pure water (3.4) is slightly higher than in ref. 23 (3.0), which indicates we have a lower grafting density³⁸ of the samples in the present article (0.25 chains per nm² here vs. 0.45 chains per nm² in ref. 23). For the same reason, the swelling ratio of our PNIPAM brush in ethanol (4.3) is also slightly higher than in ref. 23 (3.6).

Fig. 1 shows that the brush swelling has a minimum for 30 vol% ethanol in the water–ethanol mixture. In this minimum the swelling ratio is still 1.2, which indicates that there is a significant amount of solvent trapped in the brush. The entrapment of solvent in the brush is consistent with the picture that polymer collapse is induced by bridging⁶⁵ between the hydrophobic groups of the PNIPAM monomers at different parts of the polymer⁶² via molecules of the better solvent (ethanol), which is an effect that cannot be captured by mean-field theories.⁶⁵ Also, recently published attenuated total reflection infrared spectroscopy (ATR-IR) measurements on a poly(dodecyl methacrylate) brush in mixtures of toluene and ethanol have shown preferential absorption by the better solvent (toluene).⁶⁹ This would indicate that there could be ethanol-rich domains present in the PNIPAM brush. But, unfortunately, we cannot extract the chemical composition of the solvent in the brush and, thus, this remains to be speculation.

Fig. 1 also shows that the adhesive force between the PNIPAM brush and a SiO₂ colloid strongly varies with the solvent composition. In pure water, the adhesion is low (on average 8 nN), because the solvent screens the interactions between the colloid and the polymers in the brush. Upon increasing the ethanol content to 10 vol%, the brush swelling strongly decreases by 32% and the adhesion force increases to approximately 25 nN. The increase in adhesion can be

explained by the increase in polymer density in the contact as a consequence of the reduced brush swelling. For the 10 vol% ethanol mixture, we also observe a long-ranged attractive interaction over $1.6 \mu\text{m}$ (Fig. S3†), which we attribute to polymer stretching.^{23,24,70} Polymer stretching has been shown to result in high friction.²⁴ This effect is less pronounced for the adhesion force. We find that the adhesion is the highest (on average 80 nN) at 30 vol% ethanol in the ethanol–water mixture. Upon further increase of the ethanol content in the solvent mixture, the adhesion decreases and it is minimum in pure ethanol (<1 nN) where the brush swells the most. Fig. 2 shows the adhesion force between the SiO_2 colloid and PNIPAM brush by consecutively varying 4 times the composition of the solvent mixture between 100% ethanol and 30–70 vol% ethanol–water. Between each solvent exchange the brush surface is washed with ethanol and dried under a stream of nitrogen. The results in Fig. 2 show that the adhesive force can be switched from 0.7 ± 0.1 nN in pure ethanol to 81 ± 10 nN for 30 vol% of ethanol in the solvent mixture. After 4 cycles, the change in adhesion is still the same within the experimental error without showing any signs of degradation. The repeatability of the adhesion-switch shows that this system holds great potential for application in pick up and release systems.

To study the effect of the counter surface material, we use several different types colloids for the force–separation measurement: polystyrene (PS), poly(methyl methacrylate) (PMMA) and gold. The adhesion force as a function of ethanol volume fraction in water is shown in Fig. S4.† From the curve we can see the adhesion as a function of the ethanol–water composition shows the same trend for the different types of colloids. The results for all counter surfaces studied are summarized in Table 1. Though the absolute values for adhesion forces are different for the different colloid materials, we

