Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Polymer Chemistry

www.rsc.org/polymers

ROYAL SOCIETY OF CHEMISTRY

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

www.rsc.org/polymers

Journal Name

ARTICLE TYPE

- ## Thiol-Michael Addition Miniemulsion Polymerizations: Functional Nanoparticles and Reactive Latex Films

Chen Wang[a], Shunsuke Chatani[a], Maciej Podgórski[a,b] and Christopher N. Bowman[a]

Thiol-Michael addition polymerization is successfully implemented in a miniemulsion polymerization system. By off-stoichiometric polymerization between thiols and acrylates, inherently functionalized particles are facilely
10 **prepared in a single step. We demonstrate that the latex films from such particles are readily available for further modification and second-stage photo-curing.**

Although the thiol-Michael addition reaction has been well understood for half a century[1], it has received renewed attention
15 in polymer chemistry over the past decade due in large part to its inclusion as one of the click reactions[2-4]. The thiol-Michael addition reaction achieves quantitative yield in the reaction between thiols and electron deficient double bonds under benign conditions[5, 6]. As such, it is considered as one of the "click"
20 chemistries and has been shown to be a powerful tool for a wide range of applications in polymer chemistry, including the formation of polymer networks[7], polymer conjugation[8] and modification[9, 10]. Recent advances in thiol-Michael addition polymerization include initiation with spatiotemporal control[11-17],
25 synthesis of dendrimers[18, 19] and hydrogels[20], sequence controlled polymers[21, 22] and various implementations in heterogeneous systems[23, 24]. Both the thiol-Michael addition and radical mediated thiol-ene reactions generate thio-ether products; however, the thiol-Michael addition reaction is often more
30 enabling in the design of functional materials because of the absence of radicals and the great selectivity among various vinyl groups.

The study of heterogeneous polymerizations is critical for expanding the polymerization in industrial manufacturing, where
35 suspension polymerizations and emulsion polymerizations are primarily utilized. Miniemulsion polymerization techniques have emerged as a versatile approach for producing polymeric nanoparticles, especially functional nanoparticles with complex structures[25]. Because of the addition of a hydroprobe, mass
40 transfer between the monomer droplets in miniemulsions is prohibited. Hence, the droplets act as individual segregated nanoreactors, which enables the formation of encapsulated systems and organic/inorganic hybrid particles[26]. Free radical polymerizations are generally used in miniemulsions, including
45 for polymerizations of monomers such as styrene and various (meth)acrylates. In chain-growth polymerizations, monomers are often not completely consumed,[27] and the unreacted monomer contributes to the volatile organic compounds (VOC) content of

the particle system. VOCs often limit the long-term durability of
50 the product and may introduce toxicity as well.

In contrast, the existence of residual, extractable monomer is extremely rare in a step-growth polymerization. Landfester *et al.* initially reported a series of step-growth miniemulsion polymerizations, including polyurethane[28], polyester[29] and
55 polyimide[30] forming reactions, where the VOC content is significantly reduced. More interestingly, step-growth polymerizations offer an exciting library from which to choose for the design of functional nanoparticles since numerous coupling reactions have been used for polymerizations, including
60 several from the click family of reactions.

In particular, several examples of "click" polymerizations in miniemulsions have been reported. Bernard *et al.*[31] studied the implementation of copper-catalysed alkyne-azide cycloaddition reaction (CuAAC) in an interfacial miniemulsion polymerization,
65 which produces capsules with a diameter around 200 nm. Landfester *et al.*[32] demonstrated that similar nanocapsules can also be made by copper-free alkyne-azide cycloaddition polymerizations, where electron deficient alkyne monomers are used. Radical mediated thiol-ene click chemistry possesses many
70 advantages in terms of polymer synthesis[3] and has been utilized in miniemulsion systems. Jiang *et al.*[33] reported the preparation of microcapsules loaded with noble metals by thiol-ene interfacial photo-polymerization. Chemtob *et al.*[34] and Patton *et al.*[35] recently reported photo-induced thiol-ene miniemulsion
75 polymerizations, where the polymerization are completed as rapidly as a few seconds. Thiol-ene photopolymerization was also utilized in suspension polymerization systems, as described by Shipp *et al*[36, 37]. However, the investigation of other "click" chemistries has not been implemented to date, including the thiol-
80 Michael addition reaction.

