

# ChemComm

Accepted Manuscript



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

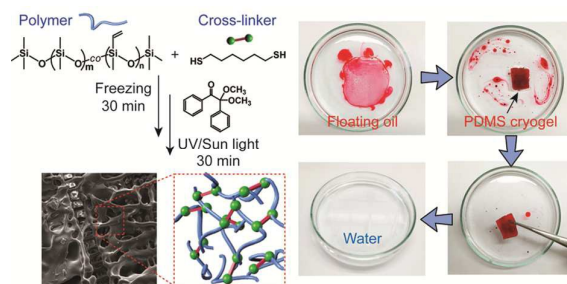
*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript*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

## Graphical Abstract

We prepared novel cryogels via facile thiol-ene reaction at low temperatures, which can selectively remove oils with excellent recyclability.



## COMMUNICATION

# A rapid and facile preparation of novel macroporous silicone-based cryogels via photo-induced thiol-ene click chemistry

Cite this: DOI: 10.1039/x0xx00000x

Mehmet Murat Ozmen<sup>a,b</sup>, Qiang Fu<sup>a</sup>, Jinguik Kim<sup>a</sup> and Greg G. Qiao<sup>a,\*</sup>

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

[www.rsc.org/](http://www.rsc.org/)

**Novel poly(dimethylsiloxane) based macroporous gels (cryogels) were prepared via a simple and rapid photo-induced thiol-ene click reaction at low temperatures. The cryogels formed were able to float on a water surface and selectively remove oils or organic solvents with excellent recyclability.**

Macroporous gels, so called cryogels, arising from gelation at low temperatures, known as cryogelation, have attracted much attention in recent years due to their superfast swelling rate, open porous structure and high degree of toughness.<sup>1</sup> Generally, the process of cryogelation involves moderately freezing the solutions of monomers or polymer precursors at temperatures below the freezing point of the reaction solvent resulting in solvent crystal formation. Thereafter, crosslinking reactions followed by thawing of the solvent crystals, subsequently, results in an interconnected macroporous network.<sup>2</sup> Cryogels continue to receive widespread interest in many applied areas such as bioseparation, scaffolds for tissue engineering, and oil absorbents.<sup>3</sup> Examples of previously prepared cryogels including butyl rubber have been found to be suitable materials as oil absorbents in removing pollution such as oil products and toxic organic solvents which can cause serious environmental problems.<sup>4</sup> Such cryogels possess the properties of ideal oil absorbents displaying high hydrophobicity, good buoyancy, high uptake capacity, have good recyclability and are of low cost to produce. However, the conventional cryogelation reactions of these materials require long reaction times of about 24 hours and the immediate initiation of crosslinking reactions before freezing limits the control on the properties of the resultant cryogels. Recently, Petrov *et al.* reported the cryogelation process in which the reactions are initiated after moderately freezing of the precursor solutions via UV irradiation giving rise to short reaction times.<sup>5</sup> Although cryogel formation was achieved in a relatively short time, this reaction relies on a powerful UV source of 400 W. Therefore, obtaining cryogels utilizing moderate UV or alternative light sources such as sunlight is considered favourable for large scale industrial production of these materials.

Thiol-ene click chemistry, which is a versatile photo-induced coupling reaction, has been attractive to researchers due to several reasons including the ability of the reaction to proceed under mild UV irradiation, tolerance to a variety of solvents and enes, minimal

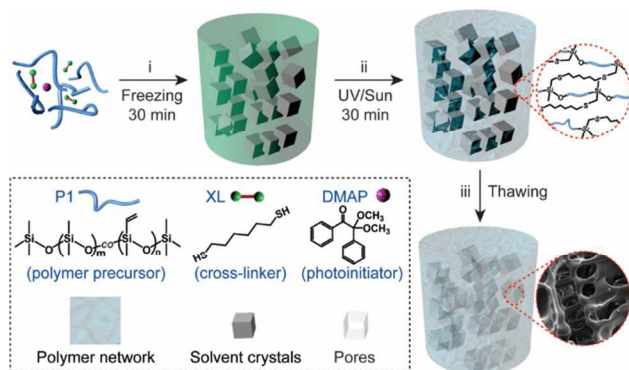
oxygen inhibition, high yields and rapid reaction rates.<sup>6</sup> Photo-induced thiol-ene chemistry has been proposed as an efficient approach for the crosslinking of polymer chains without using an expensive metal catalyst.<sup>7</sup> While it is a simple and rapid approach to complete the reactions, thiol-ene reaction has rarely been utilized directly to produce macroporous materials.<sup>8</sup>