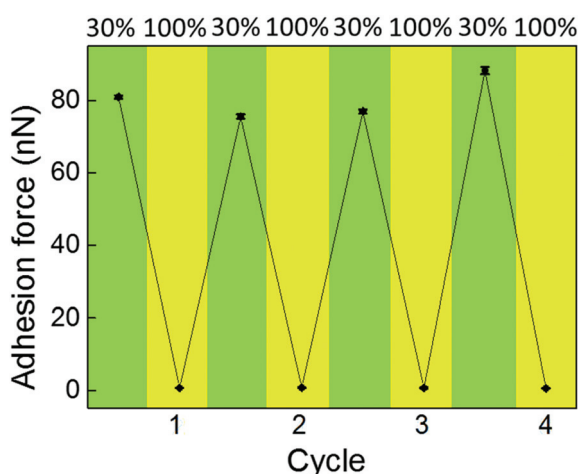


Fig. 2 Repeatability test showing that the adhesion force can be switched from 81 ± 10 nN in 30–70 vol% ethanol–water mixture to 0.7 ± 0.1 nN in ethanol and back for 4 cycles without showing signs of degradation. The error bars denote the standard error of the mean with a 95% confidence interval.

Table 1 The average adhesion force F_{adh} measured in pure water (0%), 30–70 vol% ethanol–water mixture (30%) and in pure ethanol (100%) using colloid probes of different sizes and materials, while keeping the retraction velocity ($0.8\text{--}1 \mu\text{m s}^{-1}$) and the maximum indentation force F_{max} divided by the colloid diameter D approximately constant

Material	D (μm)	F_{max} (nN)	F_{adh} 0% (nN)	F_{adh} 30% (nN)	F_{adh} 100% (nN)
SiO_2	7.75	77.5 ± 5	8.1 ± 0.37	81 ± 10	0.7 ± 0.1
Au	6	60 ± 4	1.6 ± 0.15	73 ± 6	0.2 ± 0.16
PS	5	50 ± 3	0.5 ± 0.01	33 ± 4	0.2 ± 0.03
PMMA	6	60 ± 4	0.05 ± 0.01	12 ± 2	0.08 ± 0.01

observe the same trend in the adhesion force as a function of the solvent composition for all counter surfaces. For all colloid materials we tested, the adhesion is the highest for an ethanol–water mixture that contains 30 vol% ethanol, while the adhesion is much lower in the pure solvents. We find that the largest change in adhesion is for the gold colloid. For gold, the adhesion in pure ethanol is a factor of 365 lower than in 30–70 vol% ethanol–water. The overall adhesion between the PMMA colloid and the PNIPAM brush is much lower than the adhesion for the other colloid materials. We attribute this reduction to a small preference of the solvent to move into the PMMA film,⁴¹ which could screen direct colloid–brush interactions. In bulk PMMA, there is a 2–4 vol% solvent absorbance of pure water,⁷¹ which increases to 20 vol% in 30–70 vol% ethanol–water mixture.⁷² Due to a co-solvency effect of PMMA in ethanol–water mixtures,⁴¹ there is a solubility-maximum at 80–20 vol% ethanol–water. For this composition, there is approximately 60 vol% of solvent absorbed in the PMMA film. This might be the reason for the slightly lower adherence for PMMA modified colloid compared to the other CSs. Nevertheless, for all CSs the adhesion can be switched by at least a factor 115 when switching between pure ethanol and 30–70 vol% ethanol–water, which shows that our system will be able to pick up and release different kinds of nanoparticles. We anticipate that the adhesion between PNIPAM brushes and the colloids in solvent mixtures can be switched by changing the temperature too. However, this will only be possible for solvent mixtures between 0 and 26 vol% and 52 and 64 vol% ethanol in the mixture, since for these mixtures the LCST occurs at temperatures for which the mixture is in the liquid phase.⁷³

Fig. 3 shows the pick up and release of silicon nanoparticles (diameter 80 nm) using a PNIPAM brush (dry height = 150 nm) substrate. The particles are picked up in a 30–70 vol% ethanol–water mixture. The release of particles is allowed by ultra-sonication in ethanol for 2 minutes. Fig. 3(a) is an AFM height image of the brush before immersion in solution showing that the brush is clean and homogeneous (RMS roughness 0.3 nm). In 3(b) we show the AFM height image of the PNIPAM brush after it has been immersed in a nanoparticle solution (concentration 1 mg ml^{-1}) in 30–70 vol% ethanol–water and then dried. In this “pick-up” image, there are 80 nanoparticles that are spread out over an area of