The thiol-Michael addition reaction is self-limiting; thus, off-stoichiometric polymerization results in intrinsically functionalizable polymers. For example, an acrylate-excess thiol-Michael addition polymerization followed by the
85 homopolymerization of remaining acrylates has been utilized for preparing lithographic impression materials, shape memory polymers and optical materials[38]. Lately, we reported the preparation of monodisperse microspheres by thiol-Michael addition polymerizations. Off-stoichiometric polymerizations and
90 copolymerizations yield particles with inherent capacity for functionalization including subsequent derivatization[23]. Herein, we implement the thiol-Michael addition polymerizations in

miniemulsions, with all of the above-mentioned advances incorporated.

A thiol-Michael based analogue to conventional miniemulsion polymerization was designed using the monomers listed in figure 1. For preparing miniemulsions it is necessary to process the reactants, for example, through mixing and ultra-sonication, and subsequently trigger the polymerization efficiently. We chose thermal initiation because it enables facile scale up of the process to large volumes. We selected 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as a thermal initiator for the thiol-Michael addition reaction. TEMPO is a common inhibitor for radical polymerization and also a weak base that serves to deprotonate thiols and initiate the thiol-Michael reaction. The deprotonation happens very slowly at ambient temperature but occurs rapidly and efficiently upon heating. Model reactions were performed to investigate the efficiency of TEMPO as a Michael addition catalyst. Pentaerythritol tetra(3-mercaptopropionate) (PETMP) and divinyl sulfone (DVS) were heated to 60°C with 2 wt% TEMPO, achieving 85% conversion in 20 min, as monitored by real time FT-IR (figure S1a). On the other hand, 1,3,5-triallyl-1,3,5-triazine-2,4,6-trione (TATATO), an electron-rich monomer, did not react with PETMP under similar conditions. DVS is an excellent Michael acceptor while TATATO does not react via Michael addition, indicating that TEMPO initiates the thiol-Michael addition reaction exclusively. Also, control experiments show that no polymerization happens in the absence of TEMPO (figure S1b) under these conditions. For the miniemulsion system, we chose a combination of dithiol and diacrylate as a model system, which produces a linear thio-ether polymer. Stoichiometric ethylene glycol bis(3-mercaptopropionate) (GDMP, 10 mmol, 2.38 g) and neopentyl glycol diacrylate (NDA, 10 mmol, 2.12 g) were mixed with TEMPO (0.23 g, 5 wt% to monomers) and hexadecane (HD, 0.18 g, 4 wt% to monomers). Subsequently, 18 mL water (with 0.83 wt% sodium dodecyl sulfate, SDS) was added to the monomer mixture (20 wt% oil content). The mixture was homogenized by a total of 5 min ultra-sonication on a Branson sonifier 450 W/L at 70% amplitude, and a stable emulsion was generated. After reacting at 80°C for two hours, the mixture was cooled to ambient and used without purification. Latex films were prepared by drying the emulsion in air at ambient temperature overnight.

2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959).

The conversion was characterized by FT-IR. Figure 2A shows the IR spectra for the GDMP-NDA monomer mixture, polymer particles and latex film, respectively. In the monomer mixture, a distinct thiol peak is seen from 2470-2600 cm^{-1} and an acrylate peak from 795-810 cm^{-1}. In the miniemulsion systems, the monomer concentration is nearly at bulk concentrations within each droplet. Bulk thiol-Michael addition polymerization between a stoichiometric mercaptopropionate and acrylate is shown to achieve full conversion of both functional groups within 60 min at 80°C with 5 wt% TEMPO (shown in Figure S2). Thus, to ensure complete conversion, we allow the miniemulsion polymerization to proceed for 2 h at 80°C. In the spectra for the particles and latex films, both of the peaks disappeared, indicating that the polymerization was completed.