Poly(dimethylsiloxane) (PDMS) is a very well-known member of the silicone-based polymers, possessing a combination of unique properties including high flexibility, high hydrophobicity, non-toxicity, thermal stability, non-flammability and inertness.<sup>9</sup> Recently, macroporous PDMS has attracted attention as a promising candidate for selectively separating oils or organic solvents from water.<sup>10</sup> The bond formation characteristics and the low intermolecular forces between the side chains provide low surface energy.<sup>11</sup> These properties of PDMS ensure high hydrophobicity which enables it to be very suitable for oil removal. Another advantage offered by PDMS as an ideal material for oil removal is its flame retardancy, that is, a slow burning rate and low heat release rates.<sup>12</sup> However, important to note is that previously reported macroporous PDMS materials were prepared using templating methods (generally using sugar as the template) which have common drawbacks such as the removal of templates to generate the macropores and also have long preparation times.<sup>10a</sup>

In the present communication, we report to the best of our knowledge, the first example of low temperature photo-induced thiol-ene click chemistry with short cryogelation time as a facile route to fabricate macroporous materials. Furthermore, this study represents the first report of PDMS cryogels. These cryogels were prepared in moderately frozen reaction solutions within one hour (30 minutes freezing time plus 30 minutes reaction time) via the thiol-ene coupling at low temperatures. By employing cryogelation and in the presence of solvent crystals acting as a natural template, the macropores form *in situ* during the thawing step avoiding additional work to remove the templates. As will be seen below, the resulting PDMS cryogels exhibit a high degree of toughness, superfast absorption rates and show excellent buoyancy and hydrophobicity.

The preparation of the cryogels by a typical cryogelation process involving freezing of the reaction system followed by photo-induced

thiol-ene coupling is schematically shown in Scheme 1. After the initial precursor solution was frozen, it was placed in a LED UV activation apparatus (Fig. S1, ESI†) or alternatively exposed to sunlight (see ESI† for experimental details). The crosslinking reactions were initiated in the presence of 2,2-dimethoxy-2-phenylacetophenone (DMPAP) as the photoinitiator and cyclohexane as the reaction solvent either at  $-18\text{ }^{\circ}\text{C}$  or  $0\text{ }^{\circ}\text{C}$ , designated as Cryogel-UV and Cryogel-Sun, respectively. Control samples were also prepared by UV exposure at room temperature designated as Hydrogel.



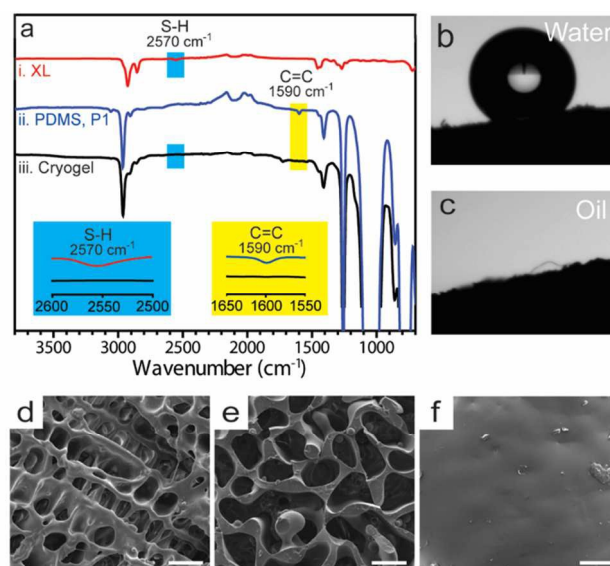
**Scheme 1.** Schematic illustration of the fabrication of silicon-based cryogels. (i) The PDMS, cross-linker and DMAP were dissolved in cyclohexane (10 w/v %) and the mixture was frozen at  $-18\text{ }^{\circ}\text{C}$  for 30 min. (ii) The mixture was exposed to under UV ( $\lambda_{\text{max}} = 390\text{ nm}$ )/sunlight irradiation for another 30 min. (iii) The gel was then thawed at R.T., washed with toluene and air dried at R.T.