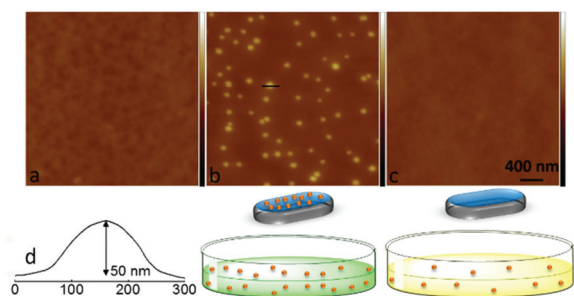


Fig. 3 AFM imaging of the dry PNIPAM brush surface of (a) before adsorption of silicon particles (scansize $3.3 \times 3.3 \mu\text{m}^2$), (b) after immersion in 30–70 vol% ethanol–water mixture containing silicon nanoparticles (diameter 80 nm, 1 mg ml^{-1}) and (c) the same PNIPAM brush surface after immersion in pure ethanol and sonication for 2 minutes. The black line in (b) denotes the position of the cross section shown in (d). The dry brush height is 150 nm, and the scale bar is 400 nm and the color bar is 200 nm.

$3.3 \times 3.3 \mu\text{m}^2$. The particles are evenly distributed over the surface, which shows that there is almost no aggregation of the nanoparticles. In Fig. 3(c) the AFM image of the brush after particle-release is shown. The brush is clean and homogeneous and there are no particles left on this part of the surface, which shows that the particles can be successfully transferred from one medium into another. The release can only be triggered when we work in pure solvent (water or ethanol): in fact, if the brush is sonicated in 30–70 vol% ethanol–water, only 5–8% of the particles are released.

The graph in Fig. 3(d) shows a cross section of a nanoparticle that is partly embedded in the dried PNIPAM brush. Approximately 38% of the particle's volume is in the brush, the other part is exposed to the air. The penetration depth of nanoparticles into a brush depends on the size^{74,75} and geometry⁷⁶ of the particles and the solvent-mediated, specific particle–polymer interactions.^{77,78} Particles that are smaller than or comparable to the distance between anchor points of the polymers are free to move into the brush. These small particles can self-organize and form clusters inside the brush.^{77,79,80} Our particles are approximately 300 times larger than the distance between the anchor points and therefore our particles reside in the top of the brush and there is no significant aggregation or cluster formation.

To test the performance of the PNIPAM pick up and release system, we compare the amount of captured particles from 30–70 vol% ethanol–water mixture, to the number of captured particles on PNIPAM in pure water (see Fig. S5†), which shows a higher adhesion than in pure ethanol (see Table 1) for PNIPAM in contact with SiO_2 colloid. Also the capability of capturing particles on a bare silicon surface is characterized (see Fig. S6†). Fig. 4(a) shows the average number of particles imaged over $10 \times 10 \mu\text{m}^2$ (see Fig. S7†) for these three test situations. The number of trapped particles for the PNIPAM brush in 30–70 vol% ethanol–water is approximately 25 times higher than for PNIPAM in pure water and 90 times higher than for the bare silicon surface.