We then carried out a similar polymerization to form a crosslinked polymer. Stoichiometric PETMP and trimethylolpropane triacrylate (TMPTA) were polymerized under similar conditions as the GDMP-NDA polymerization. The sizes of the resulting particles were measured by dynamic light scattering (figure 3A), which shows an average diameter of 200 nm with a polydispersity of 0.21, and the morphology was confirmed by transmission electron microscopy (figure 3B). The average diameter is within the range generally found for a miniemulsion system, noting that the monomers here are more viscous than most common vinyl monomers, such as styrene. If smaller particles are preferred, several methods have been reported to decrease the size of these particles, including adding diluent, using higher ultra-sonication energy and lowering the solids content[39].
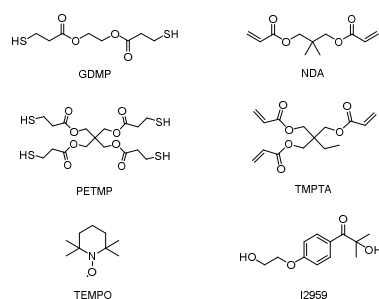

Fig 1. Monomers and initiators used in this work. Multi-thiols: ethylene glycol bis(3-mercaptopropionate) (GDMP) and pentaerythritol tetra(3-mercaptopropionate) (PETMP). Multi-acrylate: neopentyl glycol diacrylate (NDA) and trimethylolpropane triacrylate (TMPTA). Initiators:
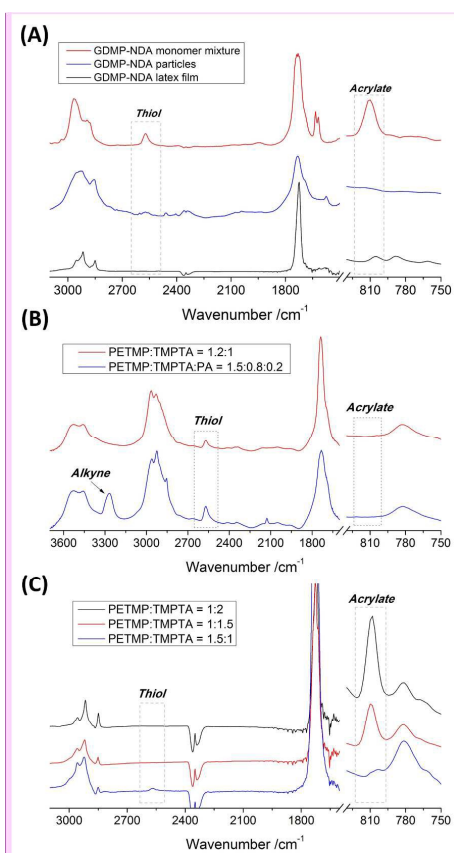
Fig 2. FT-IR spectra for (A) stoichiometric GDMP-NDA emulsions;(B) Particles prepared from thiol-excess off-stoichiometric PETMP-TMPTA system and copolymerization with propargyl acrylate (PA). (C) ATR-FTIR spectra of crosslinked latex films from off-stoichiometric PETMP-TMPTA systems. Molar ratios between thiol and acrylate groups are indicated in the legends. The emulsion polymerization was conducted with 5 wt% TEMPO at 80℃ for 2 h, and the latex films were prepared by drying in air overnight with a film thickness of 0.5 mm.
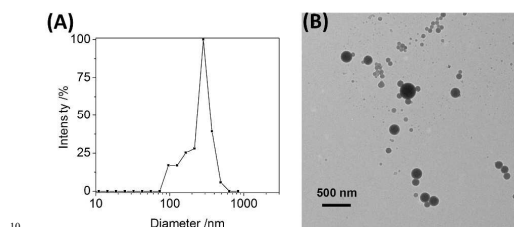

Fig 3. Characterization of crosslinked PETMP-TMPTA miniemulsion nanoparticles. (A) Dynamic light scattering tests of nanoparticle dispersion in water; (B) Transmission electron microscopy pictures. The particles were stained by OsO$_4$.

