Angewandte International Edition Chemie

Photocatalysts

International Edition: DOI: 10.1002/anie.201505325
German Edition: DOI: 10.1002/ange.201505325

Heterophase Photocatalysts from Water-Soluble Conjugated Polyelectrolytes: An Example of Self-Initiation under Visible Light

Saman Ghasimi, Simon Prescher, Zi Jun Wang, Katharina Landfester, Jiayin Yuan, and Kai A. I. Zhang**

Abstract: *We herein report a new design route to stable, heterophase photocatalysts, which function as highly dispersible conjugated polymer nanoparticles and porous monoliths under visible light in aqueous medium. They were constructed by attachment of the ionic-liquid species 1-alkyl-3-vinylimidazolium bromide onto the side chains of a photoactive polymer. The structure configuration allows not only photocatalysis in aqueous environment but also a unique self-initiation radical cross-linking process to transform the water-soluble photoactive polymer into a heterophase system, either as nanoparticles or a porous monolith. High photocatalytic activity and reusability of the heterophase system were demonstrated in the degradation of organic dyes and reduction of* Cr^{VI} *into* Cr^{III} *in water under visible-light irradiation.*

Visible-light-driven photochemistry and photocatalysis have found significantly broad utility in organic synthesis and energy materials in recent years.[1] Taking nature as a role model, where various chromophores and photocatalysts for converting solar energy into chemical energy have been used for millions of years, organic chemists have developed a vast number of systems involving photo-redox processes that mimic photosynthesis.[2] Among them, transition metal complexes are very popular due to their easy access, favorable stability, and photo-redox properties. Thus their applications range from water splitting and solar energy storage to photovoltaics and chemical transformations.[1a,3] Nevertheless, there are some intrinsic drawbacks associated with these complex systems, for instance, high cost, toxicity of these rare metals, and their limited availability in nature. From this standpoint, the development of metal-free catalysts having light-absorbing properties has caught much interest in many research groups. In fact, a number of organic dyes such as fluorescein, eosin Y, nile red, and rhodamine B have been already successfully employed in photo-redox catalysis in the last two decades.[4] However, a common disadvantage of these organic dyes as molecular catalysts is that they readily undergo solvolytic attack in the reaction medium and the photobleaching effect, which can be troublesome for catalyst recycling and long-term usage. It is therefore highly desirable to design new organic, non-metal, heterophase photocatalysts that are stable and easy to recover. From this point of view, two heterophase models are of high importance: nanoparticulate systems and porous polymers. Nanoparticles are characterized by a high surface-to-volume ratio and porous materials by a large surface area. Recent responses to the acute need for heterogeneous non-metal photocatalytic systems, especially porous carbon nitrides, a state-of-art example, have gained enormous attention. The electronic and optical properties of these efficient metal-free photocatalysts can be tuned by molecular design, copolymerization, doping, texture or morphology engineering, and surface heterojunctions.[5] Another emerging class of organic semiconductors, conjugated porous polymers, combining a photoactive π-electron backbone and porous-interface properties, have been advantageously introduced as stable heterogeneous photocatalysts for organic synthesis under irradiation by visible light.[6] Some research activities showed their applications for molecular oxygen activation,[7] hydroxylation of arylboronic acids,[8] dehalogenation reaction[9] visible-light photoinitiation for free radical polymerization,[10] and hydrogen evolution.[11]