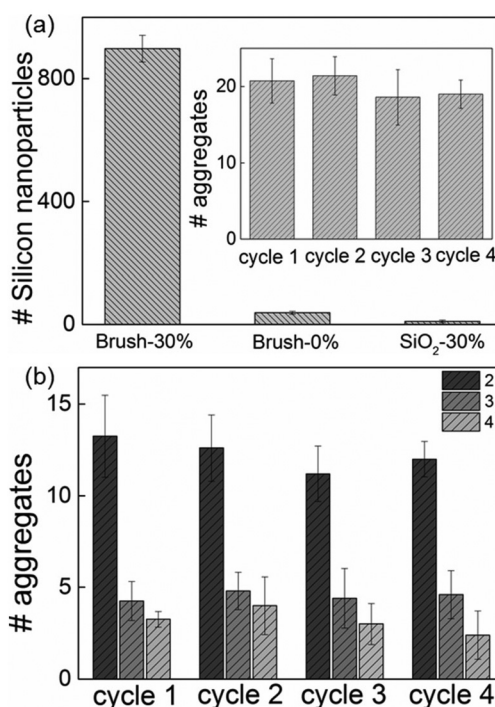


Fig. 4 (a) The amount of particles attached on the brush or SiO_2 substrates with an image size of $10 \times 10 \mu\text{m}^2$ after immersion in ethanol–water solution ($v/v = 3/7$) containing silicon particles (concentration 1 mg ml^{-1}), pure water containing silicon particles (concentration 1 mg ml^{-1}). The inset shows the number of aggregates in the image during 4 consecutive capture and release cycles using ethanol–water solution ($v/v = 3/7$) and pure ethanol. (b) The number of particles in the aggregates during the 4 consecutive capture and release cycles. The numbers 2, 3 and 4 denote the number of particles in the aggregate.

To test if the number of aggregates changes after release from the brush, we performed experiments of 4 consecutive capture and release cycles. The inset of Fig. 4(a) shows that there are on average 20 aggregates visible per image, which is 2% of the total number of captured particles. Moreover, the results in the inset show that there is no change in the number of aggregates in the picture within the experimental error in 4 cycles. However, the total number of particles picked up decreases per cycle (as shown in Fig. S8†) such that the percentage of aggregate increases to 4% after 4 cycles. We attribute this reduction in the efficiency to brush degradation (see Fig. S9†) due to sonication, which can be inhibited by employing stronger surface-anchors.⁸¹ Also the number of particles in the aggregation clusters are counted as shown in Fig. 4(b). The dominated aggregation is composed of 2 nanoparticles, and keeps almost the same numbers in 4 cycles.

Conclusions

In summary, we have shown that the adhesion force between a PNIPAM brush and SiO_2 , gold, PS and PMMA colloids can be reversibly switched by changing the solvent composition. In

30–70 vol% ethanol–water mixtures adhesion is high, while the adhesion is low in pure solvents. We employ the change in adherence to create a pick-up move and release system to transfer particles from one liquid into another. The advantage of this system is that the formation of aggregates is strongly reduced, which is an important problem in traditional approaches for nanoparticle transfer.

Acknowledgements

S. Liu is acknowledged for sharing his SiO₂ nanoparticles. We thank the MESA+ Institute for Nanotechnology of the University of Twente for financial support. YY thanks the Chinese Scholarship Council for the scholarship support. SdB and AP have been supported by the Foundation for Fundamental Research on Matter (FOM), which is financially supported by the Netherlands Organization for Scientific Research (NWO). BDk has been supported by the Dutch Technology Foundation (STW), which is part of the Netherlands Organisation for Scientific Research (NWO), which is partly funded by Ministry of Economic Affairs.