For crosslinked step-growth polymerizations, polymer networks may be formed even when off-stoichiometric reactions are performed, as guided by the Flory-Stockmayer equation. This approach, coupled with the self-limiting nature of the thiol-Michael addition reaction enables particles to be formed with residual thiol or vinyl groups simply by forming particles from an initial excess of that functionality. Thus, in the thiol-Michael addition miniemulsion polymerization, nanoparticles are inherently functionalized as a result of off-stoichiometric reactions. We initially performed a thiol-excess polymerization with a molar ratio between thiol and acrylate of 1.2:1 (thiol:acrylate). Figure 2B shows the FT-IR spectra of thiol-excess nanoparticles. No peak is observed from 795-810 cm^{-1}, which confirms complete consumption of the acrylate. However, a peak from 2470-2600 cm^{-1} is observed, indicative of the residual, unreacted thiol groups. Moreover, copolymerization was performed to incorporate additional functionalities other than thiol and acrylate. We chose propargyl acrylate (PA), an acrylic monomer bearing alkyne moiety which is widely used for CuAAC reactions, as a co-monomer in the PETMP-TMPTA system. The copolymerization was carried out with a molar ratio of functionality between PETMP:TMPTA:PA=1.5:0.8:0.2. In figure 2B, we see significant peaks at both 3190-3330 cm^{-1} and 2470-2600 cm^{-1}, indicating the immobilized alkyne and thiol species, respectively. Note that alkyne is very radically reactive with thiols, however the radical-free thiol-Michael addition reaction is orthogonal to alkynes and thus enables this *in situ* functionalization.

A series of off-stoichiometric latex films between PETMP and TMPTA were prepared, with molar ratios between thiol and acrylate of 1:2, 1:1.5 and 1.5:1 (thiol:acrylate), respectively. Figure 2C shows the attenuated total reflectance (ATR) FT-IR spectra for these latex films. Note that the acrylate peak is more significant for 100 % excess acrylate films than that for 50 % excess acrylate film. In conventional free-radical polymerizations, functional monomers are used for the design of functional latex films. For example, glycidyl methacrylate is used for the creation of an amine-reactive latex[40]. Both thiol and acrylate groups are platform functional groups capable of reacting in various thiol-X (or other) reactions, such as the radical mediated thiol-ene reaction, thiol-Michael addition, thiol-epoxy, thiol-halide and thiol-isocyanate reactions, which are readily implemented in subsequent polymer functionalization and modification reactions. In contrast to the self-limiting thiol-Michael approach, both thiols and (meth)acrylates are reactive with radicals which makes them more difficult to leave for subsequent functionalization in many radical miniemulsion polymerization approaches. Herein, these off-stoichiometric thiol-Michael latex films are inherently functionalizable.

The latex films are uniform and translucent for both linear and crosslinked polymers. Mechanical studies were performed by dynamic mechanical analysis (DMA), as shown in figure 4. The linear polymer was used primarily for latex materials, due to its mobility. As a result, the particles are able to deform to compensate for the shrinkage during drying, leading to uniform films. The linear GDMP-NDA latex film shows a glass transition temperature (Tg) of -31°C. The storage modulus drops quickly below 1 MPa when heating beyond the Tg, indicative of a linear polymer. The crosslinked latex films also have significant mechanical integrity, likely due to the small particle size. The

Polymer Chemistry Accepted Manuscript

stoichiometric PETMP-TMPTA latex film had a Tg of 23°C (figure 4) and a rubbery modulus of 6 MPa. In off-stoichiometric latex films, the Tg decreases with lower crosslinking density. As the thiol:acrylate molar ratio varies from 1:1 to 1.5, the Tg of the
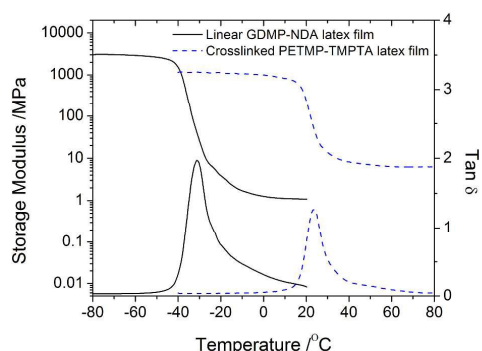5 latex films decreases from 23°C to 10°C (figure S3).

Fig 4. Dynamic mechanical analysis (DMA) of linear and crosslinked latex films. Solid line: linear GDMP-NDA latex film. Dashed line: crosslinked PEMTP-TMPTA latex film. The emulsion polymerization
10 was conducted with 5 wt% TEMPO at 80°C for 2 h, and the latex films were prepared by drying in air overnight with a thickness of 0.5 mm.
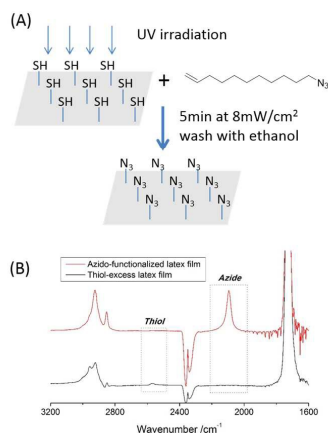

Fig 5. (A) Diagram of functionalization of a thiol-excess latex film by photo-initiated thiol-ene reactions. (B) ATR-FTIR spectra of 20% thiol-
15 excess PETMP-TMPTA latex films before (bottom) and after (top) thiol-ene functionalization with 11-azido-1-undecene.

