Preparation of mechanoresponsive hairy particles using polymeric surfactants in emulsion polymerization

Citation for published version (APA):

Li, H., Zhang, Y., Liu, Y., Sijbesma, R. P., Heuts, J. P. A., & Zhang, Q. (2017). Preparation of mechanoresponsive hairy particles using polymeric surfactants in emulsion polymerization. *Polymer Chemistry*, 8(27), 3971-3976. <https://doi.org/10.1039/c7py00468k>

Document license:
TAVERNE

DOI:
[10.1039/c7py00468k](https://doi.org/10.1039/c7py00468k)

Document status and date:
Published: 21/07/2017

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Polymer Chemistry

rsc.li/polymers

ISSN 1759-9962

PAPER

Qiuyu Zhang *et al.*

Preparation of mechanoresponsive hairy particles using polymeric surfactants in emulsion polymerization

Cite this: *Polym. Chem.*, 2017, **8**, 3971

Preparation of mechanoresponsive hairy particles using polymeric surfactants in emulsion polymerization†

Hui Li,^a Yuyu Zhang,^a Yibin Liu,^a Rint P. Sijbesma,^b Johan P. A. Heuts^b and Qiuyu Zhang^b*

We demonstrate that diblock copolymers comprising hydrophobic polystyrene and hydrophilic poly(acrylic acid) blocks connected by an off-center anthracene–maleimide Diels–Alder adduct mechanophore are mechanochemically active when sonicated in the form of micelles. Non-crosslinked and cross-linked hairy poly(butyl acrylate) latex particles were synthesized using amphiphilic block copolymers as stabilizers in emulsion polymerization. Both non-crosslinked and crosslinked hairy particles can be mechanically activated by sonication, which means that the “hairs” on the surface of particles can be selectively cleaved. The sensitivity to mechanical force enhanced with increasing crosslinking of the PBA particles, but it may also lead to particle degradation. The mechanoresponsive hairy latex particles may facilitate the design of stress-sensing probes in aqueous systems.

Received 20th March 2017,
Accepted 7th May 2017

DOI: 10.1039/c7py00468k

rsc.li/polymers

Introduction

In recent years, there has been increasing interest in exploiting functional polymers¹ which are designed to respond to stimuli, such as heat,^{2,3} light,^{4,5} electric and magnetic fields,¹ pH,^{6,7} redox potential^{8,9} or mechanical stress.^{10–13} Specifically, the rise of polymer mechanochemistry has spurred rapid development of mechanoresponsive polymers¹⁴ which find applications in force sensors, self-healing materials or biomedical purposes.^{15–20} Molecules with mechanically labile bonds, called mechanophores, are embedded within polymers and can be activated by applying a mechanical force. Recent progress in mechanophores has prompted the advent of new methods for fabricating functional polymers with force-induced functionalities, including mechanochromism,^{21–23} mechanoluminescence,^{10,24} release of therapeutics,^{25,26} cross-linking agents^{17,18} and mechanocatalysis.^{27,28} Although considerable research effort has focussed on the design and development of new mechanically activated polymeric structures, mechanochemistry on hairy particles has rarely been reported.²⁹

In general, hairy particles are particles containing polymers at their surface where these polymer chains extend into the continuous phase. They are generally synthesized by “grafting from” and/or “grafting onto” processes using functional “hairs” for applications such as optical data storage,³⁰ protein binding or biomedical applications.^{39,40} Alternatively, these hairy particles can be obtained *in situ* by using polymeric surfactants as stabilizers in emulsion polymerization.^{16,31–38} It would be of interest to obtain polymer particles with mechanically cleavable “hairs” for applications such as polymer synthesis on solid supports, heterogeneous catalysis and controlled release of agents.