References

- J. F. Wang, T. Tsuzuki, L. Sun and X. G. Wang, *ACS Appl. Mater. Interfaces*, 2010, **2**, 957–960.
- D. M. Eby, H. R. Luckarift and G. R. Johnson, *ACS Appl. Mater. Interfaces*, 2009, **1**, 1553–1560.
- I. Perelshtein, G. Apperlot, N. Perkass, E. Wehrschetz-Sigl, A. Hasmann, G. M. Guebitz and A. Gedanken, *ACS Appl. Mater. Interfaces*, 2009, **1**, 363–366.
- L. Shang, T. Bian, B. H. Zhang, D. H. Zhang, L. Z. Wu, C. H. Tung, Y. D. Yin and T. R. Zhang, *Angew. Chem., Int. Ed.*, 2014, **53**, 250–254.
- F. Costantini, E. M. Benetti, D. N. Reinhoudt, J. Huskens, G. J. Vancso and W. Verboom, *Lab Chip*, 2010, **10**, 3407–3412.
- R. P. Bagwe, C. Y. Yang, L. R. Hilliard and W. H. Tan, *Langmuir*, 2004, **20**, 8336–8342.
- R. P. Bagwe, L. R. Hilliard and W. H. Tan, *Langmuir*, 2006, **22**, 4357–4362.
- R. A. French, A. R. Jacobson, B. Kim, S. L. Isley, R. L. Penn and P. C. Baveye, *Environ. Sci. Technol.*, 2009, **43**, 1354–1359.
- M. Pena, X. G. Meng, G. P. Korfiatis and C. Y. Jing, *Environ. Sci. Technol.*, 2006, **40**, 1257–1262.
- N. L. Torad, M. Hu, S. Ishihara, H. Sukegawa, A. A. Belik, M. Imura, K. Ariga, Y. Sakka and Y. Yamauchi, *Small*, 2014, **10**, 2096–2107.
- Y. G. Lee, J. H. Park, C. Oh, S. G. Oh and Y. C. Kim, *Langmuir*, 2007, **23**, 10875–10878.
- B. L. Cushing, V. L. Kolesnichenko and C. J. O'Connor, *Chem. Rev.*, 2004, **104**, 3893–3946.
- C. Liu, B. S. Zou, A. J. Rondinone and Z. J. Zhang, *J. Am. Chem. Soc.*, 2001, **123**, 4344–4345.
- Y. Lu, Y. Yin, B. T. Mayers and Y. Xia, *Nano Lett.*, 2002, **2**, 183–186.
- B. G. Trewyn, I. I. Slowing, S. Giri, H. T. Chen and V. S. Y. Lin, *Acc. Chem. Res.*, 2007, **40**, 846–853.
- M. Grzelczak, J. Vermant, E. M. Furst and L. M. Liz-Marzán, *ACS Nano*, 2010, **4**, 3591–3605.
- C. Vauthier, B. Cabane and D. Labarre, *Eur. J. Pharm. Biopharm.*, 2008, **69**, 466–475.
- A. Frattini, N. Pellegri, D. Nicastro and O. de Sanctis, *Mater. Chem. Phys.*, 2005, **94**, 148–152.
- R. Konwarh, N. Karak, C. E. Sawian, S. Baruah and M. Mandal, *Carbohydr. Polym.*, 2011, **83**, 1245–1252.
- S. Diamanti, S. Arifuzzaman, J. Genzer and R. A. Vaia, *ACS Nano*, 2009, **3**, 807–818.
- S. T. Milner, *Science*, 1991, **251**, 905–914.
- Q. Chen, E. S. Kooij, X. F. Sui, C. J. Padberg, M. A. Hempenius, P. M. Schon and G. J. Vancso, *Soft Matter*, 2014, **10**, 3134–3142.
- Y. Yu, M. Cirelli, B. D. Kieviet, E. S. Kooij, G. J. Vancso and S. de Beer, *Polymer*, 2016, **102**, 372–378.
- Y. Yu, B. D. Kieviet, F. Liu, I. Siretanu, E. Kutnyanszky, G. J. Vancso and S. de Beer, *Soft Matter*, 2015, **11**, 8508–8516.
- Z. Y. Zhang, A. J. Morse, S. P. Armes, A. L. Lewis, M. Geoghegan and G. J. Leggett, *Langmuir*, 2011, **27**, 2514–2521.
- Z. Y. Zhang, A. J. Morse, S. P. Armes, A. L. Lewis, M. Geoghegan and G. J. Leggett, *Langmuir*, 2013, **29**, 10684–10692.
- Q. B. Wei, M. R. Cai, F. Zhou and W. M. Liu, *Macromolecules*, 2013, **46**, 9368–9379.
- H. J. Dai, Q. Chen, H. L. Qin, Y. Guan, D. Y. Shen, Y. Q. Hua, Y. L. Tang and J. Xu, *Macromolecules*, 2006, **39**, 6584–6589.
- T. Wu, P. Gong, I. Szleifer, P. Vlcek, V. Šubr and J. Genzer, *Macromolecules*, 2007, **40**, 8756–8764.
- M. K. Vyas, K. Schneider, B. Nandan and M. Stamm, *Soft Matter*, 2008, **4**, 1024–1032.
- H. S. Lim, D. Kwak, D. Y. Lee, S. G. Lee and K. Cho, *J. Am. Chem. Soc.*, 2007, **129**, 4128–4129.
- Y. Zhang, S. Furyk, L. B. Sagle, Y. Cho, D. E. Bergbreiter and P. S. Cremer, *J. Phys. Chem. C*, 2007, **111**, 8916–8924.
- R. Jakubiak, T. J. Bunning, R. A. Vaia, L. V. Natarajan and V. P. Tondiglia, *Adv. Mater.*, 2003, **15**, 241–244.
- J. M. Shen, F. Y. Gao, L. P. Guan, W. Su, Y. J. Yang, Q. R. Li and Z. C. Jin, *RSC Adv.*, 2014, **4**, 18473–18484.
- D. M. Jones, J. R. Smith, W. T. S. Huck and C. Alexander, *Adv. Mater.*, 2002, **14**, 1130–1134.
- J.-K. Chen, J.-H. Wang, J.-Y. Chang and S.-K. Fan, *Appl. Phys. Lett.*, 2012, **101**, 123701.
- S. H. Ma, D. A. Wang, Y. M. Liang, B. Q. Sun, S. N. Gorb and F. Zhou, *Small*, 2015, **11**, 1131–1137.
- I. B. Malham and L. Bureau, *Langmuir*, 2010, **26**, 4762–4768.
- C. Rodriguez-Emmenegger, C. M. Preuss, B. Yameen, O. Pop-Georgievski, M. Bachmann, J. O. Mueller, M. Bruns,