To demonstrate the utility of the thiol-functionalized latex film, we chose a photo-induced thiol-ene reaction for latex modification. A solution of 50 wt% 11-azido-1-undecene in ethyl
20 acetate, with 5 wt% 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a radical photoinitiator, was applied on the surface of a thiol-excess latex film (PETMP:TMPTA=1.2:1). The azido moiety is chosen as a model because the N=N=N stretching from azides is a strong peak in the IR region and does not overlap with
25 existing groups in the PETMP-TMPTA films. The film was subsequently sandwiched between glass slides and exposed to

UV light for 5 min as illustrated in Figure 5A. Afterward, the film was washed extensively with ethanol and dried. Figure 5B shows that, the thiol peak diminishes after the irradiation and a
30 significant peak at 2000-2300 cm^{-1} indicative of the azide is observed on ATR-FTIR, indicating the progress of the thiol-ene reaction and the covalent incorporation of an azido moiety. A control experiment was performed using a nonreactive azide (6-azido-1-hexanol), which confirmed the covalent immobilization
35 of the azido-moiety by the thiol-ene reaction (Figure S4). The azido groups can be utilized for further modifications such as CuAAC reactions.

Table 1. Dynamic Mechanical Analysis (DMA) shows the glass transition temperatures and rubbery moduli for both stage 1 and stage 2
40 for PETMP-TMPTA latex films.

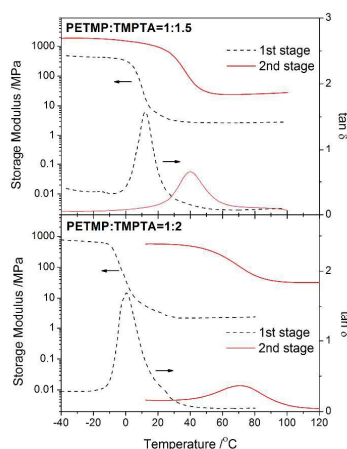| Acrylate/thiol ratio	Stage 1 Tg (°C)	Stage 1 rubbery modulus (Mpa)	Stage 2 Tg (°C)	Stage 2 rubbery modulus (Mpa)
1:1	23±1	6±1	/	/
1.5:1	10±2	3±1	41±2	23±2
2:1	-1±2	2±1	69±2	32±1

Fig 6. Dynamic mechanical analysis (DMA) of dual-cure latex films from PETMP-TMPTA particles with excess acrylate. Top: 50% excess
45 acrylate; bottom: 100% excess acrylate. Dashed line: 1st stage (latex film from the thiol-Michael miniemulsion polymerization). Solid line: 2nd stage (latex film after radical photopolymerization of the residual acrylates). The second stage curing was conducted by irradiating under a Black ray lamp (8 mW/cm^2 at 365 nm) for 10 min.

50 We further demonstrate the application of dual-cure latex films by using the residual acrylates. Non-radical mediated polymerizations are ideal candidates for the first stage curing in a dual-cure system. Thus, simple free-radical polymerizations are able to be used as a second-stage of curing to modify the
55 chemomechanical behaviour of the film after its initial formation from the latex. We used an acrylate-excess latex film as the first stage network, and subsequently the photopolymerization of the residual acrylates was used as increase the crosslink density, mechanical integrity and Tg of the film in a second curing stage.

The formulas for various acrylate-excess films are summarized in Table 1. The stage 1 film Tg decreases from 23º C to -1ºC as the acrylate content increases, which is consistent with that of thiol-excess latex films. The rubbery modulus also decreases as the crosslinking density is reduced.