As can be seen in Scheme 1, by applying a photo-induced thiol-ene coupling reaction, we successfully prevented the reagents from reacting and crosslinking before freezing of the reaction system until the initiator was triggered by UV or sunlight. As mentioned above, thiol-ene reactions enable high yields of the material formed. Indeed, in this study we observed that the gel fraction which was determined by the extraction of the gels in toluene and then drying the insoluble polymer to constant mass, was found to be  $89 \pm 5\%$  and  $90 \pm 3\%$  for Cryogel-Sun and Cryogel-UV, respectively. This result indicates high crosslinking efficiency of the crosslinker (XL, 1,6-hexanedithiol) even at low reaction temperatures. Fourier-transform infrared spectroscopy (FT-IR) spectra of the PDMS cryogel indicated the thiol-ene reaction of the vinyl group containing polymer (P1) with crosslinker (XL) as evident from the complete disappearance of the characteristics peaks of the thiol ( $2570\text{ cm}^{-1}$ , Fig. 1a-i) and vinyl ( $1590\text{ cm}^{-1}$ , Fig. 1a-ii) groups. The successful formation of cross-linked PDMS cryogel was also confirmed by X-ray photoelectron spectroscopy (XPS) analysis. The detected elements (At. %) are indicated as follow:  $\sim 20.7\text{ At. \%}$  of O1s,  $\sim 54.0\text{ At. \%}$  of C1s,  $\sim 1.6\text{ At. \%}$  of S2p and  $\sim 23.7\text{ At. \%}$  Si2p (Fig. S2a, ESI†). In addition, as shown in Fig. S2b-e, the high resolution XPS spectra of these elements provides detailed information about internal chemical composition. All of these results demonstrate the successful preparation of cross-linked cryogels *via* the rapid and robust thiol-ene click chemistry. Control experiments were also performed in which photoinitiator or crosslinker was selectively omitted and the results revealed that thiol-ene reactions do not proceed without addition of either initiator or crosslinker.

Contact angle measurements were carried out to investigate the hydrophobic/oleophilic character of the cryogels by quantifying the

water-repellence of the samples. Images of water and oil droplets on the cryogel were taken as shown in Fig. 1b-c, respectively. Whilst the water droplet on the cryogel surface assumed a large contact angle of  $140^{\circ}$ , the oil droplet immediately penetrated into the cryogel with a contact angle measured to be  $0^{\circ}$ . These results indicated that the cryogels exhibit simultaneous hydrophobic and oleophilic properties and absorb oil while repelling water.

The internal morphology of the dried cryogels was then investigated by environmental scanning electron microscope (E-SEM). Fig. 1d-f shows E-SEM images of cross-sections of the PDMS gels with 10 w/v% mass loading. As can be seen from the images, while the Hydrogel sample has a non-porous structure (Fig. 1f), the cryogels exhibited an aligned porous morphology (Fig. 1d-e). These aligned interconnected structures are in good agreement with the macroporous networks of butyl rubber cryogels which resulted from using cyclohexane as the solvent.<sup>4b</sup> Additionally, this system of large interconnected pores is the main characteristic feature of the cryogels giving them a spongy morphology. Moreover, this pore structure affords the cryogels sufficient mechanical strength due to the dense pore walls as observed during investigation of their mechanical properties when swollen in toluene by compression testing. As shown in Fig. S3, while the Hydrogel sample could not withstand deformations as large as 20 %, the PDMS cryogels could be compressed up to 80 % deformation. At 50 % strain, the samples displayed a stress of 0.014 MPa for Cryogel-UV and 0.019 MPa for Cryogel-Sun. The absorbed cryogel samples could also be completely squeezed between the fingers without suffering any mechanical damage. Once the forces were removed, these tough samples adopted their initial shapes without any crack development.



**Fig 1.** a) ATR FT-IR spectra of (i) cross-linker, (ii) PDMS precursor, P1 and (iii) the formed Cryogel-UV. The inserted figures reflect the enlarged colour regions. b-c) Contact angle measurements of a water and an oil droplet on the Cryogel-UV. E-SEM characterization on the internal morphology of d) PDMS Cryogel-UV, e) PDMS Cryogel-Sun and f) The control PDMS Hydrogel prepared at room temperature. The scale bars represent  $50\text{ }\mu\text{m}$ .