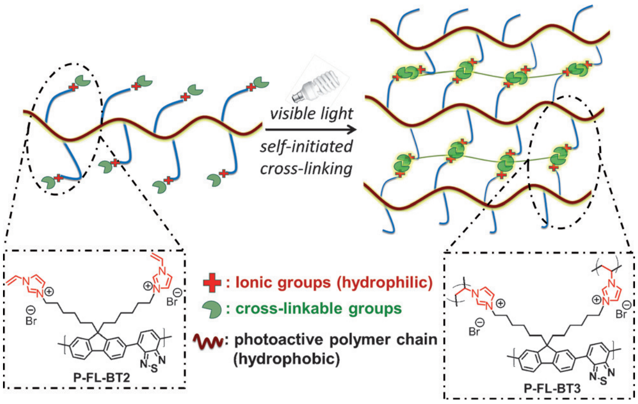
Apart from the materials design perspective, a more technologically relevant concept of using economically and environmentally friendly reaction media, that is, to employ "green" solvents instead of hazardous organic solvents, is often considered for the photocatalyst design, given the fact that the use of organic solvents produces a vast volume of liquid waste in laboratory and industrial processes. Water, in particular, has been considered as a cheap, easy-to-recycle green solvent for organic reactions.[12]

Here, we report the design and synthesis of water-compatible conjugated nanoparticles and porous polymers bearing imidazolium-based ionic-liquid (IL) units[13] as highly efficient metal-free visible-light photocatalysts in aqueous environment. Through the attachment of cross-linkable vinylimidazolium side chains onto the conjugated poly(benzothiadiazolylfluorene) backbone, both nanoparticles and porous monoliths, depending on the polymer concentration, were produced via a unique self-initiated intramolecular radical cross-linking process under visible-light irradiation. High photocatalytic activity of the as-synthesized polymer in aqueous medium was demonstrated for the degradation of rhodamine B and methylene blue dyes and the photoreduction of Cr^{VI} into Cr^{III} under visible-light irradiation.

---

[*] S. Ghasimi, Z. J. Wang, Prof. K. Landfester, Dr. K. A. I. Zhang
Max Planck Institute for Polymer Research
Department of Physical Chemistry of Polymers
55128 Mainz (Germany)
E-mail: kai.zhang@mpip-mainz.mpg.de
Dr. S. Prescher, Dr. J. Yuan
Max Planck Institute of Colloids and Interfaces
Department of Colloid Chemistry
14476 Potsdam (Germany)
E-mail: jiayin.yuan@mpikg.mpg.de

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/anie.201505325.



Scheme 1. The side-product-free synthesis of the heterophase photocatalyst from the photoactive conjugated polymer bearing cross-linkable imidazolium-based ionic liquid units by visible-light-promoted self-initiated cross-linking.

The synthetic principle of targeted conjugated polymers is illustrated in Scheme 1. The water-soluble conjugated polymer P-FL-BT-2 bearing cross-linkable vinylimidazolium side groups was obtained by functionalization of the hydrophobic conjugated polymer P-FL-BT-1 bearing bis(6-bromohexyl)-fluorene units with *N*-vinylimidazole. (The experimental details and characterization data are provided in the Supporting Information.) It should be noted that the reaction mixture is heated stepwise from 60 to 100 °C to achieve a high degree of quaternization without the occurrence of dehydrobromination side reactions. NMR spectroscopy indicated a 92 % conversion of bromohexyl groups in P-FL-BT-1 to vinylimidazolium bromide in P-FL-BT-2 (see Figure S2). Thermogravimetry analysis (TGA) showed comparable thermal behavior of P-FL-BT-1 and P-FL-BT-2 until about 230 °C (see Figure S4). UV/Vis absorption and fluorescence emission spectra showed a bathochromic shift of P-FL-BT-2 compared to P-FL-BT-1 (see Figure S6). A slight increase of the band gap from 2.49 eV for P-FL-BT-1 to 2.37 eV for P-FL-BT-2 can be derived from the absorption edges.

It was previously shown that conjugated macromolecular systems could mediate electron transfer under visible-light irradiation and thus act as photosensitizers.[7a,10,14] Therefore in our opinion the conjugated structure of P-FL-BT-2 should fulfill the requirements as a visible-light-active photoinitiator. Additionally, given the fact that P-FL-BT-2 consists of hydrophilic imidazolium side chains and a hydrophobic polymer main chain, which creates an amphiphilic pattern, it could simultaneously act as a stabilizer for colloidal systems, a concept that has been proven previously for such IL-based polyelectrolytes.[15] The critical micelle concentration (CMC) of P-FL-BT-2 was measured to be 0.90 mM (see Figure S5). This value is similar to that of hexacetyltrimethylammonium bromide (CTAB, 0.92 mM), a widely used cationic surfactant in aqueous media.