The second stage curing was performed by UV exposure with I2959 as an initiator. For 50 % acrylate excess films, the Tg and rubbery modulus increase from 10ºC to 41ºC and from 3 MPa to 23 MPa, respectively. For 100 % acrylate excess films, the Tg and rubbery modulus increase from -1ºC to 69ºC and from 2 MPa to 32 MPa, respectively. It is worth noting that the Tg values are in good agreement with those for bulk films of similar composition that were previously reported[38]. However the rubbery modulus for the latex films are lower than those of bulk films, due to the fact that those films are mixtures of polymer, surfactant and residual water. The DMA curves from the abovementioned materials are shown in figure 6. The Tg curves after the initial latex film formation are narrow (with a half-width ~10ºC), indicative of a homogeneous step-growth network. The loss tangent curves become much broader after the acrylate photopolymerization, representing the heterogeneity of the mixed-mode networks[41]. In summary, these films are rubbery following the first stage and become glassy after subsequent reaction of the residual acrylates. The on-demand second-stage curing is useful in applications such as coatings, binders and adhesives, where a rubbery initial material provides good substrate adhesion while the rigid, glassy final polymer delivers higher strength and long-term stability.

Conclusions

Thiol-Michael addition polymerizations are implemented in a miniemulsion polymerization system for the development of functional nanoparticles and latex materials via off-stoichiometric thiol-Michael polymerizations. Photo-induced thiol-ene reactions are demonstrated to facilely modify thiol-excess latex films. Latex films with excess acrylate are shown to enable acrylate homopolymerization as a second-stage photo-curing that is useful for altering the mechanical behavior. We expect that these thiol-Michael nanoparticles and latex materials will be platforms for various applications such as drug carriers and stimuli-responsive functional coatings.

Acknowledgement

Notes and references

a Department of Chemical and Biological Engineering, University of Colorado, UCB 596, Boulder, Colorado 80303, United States. Email: Christopher.bowman@colorado.edu
b Faculty of Chemistry, Department of Polymer Chemistry, MCS University, pl. Marii Curie Skłodowskiej 5, 20-031 Lublin, Poland
† Electronic Supplementary Information (ESI) available: experimental details and material chracterizations. See DOI: 10.1039/b000000x/
‡ The authors declare no competing financial interest.