Inspired by the work reported by Moore and co-workers⁴¹ in which mechanophore anchored poly(methyl acrylate) (PMA) chains are grafted onto the surface of silica nanoparticles and the high capability of the anthracene–maleimide Diels–Alder adduct to optically report over covalent bond scission, we previously synthesized mechanoresponsive block copolymer micelles.⁴² In that work, asymmetric block copolymers comprising a long hydrophilic poly(acrylic acid) (PAA) and a short hydrophobic poly(butyl acrylate) (PBA) block connected by the anthracene–maleimide were synthesized and micellar solutions were prepared (Fig. 1a). We then demonstrated that noncovalent micellar aggregation can promote the mechanochemistry of covalent bonds.

In the current work, we wish to take this approach one step further and use similar mechanophore-containing block copolymer micelles as a starting material for the synthesis of mechanoresponsive hairy polymer particles. Different from our previous work, here asymmetric poly(styrene)-*b*-poly(acrylic acid) (PS-*b*-

^aKey Laboratory of Applied Physics and Chemistry in Space of Ministry of Education, School of Science, Northwestern Polytechnical University, 710072 Xi'an, Shaanxi, China. E-mail: qyuzhang1803@gmail.com

^bLaboratory of Supramolecular Polymer Chemistry, Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

† Electronic supplementary information (ESI) available: The experimental details and structural characterization. See DOI: 10.1039/c7py00468k

Fig. 1 (a) Illustration of the force-induced scission of the anthracene-maleimide mechanophore when (b) embedded in block copolymer micelles or hairy latex particles.

PAA) copolymers connected by the anthracene-maleimide Diels-Alder adduct (Fig. 1a) were synthesized and used in emulsion polymerization of butyl acrylate (BA) to prepare mechano-responsive hairy latex particles using the mechanophore-containing PS-*b*-PAA block copolymers as polymeric surfactants. The overall objective of this work is to evaluate this synthesis strategy for the preparation of hairy latex particles with mechano-responsive cleavable “hairs” as this would be helpful in further designing stress-sensing probes in aqueous systems.

Results and discussion

Synthesis of the block copolymers

The synthetic route towards mechanophore-containing amphiphilic block copolymers is depicted in Scheme 1.

Scheme 1 Synthetic route towards PS₄₆-*b*-PAA₁₄₂ **5** containing the maleimide-anthracene Diels-Alder adduct mechanophore.

Fig. 2 Molecular weight distributions of anthracene-PtBA₁₄₂ **3**, maleimide-PS₄₆ **4**, and DA adduct. Values reported are relative to polystyrene standards.

First, the functionalized initiators **1** and **2** were synthesized according to modified procedures of Moore and co-workers⁴¹ and Haddleton and co-workers.⁴³ Anthracene-PtBA₁₄₂ ($M_n = 18.5$ kDa, $\bar{D} = 1.29$) was synthesized by atom transfer radical polymerization (ATRP) at room temperature employing **1** as the initiator. Subsequently, initiator **2** was used to prepare maleimide-PS₄₆ **4** ($M_n = 5.1$ kDa, $\bar{D} = 1.14$) *via* Cu(0)-mediated living radical polymerization (SET-LRP). Then the PS₄₆-*b*-PtBA₁₄₂ diblock copolymer was obtained by a Diels-Alder reaction between **3** and a slight excess of **4** ($M_n = 17.5$ kDa, $\bar{D} = 2.03$). The molecular weight distributions of these polymers were determined by gel permeation chromatography (GPC), the traces of which are shown in Fig. 2.

It can be seen clearly from Fig. 2 that the molecular weight distribution of the block copolymer contains minor peaks besides that of the desired block. The small peak at $M \approx 5.1$ kDa was ascribed to maleimide-PS₄₆ **4** as this reagent was added in slight excess in order to optimize conversion of the anthracene moiety. The high molecular weight shoulder around 45–50 kDa originates from the anthracene-PtBA, which also contains a similar shoulder around 40 kDa and which we ascribe to polymer chains that were terminated by chain coupling. Since these PtBA chains contain two anthracene groups, it is very likely that both these groups react with maleimide-PS (which is in excess) resulting in a triblock copolymer with a molecular weight corresponding to the high M shoulder of the coupling product.