To investigate the double role of P-FL-BT-2 as a visible-light photoinitiator and as a stabilizer for colloidal systems, the following two experiments were performed. First, a dilute solution of P-FL-BT-2 in water (0.1 mg mL^{-1}) was irradiated with a white LED lamp without using any additional radical initiator, yielding a stable dispersion (Figure 1 a). Transmission electron microscopy (TEM) analysis showed particles with a diameter of (85 ± 10) nm, indicating the formation of nanoparticles of the cross-linked polymer P-FL-BT-3 (Figure 1 b). The dynamic light scattering (DLS) characterization gave a larger number average apparent diameter of ca. 141 nm. This can be explained by the fact that the nanoparticles in solution are in a swollen state with a hydration shell, which leads to a size expansion. The zeta-potential of the nanoparticle dispersion (+34.7 mV) confirmed a stable colloidal system.

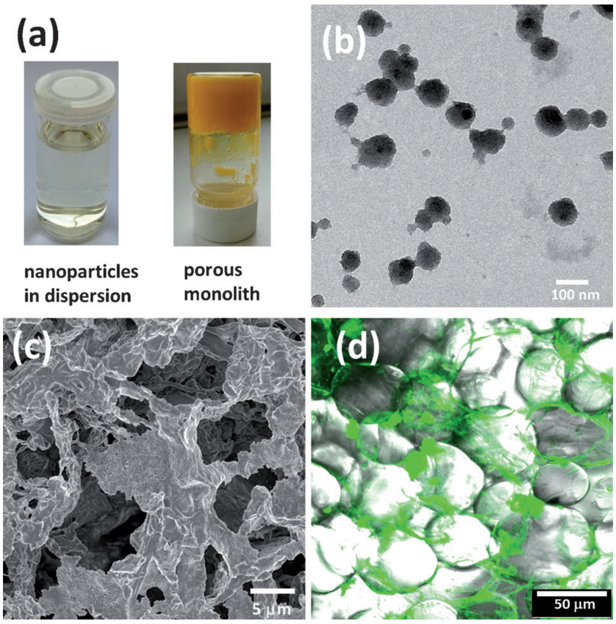


Figure 1. a) Photographs of P-FL-BT-3 as nanoparticles in aqueous dispersion (0.10 mg mL^{-1}) and as a porous monolith (0.67 mg mL^{-1}). b) TEM image of P-FL-BT-3 as nanoparticles. c) SEM image of a freeze-dried P-FL-BT-3 monolith. d) Confocal microscope image of a P-FL-BT-3 monolith with its own fluorescence.

Second, the high interfacial activity of P-FL-BT-2 for a two-phase emulsion system was demonstrated by the build-up of a porous polymer monolith by using the high internal phase emulsion polymerization technique (polyHIPE).[16] Without the addition of any surfactant, a stable water-in-oil emulsion formed using a small amount of P-FL-BT-2 (4 mg in 5 mL H_2O/hexadecane (volume ratio 1:4)). Under visible-light irradiation, self-initiation and cross-linking took place and eventually resulted in a porous monolith (Figure 1 a), which is insoluble in the common organic solvents and aqueous media tested. The SEM images of a freeze-dried sample showed a porous structure with interconnected pores inside the monolith (Figure 1 c). In the confocal microscope image, water droplets of about 50 μm were observed inside the monolith in a wet state, indicating a large pore structure inside the polymer monolith (Figure 1 d). Solid-state ^{13}C CP MAS NMR measurements showed the characteristic signals at about 113 and 120 ppm, which can be assigned to the carbons of the vinyl groups of P-FL-BT-2. These signals disappeared after the light-induced cross-linking process and merged with the signals of the aliphatic carbons between 20 and 60 ppm (see Figure S3).