Thereafter, a series of absorption tests were carried out. The buoyancy, the absorption capacities, the absorption kinetics and the recyclability of the samples were investigated. Fig. 2a, reveals the process of removing oil from water when the cryogel was floated on the water surface. As soon as the cryogel was in contact with the oil floating on the surface of the water, the oil was quickly and completely absorbed by the cryogel. This buoyancy and selectivity of the cryogels clearly suggests their potential use as selective absorbent to remove oils and organic solvents from water. In order to measure the absorption capacity of the cryogels, samples were immersed in oils or solvents without water and the maximum absorption capacities were determined by mass change. Fig. 2b shows the absorption capacities of the cryogel for various oils and organic solvents. For example, the oil (Gasoline) uptake was ~1,600 % weight gain (or 16 g per gram) of absorbent and the toluene uptake was ~1,400 % weight gain of absorbent. To further investigate the uptake rate and recyclability, toluene was used as a model organic compound. Fig. 2c shows the superfast absorption rate of the cryogels in toluene compared to the Hydrogel sample. Specifically, by dipping the gels into toluene, the cryogels quickly absorbed the solvent and reached their highest uptake within 5 seconds. This superfast absorption is due to the interconnected macroporous structure which ensures unhindered convectional transport of solvents within the cryogels. In contrast, the absorption was much slower for the non-porous hydrogel due to the slow diffusion of the solvent into the hydrogel. Fig. 2c also shows that the water absorption of the gels is almost zero which also reveals the hydrophobic nature of these materials.

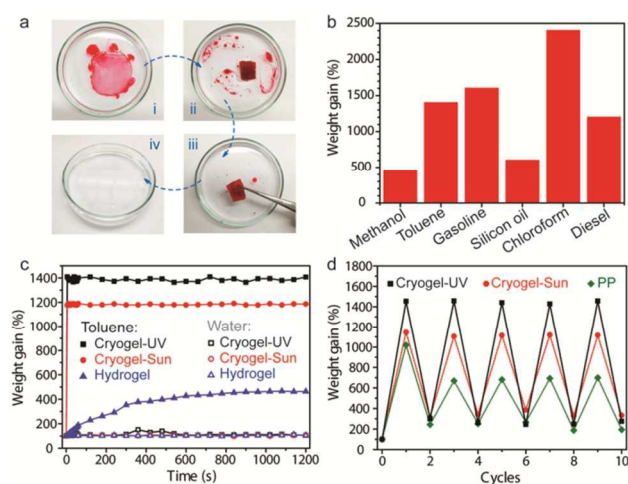


Fig. 2 a) Digital images of removal of oil which was dyed with Oil Red O from the surface of water using the PDMS Cryogel-UV. b) Absorption capacity of PDMS Cryogel-UV (10 w/v %) for different organic solvents and oils. c) Superfast absorption rate of PDMS cryogels in toluene. d) Comparison of the absorption of the cryogels obtained by sunlight and UV initiation in this study with commercial non-woven polypropylene absorbent.

For recyclability tests, the swollen absorbents were mechanically pressed to collect absorbed oil and then load was removed to recover the absorbents for further absorption use. As shown in Fig. 2d, the recyclability of the cryogels was investigated by repeated absorption-squeezing cycles. The cryogels exhibited excellent robustness even after recycling 10 times (further experiments up to 100 cycles are shown in Fig. S4). Furthermore, the cryogels maintained their absorption capacities during reuse and the values were close to their maximum uptake capacities (1,400 % weight-gain or 14 g per gram of absorbents). The recyclability was further investigated for the cryogels in comparison with commercially

available non-woven polypropylene mat (PP). Fig. 2d reveals that while the high absorbency was maintained for Cryogel-Sun and cryogel-UV, the PP could not keep its absorbency efficiency during recycling (~ 400 % weight-gain loss). Moreover, the emulsion separation ability of the cryogel was investigated. Oil (toluene) in water emulsion (5 % v/v) was prepared and then immediately poured into a syringe in which a piece of cryogel was inserted in its lower part (See ESI† for details). While the oil was absorbed by the cryogel, the water passed through the cryogel as drops which were collected in a glass vial located under the syringe. The concentration of the toluene after separation was calculated by UV-Vis spectrophotometry (Fig. S5). It was found that, after separation, the concentration of toluene decreases from 5 % v/v to less than 0.16 % v/v. This result indicates that more than 96 % of oil in the emulsion is separated due to the absorption of toluene by the cryogel and henceforth, the cryogel can also separate emulsified oils.