- A. S. Goldmann, M. Bastmeyer and C. Barner-Kowollik, *Adv. Mater.*, 2013, **25**, 6123–6127.
- 40 X. F. Sui, A. Di Luca, M. K. Gunnewiek, E. S. Kooij, C. A. van Blitterswijk, L. Moroni, M. A. Hempenius and G. J. Vancso, *Aust. J. Chem.*, 2011, **64**, 1259–1266.
- 41 Y. Yu, B. D. Kieviet, E. Kutnyanszky, G. J. Vancso and S. de Beer, *ACS Macro Lett.*, 2015, **4**, 75–79.
- 42 E. M. Benetti, S. Zapotoczny and J. Vancso, *Adv. Mater.*, 2007, **19**, 268–271.
- 43 S. de Beer, *Langmuir*, 2014, **30**, 8085–8090.
- 44 S. de Beer, E. Kutnyanszky, P. M. Schon, G. J. Vancso and M. H. Muser, *Nat. Commun.*, 2014, **5**, 3781.
- 45 P. W. Zhu and D. H. Napper, *J. Colloid Interface Sci.*, 1996, **177**, 343–352.
- 46 T. Gilanyi, I. Varga, R. Meszaros, G. Filipcsei and M. Zrinyi, *Phys. Chem. Chem. Phys.*, 2000, **2**, 1973–1977.
- 47 J. Zhang, L. Y. Chu, Y. K. Li and Y. M. Lee, *Polymer*, 2007, **48**, 1718–1728.
- 48 R. Liu, M. Fraylich and B. R. Saunders, *Colloid Polym. Sci.*, 2009, **287**, 627–643.
- 49 T. G. McKenzie, E. H. Wong, Q. Fu, S. J. Lam, D. E. Dunstan and G. G. Qiao, *Macromolecules*, 2014, **47**, 7869–7877.
- 50 A. Halperin, M. Kroger and F. M. Winnik, *Angew. Chem., Int. Ed.*, 2015, **54**, 15342–15367.
- 51 A. Halperin and M. Kroger, *Macromolecules*, 2011, **44**, 6986–7005.
- 52 R. Liu, P. De Leonardis, N. Tirelli and B. R. Saunders, *J. Colloid Interface Sci.*, 2009, **340**, 166–175.
- 53 J. Guo, W. Yang, Y. Deng, C. Wang and S. Fu, *Small*, 2005, **1**, 737–743.
- 54 F. Tanaka, T. Koga and F. M. Winnik, *Phys. Rev. Lett.*, 2008, **101**, 028302.
- 55 F. M. Winnik, M. F. Ottaviani, S. H. Bossmann, M. Garcia-Garibay and N. J. Turro, *Macromolecules*, 1992, **25**, 6007–6017.
- 56 F. M. Winnik, M. F. Ottaviani, S. H. Bossmann, W. Pan, M. Garcia-Garibay and N. J. Turro, *Macromolecules*, 1993, **26**, 4577–4585.
- 57 D. Mukherji and K. Kremer, *Macromolecules*, 2013, **46**, 9158–9163.
- 58 F. M. Winnik, H. Ringsdorf and J. Venzmer, *Macromolecules*, 1990, **23**, 2415–2416.
- 59 C. Scherzinger, A. Schwarz, A. Bardow, K. Leonhard and W. Richtering, *Curr. Opin. Colloid Interface Sci.*, 2014, **19**, 84–94.