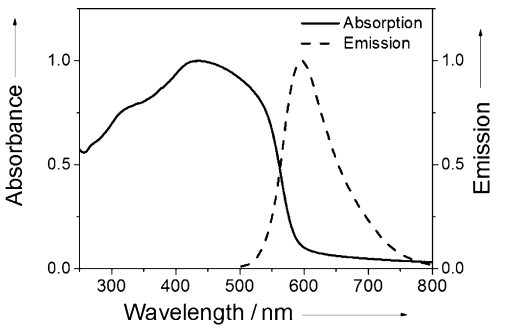


Figure 2. UV/Vis DRS and fluorescence emission spectra of monolithic P-FL-BT-3 (normalized curves).

In the UV/Vis diffuse reflectance spectra (DRS) (Figure 2) the absorption band of P-FL-BT-3 was slightly broader than that of P-FL-BT-1 and P-FL-BT-2 (see Figure S6). A similar emission range with a maximum at 600 nm can be seen in comparison, that is, in the visible-light range. A band gap of ca. 2.11 eV can be derived from the absorption edge. This corresponds to the observed band gap of 2.07 eV measured by cyclic voltammetry (CV) (see Figure S8).

Both aforementioned experiments demonstrated the ability of P-FL-BT-2 to serve as a visible-light initiator for radical polymerization and simultaneously as a stabilizer for emulsions. We suggest a modified initiation mechanism similar to that discussed in the literature.[17] Under visible-light irradiation, P-FL-BT-2 undergoes a transition to a long-lived triplet state, in which the vinyl group of the imidazolium unit is activated, forming an alkyl radical and a radical cation. The alkyl radical attacks other vinyl groups and initiates cross-linking. The radical cation of P-FL-BT-2 likely abstracts a proton from the adjacent environment, most likely water, and then returns to the ground state to complete the catalytic cycle. To demonstrate the ability of the conjugated polymer backbone to serve as a visible-light photoinitiator, we conducted a control experiment: the free radical polymerization of methyl methacrylate (MMA) with the hydrophobic polymer P-FL-BT-1 as the photoinitiator. As expected, PMMA was obtained under the same irradiation conditions without other initiators (see Figure S13), proving the photoactivity of the conjugated backbone of the polymer.

The feasibility of the monolithic P-FL-BT-3 as a heterogeneous photocatalyst in aqueous medium was tested. As organic dyes and heavy metals are well-known pollutants in industrial wastewater, the photocatalytic degradation of rhodamine B and methylene blue as two model dyes, and the photoreduction of aqueous Cr^{VI} were carried out under visible-light irradiation using the same lamp. As displayed in Figure 3a, the two organic dyes showed over 90% degradation after irradiation for roughly 70 min. This catalysis is comparable to that of porous carbon nitride (C_3N_4), a state-of-art non-metal-based visible-light photocatalyst, given the fact that the concentration of P-FL-BT-3 used here was about 10 times lower (0.1 $mg\,mL^{-1}$).[5e] Figure 3b displays the results of the photocatalytic reduction of Cr^{VI}, with an almost quantitative conversion from the highly toxic Cr^{VI} to much less harmful Cr^{III} [18] after 120 min. The efficiency of P-FL-BT-3 for Cr^{VI} reduction was found to be also comparable to that recently reported for metal-based photocatalysts such as $BiVO_4/Bi_2S_3$[19] and SnS_2/SnO_2[20] under similar reaction conditions. The photodegradation of the organic dyes in water is likely mediated by photochemically generated singlet oxygen, similar the mechanism proposed in a previous study.[6f] By absorption of light, the P-FL-BT-3 photosensitizer is excited to its singlet state (S) followed by subsequent intersystem crossing and population of a triplet state (T). The excited P-FL-BT-3 can transfer energy and spin to the ground-state triplet oxygen, thus forming the excited singlet oxygen that attacks the organic dyes.[21] The potential required for the redox reaction from Cr^{VI} to Cr^{III} is 1.33 V (vs. NHE).[22] P-FL-BT-3 has a band gap of 2.07 eV and the conduction band lies at -1.13 V (vs. NHE; see Table S2) in the excited state, which is sufficient for the reduction of Cr^{VI} to Cr^{III}.