Furthermore, the stability of the cryogels upon exposure to harsh conditions such as immersion of the samples in acid-base and organic solvents or storage at high or low temperatures on their absorbency capacities was investigated. As shown in Table S1, there were negligible changes in the toluene absorption capacities of the cryogel upon storage at -80 °C or 200 °C and likewise when immersed in acid-base and toluene for 24 h compared to non-exposed samples. Finally, the flame retardancy of the cryogel was examined. As shown in Fig. S6, when the cryogel is ignited using a lighter, it displays flame retardancy whereby it is evident that the carbonaceous cryogel retains its skeleton intact.

In summary, a simple, rapid and efficient method was developed to produce macroporous materials by utilizing thiol-ene click chemistry with cryogelation. The obtained novel PDMS cryogels revealed aligned porous structure with micrometre sized pores. Both Cryogel-UV and Cryogel-Sun samples show high compressibility and efficiency for the removal of oil from water. The high hydrophobicity and oleophilicity of these cryogels allowed them to absorb oil and organic solvents but repel water. Absorption kinetic measurements showed that the solvent was absorbed superfast by the cryogels in just a few seconds. These materials exhibited strong durability which can be recovered by simple mechanical pressing. Furthermore, these materials could be recycled more than 100 times without any crack development and whilst still maintaining a high absorbance capacity. It was also evident that the cryogels show very good stability when exposed to harsh conditions as well as flame retardancy when ignited. The absorbing characteristics indicate that such porous silicone-based cryogels have the potential to play an important role as an absorbent for oil spill clean-ups as well as for emulsified oil separation. Moreover, using the facile thiol-ene coupling reactions to obtain cryogels enabled the efficient control of the cryogelation reactions by sunlight or UV and the preparation of these cryogels in a short preparation time (i.e. 1 h). Further exploration and application of the reported versatile strategy which can be potentially triggered by sunlight provides many opportunities to design and develop macroporous materials for various applications such as tissue engineering and bioseparation.

M.M. Ozmen acknowledges the support of The Scientific and Technological Research Council of Turkey, 2219-International Postdoctoral Research Program Fellowship.

<sup>a</sup>Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia

<sup>b</sup>Department of Bioengineering, Yildiz Technical University, Esenler, 34220, Istanbul, Turkey

†Electronic Supplementary Information (ESI) available: [details of materials, characterization methods and experiments]. See DOI: 10.1039/c000000x/