Finally, after selective acidic hydrolysis of *t*-butyl groups in PS₄₆-*b*-PtBA₁₄₂, the desired amphiphilic diblock copolymer, PS₄₆-*b*-PAA₁₄₂ was obtained (the triblock copolymer was not removed). The experimental details and structural characterization can be found in the ESI.†

Preparation and characterization of micelles

The amphiphilic block copolymer PS₄₆-*b*-PAA₁₄₂ did not directly dissolve in water. Therefore, micelles were prepared by

Fig. 3 Number and intensity size distributions of PS₄₆-b-PAA₁₄₂ micelles in water (0.5 mg mL⁻¹) as measured by DLS at 25 °C.

introducing an amount of PS₄₆-b-PAA₁₄₂ and K₂CO₃ into de-ionized water.³² The sample was heated to 70 °C under vigorous stirring for about two hours for complete solubilization (pH = 8). In Fig. 3 the size distributions of the resulting micelles (at a block copolymer concentration of 0.5 mg mL⁻¹) as determined by Dynamic Light Scattering (DLS) are shown. The great majority of the micelles have a diameter of around 70 nm. The peak around 300–400 nm in the intensity distribution is ascribed to (reversible) aggregation of micelles.

Fig. 4 Fluorescence measurements of PS₄₆-b-PAA₁₄₂ micelles during sonication (λ_{exc} = 260 nm, λ_{em} = 420 nm).

These results are in line with previously reported results on block copolymer micelles.^{16,44–46}

Mechanochemistry of PS₄₆-b-PAA₁₄₂ micelles

We first investigated whether the PS₄₆-b-PAA₁₄₂ micelles could also be mechanochemically activated, just as we previously observed for PBA₃₂-b-PAA₂₁₄ micelles.⁴² Although we did not expect to see any differences, we wanted to be certain that there were no undesired effects because of the higher glass transition temperature (T_g) of the hydrophobic core. Fig. 4 shows the effect of sonicating a micellar solution of PS₄₆-b-PAA₁₄₂ on the fluorescence emission and excitation spectra. The intensities of the anthracene fluorescence increase with increasing sonication time of a PS₄₆-b-PAA₁₄₂ micellar solution, indicating the cleavage of the anthracene–maleimide mechanophore. We estimate that about 45% of the Diels–Alder adducts are cleaved after 120 min of sonication (see Fig. S6 in the ESI†). Therefore, the glassy micellar core formed by PS₄₆ segments also provides an effective anchor point to render the PS₄₆-b-PAA₁₄₂ micelles mechanochemically active.^{42,47,48}

Preparation of mechanoresponsive hairy particles by emulsion polymerization of butyl acrylate using PS₄₆-b-PAA₁₄₂ as a stabilizer

In order to prepare hairy latex particles with cleavable “hairs”, emulsion polymerizations of butyl acrylate (BA) were performed using PS₄₆-b-PAA₁₄₂ as a polymeric surfactant. Crosslinked and non-crosslinked poly(butyl acrylate) latices were prepared using Na₂S₂O₃/(NH₄)₂S₂O₈ as a redox initiator at 35 °C. The recipes used for these emulsion polymerizations are summarized in Table 1. High monomer conversions (and stable latices) were obtained for all experiments as can be seen from the evolution of monomer conversions plotted in Fig. 5a. Additionally, DLS (Fig. 5b) and scanning electron microscopy (SEM) analyses (Fig. 6) show that the corresponding latex particles stabilized by PS₄₆-b-PAA₁₄₂ were spherical, and the particle size distribution became more monodisperse with an increasing amount of the crosslinking agent.