- 60 C. W. Tu and S. W. Kuo, *J. Polym. Res.*, 2014, **21**, 476.
- 61 P. W. Zhu and D. H. Napper, *Chem. Phys. Lett.*, 1996, **256**, 51–56.
- 62 F. Rodriguez-Ropero, T. Hajari and N. F. A. van der Vegt, *J. Phys. Chem. B*, 2015, **119**, 15780–15788.
- 63 M. Z. Liu, F. L. Bian and F. L. Sheng, *Eur. Polym. J.*, 2005, **41**, 283–291.
- 64 D. Mukherji, C. M. Marques and K. Kremer, *Nat. Commun.*, 2014, **5**, 4882.
- 65 D. Mukherji, C. M. Marques, T. Stuehn and K. Kremer, *J. Chem. Phys.*, 2015, **142**, 114903.
- 66 Y. Ito, T. Ito, H. Takaba and S. Nakao, *J. Membr. Sci.*, 2005, **261**, 145–151.
- 67 Y. M. Sun, W. Wang, Y. Y. Wei, N. N. Deng, Z. Liu, X. J. Ju, R. Xie and L. Y. Chu, *Lab Chip*, 2014, **14**, 2418–2427.
- 68 L. Liu, X. L. Song, X. J. Ju, R. Xie, Z. Liu and L. Y. Chu, *J. Phys. Chem. B*, 2012, **116**, 974–979.
- 69 C. H. Mathis, M. Divandari, R. Simic, V. V. Naik, E. M. Benetti, L. Isa and N. D. Spencer, *Langmuir*, 2016, **32**, 7588–7595.
- 70 J. D. Willott, T. J. Murdoch, G. B. Webber and E. J. Wanless, *Macromolecules*, 2016, **49**, 2327–2338.
- 71 R. Hoogenboom, C. R. Becer, C. Guerrero-Sanchez, S. Hoepfener and U. S. Schubert, *Aust. J. Chem.*, 2010, **63**, 1173–1178.
- 72 S. M. Lee and Y. C. Bae, *Polymer*, 2014, **55**, 4684–4692.
- 73 I. Bischofberger, D. C. E. Calzolari and V. Trappe, *Soft Matter*, 2014, **10**, 8288–8295.
- 74 J. U. Kim and B. O'Shaughnessy, *Macromolecules*, 2006, **39**, 413–425.
- 75 A. Milchev, D. I. Dirnitrova and K. Binder, *Polymer*, 2008, **49**, 3611–3618.
- 76 S. de Beer, L. I. S. Mensink and B. D. Kieviet, *Macromolecules*, 2016, **49**, 1070–1078.
- 77 O. A. Guskova, S. Pal and C. Seidel, *Europhys. Lett.*, 2009, **88**, 38006.
- 78 A. Halperin and M. Kroger, *Langmuir*, 2012, **28**, 16623–16637.
- 79 R. Oren, Z. Q. Liang, J. S. Barnard, S. C. Warren, U. Wiesner and W. T. S. Huck, *J. Am. Chem. Soc.*, 2009, **131**, 1670–1671.
- 80 T. Curk, F. J. Martinez-Veracoechea, D. Frenkel and J. Dobnikar, *Soft Matter*, 2013, **9**, 5565–5571.
- 81 R. Quintana, M. Gosa, D. Janczewski, E. Kutnyanszky and G. J. Vancso, *Langmuir*, 2013, **29**, 10859–10867.