### Notes and references

- (a) V. I. Lozinsky and O. Okay, in *Polymeric Cryogels*, Springer, 2014, pp. 49-101; (b) O. Okay and V. I. Lozinsky, in *Polymeric Cryogels*, Springer, 2014, pp. 103-157; (c) M. M. Ozmen and O. Okay, *Polymer*, 2005, **46**, 8119-8127; (d) M. V. Dinu, M. M. Ozmen, E. S. Dragan and O. Okay, *Polymer*, 2007, **48**, 195-204.
- (a) A. Kumar and A. Srivastava, *Nature protocols*, 2010, **5**, 1737-1747; (b) V. I. Lozinsky, F. M. Plieva, I. Y. Galaev and B. Mattiasson, *Bioseparation*, 2001, **10**, 163-188.
- (a) G. Ertürk and B. Mattiasson, *Journal of Chromatography A*, 2014, **1357**, 24-35; (b) N. Kathuria, A. Tripathi, K. K. Kar and A. Kumar, *Acta Biomaterialia*, 2009, **5**, 406-418; (c) D. Ceylan and O. Okay, *Macromolecules*, 2007, **40**, 8742-8749.
- (a) D. Ceylan, S. Dogu, B. Karacik, S. D. Yakan, O. S. Okay and O. Okay, *Environmental science & technology*, 2009, **43**, 3846-3852; (b) S. Dogu and O. Okay, *Polymer*, 2008, **49**, 4626-4634; (c) Y. Hu, X. Liu, J. Zou, T. Gu, W. Chai and H. Li, *ACS applied materials & interfaces*, 2013, **5**, 7737-7742; (d) I. Karakutuk and O. Okay, *Reactive and Functional Polymers*, 2010, **70**, 585-595; (e) Z. Oztoprak, T. Hekimoglu, I. Karakutuk, D. C. Tuncaboylu and O. Okay, *Polymer bulletin*, 2014, **71**, 1983-1999.
- (a) P. D. Petrov and C. B. Tsvetanov, in *Polymeric Cryogels*, Springer, 2014, pp. 199-222; (b) V. Stoyneva, D. Momekova, B. Kostova and P. Petrov, *Carbohydrate polymers*, 2014, **99**, 825-830; (c) P. Petrov, E. Petrova and C. B. Tsvetanov, *Polymer*, 2009, **50**, 1118-1123; (d) P. Petrov, E. Petrova, B. Tchorbanov and C. B. Tsvetanov, *Polymer*, 2007, **48**, 4943-4949.
- (a) C. E. Hoyle and C. N. Bowman, *Angewandte Chemie International Edition*, 2010, **49**, 1540-1573; (b) A. B. Lowe, *Polymer Chemistry*, 2014, **5**, 4820-4870; (c) D. P. Nair, M. Podgórski, S. Chatani, T. Gong, W. Xi, C. R. Fenoli and C. N. Bowman, *Chemistry of Materials*, 2013, **26**, 724-744; (d) A. Shen, Z. Guo, L. Yu, L. Cao and X. Liang, *Chemical Communications*, 2011, **47**, 4550-4552; (e) J. D. McCall and K. S. Anseth, *Biomacromolecules*, 2012, **13**, 2410-2417; (f) O. Altintas, T. Josse, J. De Winter, N. M. Matsumoto, P. Gerbaux, M. Wilhelm and C. Barner-Kowollik, *Polymer Chemistry*, 2015; (g) Y. Xia, H. Yao, Z. Miao, Y. Ma, M. Cui, L. Yan, H. Ling and Z. Qi, *RSC Advances*, 2015, **5**, 50955-50961.
- (a) O. van den Berg, L.-T. T. Nguyen, R. F. Teixeira, F. Goethals, C. Ozdilek, S. Berghmans and F. E. Du Prez, *Macromolecules*, 2014, **47**, 1292-1300; (b) L. Xue, Y. Zhang, Y. Zuo, S. Diao, J. Zhang and S. Feng, *Materials Letters*, 2013, **106**, 425-427; (c) K. Goswami, A. L. Skov and A. E. Daugaard, *Chemistry-A European Journal*, 2014, **20**, 9230-9233; (d) S. Mongkhontreerat, K. Öberg, L. Erixon, P. Löwenhielm, A. Hult and M. Malkoch, *Journal of Materials Chemistry A*, 2013, **1**, 13732-13737.
- (a) F. Alves and I. Nischang, *Chemistry-A European Journal*, 2013, **19**, 17310-17313; (b) Z. Liu, J. Ou, H. Lin, Z. Liu, H. Wang, J. Dong and H. Zou, *Chemical Communications*, 2014, **50**, 9288-9290.
- E. Yilgör and I. Yilgör, *Progress in Polymer Science*, 2014, **39**, 1165-1195.
- (a) S.-J. Choi, T.-H. Kwon, H. Im, D.-I. Moon, D. J. Baek, M.-L. Seol, J. P. Duarte and Y.-K. Choi, *ACS applied materials & interfaces*, 2011, **3**, 4552-4556; (b) A. Zhang, M. Chen, C. Du, H. Guo, H. Bai and L. Li, *ACS applied materials & interfaces*, 2013, **5**, 10201-10206; (c) X. Zhao, L. Li, B. Li, J. Zhang and A. Wang, *Journal of Materials Chemistry A*, 2014, **2**, 18281-18287; (d) L. Li, B. Li, L. Wu, X. Zhao and J. Zhang, *Chemical Communications*, 2014, **50**, 7831-7833; (e) G. Hayase, K. Kanamori, M. Fukuchi, H. Kaji and K. Nakanishi, *Angewandte Chemie International Edition*, 2013, **52**, 1986-1989.
- J. E. Mark, *Accounts of chemical research*, 2004, **37**, 946-953.
- S. Hamdani, C. Longuet, D. Perrin, J.-M. Lopez-cuesta and F. Ganachaud, *Polymer Degradation and Stability*, 2009, **94**, 465-495.