Transmission electron microscopy (TEM) was employed to further analyze the morphology and particle size of the final latices (Fig. 6). Interestingly, the TEM images of the particles present an apparent core–shell structure which we ascribe to the fact that the PS hydrophobic segments of the polymeric surfactant are not miscible with the bulk material of the PBA

Table 1 The recipes used for emulsion polymerization of butyl acrylate with PS₄₆-b-PAA₁₄₂ block copolymers as stabilizers

Sample	BA ^a (wt%)	EGDMA ^b (wt%)	Surfactant ^c (wt%)	Initiator ^d (wt%)	<i>T</i> (°C)	<i>D</i> _{DLS} ^e (nm)	PDI by DLS	<i>D</i> _{TEM} ^f (nm)	<i>M</i> _n (kDa)	PDI by GPC
1	15	0	3.0	0.8	35	366	0.265	92 ± 10	916	1.61
2	15	1	3.0	0.8	35	278	0.124	105 ± 10	550	1.67
3	15	3	3.0	0.8	35	295	0.197	110 ± 10	—	—

^a BA content was based on the overall composition. ^b The dosage of EGDMA was based on butyl acrylate. ^c The amount of PS₄₆-b-PAA₁₄₂ was based on the total monomer content. ^d Redox initiator system (Na₂S₂O₃/(NH₄)₂S₂O₈) based on the total monomer content was used in all the polymerizations at 35 °C. ^e z-Average particle diameter as measured by DLS. ^f Number-average particle diameter was calculated from TEM using software ImageJ.

Fig. 5 (a) Evolution of monomer conversion with time for the emulsion polymerization of butyl acrylate using a PS₄₆-b-PAA₁₄₂ block copolymer as a surfactant and (b) particle size distribution of poly(butyl acrylate) latices by number measured by DLS at 25 °C.

Fig. 6 SEM images (above) and TEM images (below) of poly(butyl acrylate) latices with different amounts of the crosslinker (EGDMA) before sonication.

particles, hence creating a block copolymer shell.³⁴ The z-average particle diameters measured by DLS for these three samples were found to be 366 nm, 278 nm and 295 nm, respectively (see Table 1), all significantly larger than those obtained from the TEM images (see Fig. 6 and Table 1). This difference is commonly observed in this type of system¹⁶ and is caused by the inclusion of the solvated layer of polyacrylic acid chains in the hydrodynamic radius measured by DLS, whereas these chains are collapsed onto the particles in the TEM measurements.

The mechanochemical response of these hairy particles was investigated using ultrasonication. Fig. 7a shows the evolution of anthracene fluorescence intensity at the emission maximum $\lambda_{em} = 420$ nm with ultrasonication time.

Fig. 7 (a) Evolution of the emission intensity at $\lambda_{em} = 420$ nm as a function of sonication time (b) evolution of the z-average diameter D_z of latices during sonication.

It is clear from the results shown in Fig. 7a that an increasing sonication time leads to an increase in free anthracene groups, which means that an increasing number of chain scissions take place at the mechanophore. Especially for the sample containing the highest amount of crosslinker (3%) this effect was very strong and the intensity of the fluorescence emission was much higher than those of the samples containing 1% and 0% crosslinker. This result implies that more heavily crosslinked particles are better anchors for the mechanophore-containing block copolymers.^{42,47,48} Thus, during sonication the “hairs” on the particle surfaces were cleaved, releasing the hydrophilic anthracene-terminated PAA chains, which in turn resulted in a fluorescence signal. A rough calculation, based on a calibration performed by fluorescence of small molecule anthracene in an aqueous sodium dodecyl benzene sulfonate solution (see Fig. S6, ESI†), leads to an estimated fraction of ~15% of the Diels–Alder adducts that were cleaved after sonication for 150 min of the sample containing 3% crosslinker.

The evolution of the z-average diameter D_z of the latices over the course of sonication is shown in Fig. 7b and it is clear from this figure that ultrasonication leads to a reduction in particle size. D_z was reduced from 278 to 233 nm and from 295 to 142 nm after sonication for 180 min for samples with 1% and 3% crosslinker, respectively, whereas there was no clear observable reduction in the case of the uncrosslinked particles. The observed reductions are consistent with what would be expected when the hydrophilic segment PAA₁₄₂ chains are cleaved off; these chains have a length of 40–45 nm when fully stretched and a maximum decrease of 80–90 nm in particle diameter (see also Fig. 3) can be expected (if all chains are cleaved off). Since the reduction in the particle diameter of sample 3 (3% of crosslinker) is significantly larger than 90 nm, these results suggest that some of the particles themselves were also broken. This is confirmed by the presence of small particles in the case of sample 3 as clearly seen in Fig. 8, which shows SEM and TEM images of the latices after soni-

Fig. 8 SEM images (above) and TEM images (below) of a poly(butyl acrylate) latex with different amounts of the crosslinker (EGDMA) after sonication for 180 min.