1. C. F. H. Allen, J. O. Fournier and W. J. Humphlett, *Canadian Journal of Chemistry*, 1964, 42, 2616-2620.
2. D. P. Nair, M. Podgórski, S. Chatani, T. Gong, W. Xi, C. R. Fenoli and C. N. Bowman, *Chemistry of Materials*, 2013, DOI: 10.1021/cm402180t.
3. A. B. Lowe, *Polymer Chemistry*, 2014, 5, 4820-4870.
4. W. Xi, T. F. Scott, C. J. Kloxin and C. N. Bowman, *Advanced Functional Materials*, 2014, 24, 2572-2590.
5. J. W. Chan, C. E. Hoyle and A. B. Lowe, *Journal of the American Chemical Society*, 2009, 131, 5751-5753.
6. J. W. Chan, C. E. Hoyle, A. B. Lowe and M. Bowman, *Macromolecules*, 2010, 43, 6381-6388.
7. Y. Meng, C. R. Fenoli, A. Aguirre-Soto, C. N. Bowman and M. Anthamatten, *Advanced Materials*, 2014, 26, 6497-6502.
8. Y. Li, H. Su, X. Feng, Z. Wang, K. Guo, C. Wesdemiotis, Q. Fu, S. Z. D. Cheng and W.-B. Zhang, *Polymer Chemistry*, 2014, 5, 6151-6162.
9. S. E. R. Auty, O. C. J. Andren, F. Y. Hern, M. Malkoch and S. P. Rannard, *Polymer Chemistry*, 2015, 6, 573-582.
10. B. B. Uysal, U. S. Gunay, G. Hizal and U. Tunca, *Journal of Polymer Science Part A: Polymer Chemistry*, 2014, 52, 1581-1587.
11. D. Guzmán, X. Ramis, X. Fernández-Francos and A. Serra, *European Polymer Journal*, 2014, 59, 377-386.
12. S. Chatani, T. Gong, B. A. Earle, M. Podgórski and C. N. Bowman, *ACS Macro Letters*, 2014, 3, 315-318.
13. W. Xi, H. Peng, A. Aguirre-Soto, C. J. Kloxin, J. W. Stansbury and C. N. Bowman, *Macromolecules*, 2014, 47, 6159-6165.
14. Z. Liu, Q. Lin, Y. Sun, T. Liu, C. Bao, F. Li and L. Zhu, *Advanced Materials*, 2014, 26, 3912-3917.
15. Z. Liu, T. Liu, Q. Lin, C. Bao and L. Zhu, *Angewandte Chemie International Edition*, 2015, 54, 174-178.
16. K. Suyama, S. Ozaki and M. Shirai, *Reactive and Functional Polymers*, 2013, 73, 518-523.
17. H. Salmi, X. Allonas, C. Ley, A. Defoin and A. Ak, *Polymer Chemistry*, 2014, 5, 6577-6583.
18. S. Chatani, M. Podgórski, C. Wang and C. N. Bowman, *Macromolecules*, 2014, 47, 4894-4900.
19. S. E. R. Auty, O. Andren, M. Malkoch and S. P. Rannard, *Chemical Communications*, 2014, 50, 6574-6577.
20. T. M. O'Shea, A. A. Aimetti, E. Kim, V. Yesilyurt and R. Langer, *Advanced Materials*, 2015, 27, 65-72.
21. L. Yu, L.-H. Wang, Z.-T. Hu, Y.-Z. You, D.-C. Wu and C.-Y. Hong, *Polymer Chemistry*, 2015, DOI: 10.1039/C4PY01363H.
22. M. Porel and C. A. Alabi, *Journal of the American Chemical Society*, 2014, 136, 13162-13165.
23. C. Wang, M. Podgorski and C. N. Bowman, *Materials Horizons*, 2014, 1, 535-539.
24. C. O. Bounds, R. Goetter, J. A. Pojman and M. Vandersall, *Journal of Polymer Science Part A: Polymer Chemistry*, 2012, 50, 409-422.
25. K. Landfester, *Angewandte Chemie International Edition*, 2009, 48, 4488-4507.
26. J. M. Asua, *Progress in Polymer Science*, 2002, 27, 1283-1346.
27. G. Odian, *Principles of polymerization*, Wiley-Interscience New York, 2004.
28. F. Tiarks, K. Landfester and M. Antonietti, *Journal of Polymer Science Part A: Polymer Chemistry*, 2001, 39, 2520-2524.
29. M. Barrère and K. Landfester, *Polymer*, 2003, 44, 2833-2841.
30. H. Frank, U. Ziener and K. Landfester, *Macromolecules*, 2009, 42, 7846-7853.
31. R. Roux, L. Sallet, P. Alcouffe, S. Chambert, N. Sintes-Zydowicz, E. Fleury and J. Bernard, *ACS Macro Letters*, 2012, 1, 1074-1078.
32. J. M. Siebert, G. Baier, A. Musyanovych and K. Landfester, *Chemical Communications*, 2012, 48, 5470-5472.
33. D. Liu, X. Jiang and J. Yin, *Langmuir*, 2014, 30, 7213-7220.

34. F. Jasinski, E. Lobry, B. Tarablsi, A. Chemtob, C. Croutxé-Barghorn, D. Le Nouen and A. Criqui, *ACS Macro Letters*, 2014, 3, 958-962.
35. D. V. Amato, D. N. Amato, A. S. Flynt and D. L. Patton, *Polymer Chemistry*, 2015, DOI: 10.1039/C4PY01449A.
36. O. Z. Durham, S. Krishnan and D. A. Shipp, *ACS Macro Letters*, 2012, 1, 1134-1137.
37. O. Z. Durham and D. A. Shipp, *Polymer*, 2014, 55, 1674-1680.
38. D. P. Nair, N. B. Cramer, J. C. Gaipa, M. K. McBride, E. M. Matherly, R. R. McLeod, R. Shandas and C. N. Bowman, *Advanced Functional Materials*, 2012, 22, 1502-1510.
39. T. Delmas, H.Piraux, A.-C. Couffin, I. Texier, F. Vinet, P. Poulin, M. E. Cates and J. Bibette, *Langmuir*, 2011, 27, 1683-1692.
40. E. Žůrková, K. Bouchal, D. Zdeňková, Z. Pelzbauer, F. Švec, J. Kálal and H. G. Batz, *Journal of Polymer Science: Polymer Chemistry Edition*, 1983, 21, 2949-2960.
41. M. A. Rakas and A. F. Jacobine, *The Journal of Adhesion*, 1992, 36, 247-263.