Fig. 9 Molecular weight distributions for latices containing different amounts of the crosslinker before and after sonication and the maleimide-PS₄₆ block. (a) Molecular weight distributions for sample 1 (0% crosslinker), (b) molecular weight distributions for sample 2 (1% crosslinker) and (c) chromatograms for sample 3 (3% crosslinker).

cation for 180 min. A possible break up of the crosslinked particles by ultrasound is an unexpected result as, to the best of our knowledge, the break up of latex particles by ultrasound has not been reported to date. In fact ultrasound has been investigated extensively as an initiation-source in emulsion polymerization.⁴⁹ A further investigation of the potential effect of crosslinking on latex stability against ultrasonication would be very interesting, but is beyond the scope of the current paper.

We also analyzed the molecular weight distributions of the three samples before and after sonication (Fig. 9) using GPC (eluent THF, so no free PAA chains are observed). From Fig. 9a and b, it can be seen that the molecular weight decreases for samples containing 0% and 1% crosslinker after sonication for 180 min, suggesting that not only the mechanophore-containing block copolymers were cleaved during sonication, but also a small number of the polymer chains inside the particles.⁵⁰ Furthermore, a peak appeared at $M \approx 5.1$ kDa, which corresponds to the maleimide-PS₄₆ block and this clearly suggests that mechanical activation of amphiphilic block copolymers on the surface of the latex particles occurred. The situation is different for the sample with 3% crosslinker, where no soluble polymer chains were detected (Fig. 9c); even the maleimide-PS₄₆ fragments were trapped in the crosslinked PBA particles. In summary and considering the results presented so far it is safe to state that crosslinking of the PBA particle resulted in an enhanced mechanochemical activity of the hairy polymer particles.

Conclusions

In this paper we report the synthesis of an asymmetric amphiphilic block copolymer PS₄₆-*b*-PAA₁₄₂ comprising an off-center anthracene-maleimide Diels-Alder adduct mechanophore. Mechanochemical activation of PS₄₆-*b*-PAA₁₄₂ block copolymer micelles in water was confirmed; the aggregation of the block

copolymers into a large superstructure resulted in a high effective contour length susceptible to mechanical activation. Subsequently, the PS₄₆-*b*-PAA₁₄₂ block copolymers were shown to be effective surfactants in the emulsion polymerization of butyl acrylate, both in the absence and presence of a crosslinker. The resulting hairy polymer particles were subjected to ultrasonication and it was found that the mechanophores in the block copolymer surfactants were activated and the PAA-chains were cleaved off selectively. Crosslinking of the particles leads to a greater mechanochemical activity, but our preliminary results suggest that it may also increase the susceptibility of the particles to ultrasound degradation. Overall we have clearly demonstrated that particles synthesized by emulsion polymerization using mechanophore-containing PS₄₆-*b*-PAA₁₄₂ as stabilizers can be mechanically activated, which further opens up ways for the application of polymer mechanochemistry in aqueous systems.

Acknowledgements

H. L. was supported by the Excellent Doctorate Foundation of Northwestern Polytechnical University and the National Natural Science Foundation of China (No. 51673156). This work was supported by the Dutch Ministry of Education, Culture, and Science (Gravity program 024.001.035).

Notes and references

- 1 M. M. Caruso, D. A. Davis, Q. Shen, S. A. Odom, N. R. Sottos, S. R. White and J. S. Moore, *Chem. Rev.*, 2009, **109**, 5755–5798.
- 2 K. M. Wiggins, J. N. Brantley and C. W. Bielawski, *ACS Macro Lett.*, 2012, **1**, 623–626.
- 3 F. D. Jochum and P. Theato, *Chem. Soc. Rev.*, 2013, **42**, 7468–7483.
- 4 A. L. Black, J. M. Lenhardt and S. L. Craig, *J. Mater. Chem.*, 2011, **21**, 1655–1663.
- 5 Y. Zhao, *Macromolecules*, 2012, **45**, 3647–3657.
- 6 D. Schmaljohann, *Adv. Drug Delivery Rev.*, 2006, **58**, 1655–1670.
- 7 K. M. Huh, H. C. Kang, Y. J. Lee and Y. H. Bae, *Macromol. Res.*, 2012, **20**, 224–233.
- 8 H. Cho, J. Bae, V. K. Garripelli, J. M. Anderson, H. W. Jun and S. Jo, *Chem. Commun.*, 2012, **48**, 6043–6045.
- 9 Y. Wen, Z. Zhang and J. Li, *Adv. Funct. Mater.*, 2014, **24**, 3874–3884.
- 10 Y. Chen, A. J. H. Spiering, S. Karthikeyan, G. W. Peters, E. W. Meijer and R. P. Sijbesma, *Nat. Chem.*, 2012, **4**, 559–562.
- 11 A. Piermattei, S. Karthikeyan and R. P. Sijbesma, *Nat. Chem.*, 2009, **1**, 133–137.
- 12 J. N. Brantley, K. M. Wiggins and C. W. Bielawski, *Science*, 2011, **333**, 1606–1609.

- 13 H. M. Klukovich, T. B. Kouznetsova, Z. S. Kean, J. M. Lenhardt and S. L. Craig, *Nat. Chem.*, 2013, **5**, 110–114.
- 14 M. W. Urban, *Handbook of Stimuli-Responsive Materials*, Wiley-VCH, Weinheim, 2011.
- 15 C. K. Lee, B. A. Beiermann, M. N. Silberstein, J. Wang, J. S. Moore, N. R. Sottos and P. V. Braun, *Macromolecules*, 2013, **46**, 3746–3752.
- 16 A. Muñoz-Bonilla, A. M. van Herk and J. P. A. Heuts, *Macromolecules*, 2010, **43**, 2721–2731.
- 17 J. Wang, I. Piskun and S. L. Craig, *ACS Macro Lett.*, 2015, **4**, 834–837.
- 18 A. L. B. Ramirez, Z. S. Kean, J. A. Orlicki, M. Champhekar, S. M. Elsagr, W. E. Krause and S. L. Craig, *Nat. Chem.*, 2013, **5**, 757–761.
- 19 S. R. White, M. M. Caruso and J. S. Moore, *Mrs Bull.*, 2008, **33**, 766–769.
- 20 Z. S. Kean, Z. Niu, G. B. Hewage, A. L. Rheingold and S. L. Craig, *J. Am. Chem. Soc.*, 2013, **135**, 13598–13604.
- 21 Y. Chen, H. Zhang, X. Fang, Y. Lin, Y. Xu and W. Weng, *ACS Macro Lett.*, 2014, **3**, 141–145.
- 22 H. Zhang, Y. Chen, Y. Lin, X. Fang, Y. Xu, Y. Ruan and W. Weng, *Macromolecules*, 2014, **47**, 6783–6790.
- 23 X. Fang, H. Zhang, Y. Chen, Y. Lin, Y. Xu and W. Weng, *Macromolecules*, 2013, **46**, 6566–6574.
- 24 Y. Chen and R. P. Sijbesma, *Macromolecules*, 2014, **47**, 3797–3805.
- 25 R. Langer, *Nature*, 1998, **392**, 5–10.
- 26 K. Y. Lee, M. C. Peters, K. W. Anderson and D. J. Mooney, *Nature*, 2000, **408**, 998–1000.
- 27 J. M. Paulusse and R. P. Sijbesma, *Chem. Commun.*, 2008, **37**, 4416–4418.
- 28 R. Groote, R. T. Jakobs and R. P. Sijbesma, *Polym. Chem.*, 2013, **4**, 4846–4859.
- 29 L. J. Wang, X. J. Zhou, X. H. Zhang and B. Y. Du, *Macromolecules*, 2015, **49**, 98–104.
- 30 E. Kumacheva, O. Kalinina and L. Lilge, *Adv. Mater.*, 1999, **11**, 231–234.
- 31 G. Riess and C. Labbe, *Macromol. Rapid Commun.*, 2004, **25**, 401–435.
- 32 C. Burguière, S. Pascual, C. Bui, J. P. Vairon, B. Charleux, K. A. Davis, K. Matyjaszewski and I. Bétremieux, *Macromolecules*, 2001, **34**, 4439–4450.
- 33 A. Muñoz-Bonilla, A. M. van Herk and J. P. A. Heuts, *Polym. Chem.*, 2010, **1**, 624–627.
- 34 A. Muñoz-Bonilla, S. I. Ali, A. Del Campo, M. Fernández-García, A. M. van Herk and J. P. A. Heuts, *Macromolecules*, 2011, **44**, 4282–4290.
- 35 A. Muñoz-Bonilla, J. P. A. Heuts and M. Fernández-García, *Soft Matter*, 2011, **7**, 2493–2499.
- 36 J. Jacobs, A. Byrne, N. Gathergood, T. E. Keyes, J. P. A. Heuts and A. Heise, *Macromolecules*, 2014, **47**, 7303–7310.
- 37 M. Álvarez-Paino, A. Muñoz-Bonilla, F. López-Fabal, J. L. Gómez-Garcés, J. P. A. Heuts and M. Fernández-García, *Polym. Chem.*, 2015, **6**, 6171–6181.
- 38 J. Jacobs, N. Gathergood, J. P. A. Heuts and A. Heise, *Polym. Chem.*, 2015, **6**, 4634–4640.
- 39 H. Kawaguchi, *Prog. Polym. Sci.*, 2000, **25**, 1171–1210.
- 40 D. Li, X. Sheng and B. Zhao, *J. Am. Chem. Soc.*, 2005, **127**, 6248–6256.
- 41 J. Li, T. Shiraki, B. Hu, R. A. Wright, B. Zhao and J. S. Moore, *J. Am. Chem. Soc.*, 2014, **136**, 15925–15928.
- 42 H. Li, R. Göstl, M. Delgove, J. Sweeck, Q. Zhang, R. P. Sijbesma and J. P. A. Heuts, *ACS Macro Lett.*, 2016, **5**, 995–998.
- 43 J. A. Syrett, G. Mantovani, W. R. Barton, D. Price and D. M. Haddleton, *Polym. Chem.*, 2010, **1**, 102–106.
- 44 K. Mortensen, W. Brown, K. Almdal, E. Alami and A. Jada, *Langmuir*, 1997, **13**, 3635–3645.
- 45 L. M. Bronstein, D. M. Chernyshov, G. I. Timofeeva, L. V. Dubrovina, P. M. Valetsky and A. R. Khokhlov, *Langmuir*, 1999, **15**, 6195–6200.
- 46 D. Lombardo, N. Micali, V. Villari and M. A. Kiselev, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 2004, **70**, 021402.
- 47 P. A. May, N. F. Munaretto, M. B. Hamoy, M. J. Robb and J. S. Moore, *ACS Macro Lett.*, 2016, **5**, 177–180.
- 48 M. Schaefer, B. Icli, C. Weder, M. Lattuada, A. F. Kilbinger and Y. C. Simon, *Macromolecules*, 2016, **49**, 1630–1636.
- 49 M. A. Bradley, S. W. Prescott, H. A. S. Schoonbrood, K. Landfester and F. Grieser, *Macromolecules*, 2005, **38**, 6346–6351.
- 50 H. H. Jellinek, *Degradation of vinyl polymers*, Academic Press, 1955.