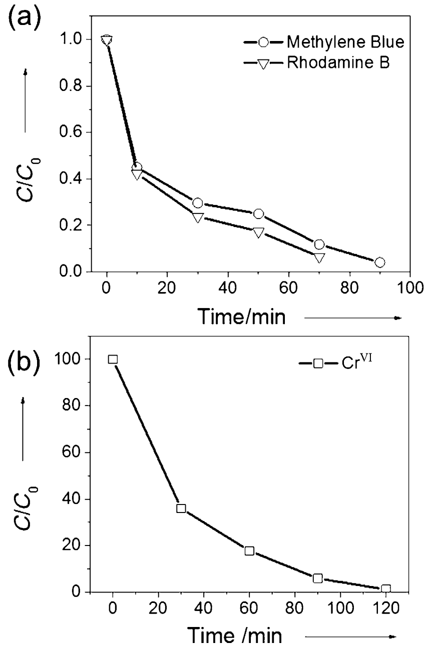


Figure 3. a) Photocatalytic degradation of rhodamine B and methylene blue and b) photocatalytic reduction of Cr^{VI} using P-FL-BT-3 in water under visible-light irradiation. C is the concentration of the organic dyes or Cr^{VI}, and C_0 is the initial concentration after reaching adsorption/desorption equilibrium in the dark.

We then studied the stability and reusability of the monolithic P-FL-BT-3 as a heterogeneous photocatalyst by conducting the same photodegradation reaction of rhodamine B for 10 repeated cycles (see Figure S12). Rhodamine B was degraded almost quantitatively in each run, demonstrating that P-FL-BT-3 can be used as a highly effective and stable water-compatible photocatalyst. It is worth noting that in the absence of P-FL-BT-3 these photoreactions did not occur at all under the same reaction conditions. A study with different scavengers[23] showed that reactive species such as superoxide ($^{\bullet}O_2^{-}$) play a crucial role in the photodegradation of the organic dye. Other active species such as photogenerated holes (h^+) and H_2O_2 have only a minor part in the catalytic process, while the effect of singlet oxygen ($^1O_2$) and hydroxyl radical ($^{\bullet}OH$) was minimal existent (see Figure S14).

In conclusion, we have demonstrated the successful synthesis and application of a conjugated polyelectrolyte photocatalyst working in a heterophase aqueous environment. The attachment of 1-alkyl-3-vinylimidazolium bromide units to the linear conjugated polymer backbone, a synthetically simple step, causes multiple synergistic effects: water-solubility, self-photoinitiation ability, and interfacial activity. The obtained monolithic polymer can serve as an efficient, recyclable, cost-effective heterogeneous photocatalyst for use under visible light and in water to degrade organic dyes and reduce heavy-metal ions such as $\mathrm{Cr^{VI}}$ to $\mathrm{Cr^{III}}$. We believe the design strategy and principle reported here can offer a very clean and side-product-free, and especially surfactant-free, synthetic pathway to obtain water-compatible photoactive polymers with desired morphology and a broader potential for other applications in aqueous medium under sustainable and environmentally friendly conditions.

Acknowledgements

We acknowledge the Max Planck Society for financial support, Dr. D. Hoffmann for the confocal microscopy images, Dr. R. Graf for the solid-state NMR measurements, and Prof. G. Wegner for fruitful discussions.

Keywords: chromium reduction · organic photocatalysts · photochemistry · self-initiation · visible light

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 14549–14553
Angew. Chem. **2015**, *127*, 14757–14761

---

[1] a) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* **2011**, *40*, 102–113; b) M. Fagnoni, D. Dondi, D. Ravelli, A. Albini, *Chem. Rev.* **2007**, *107*, 2725–2756; c) N. Hoffmann, *Chem. Rev.* **2008**, *108*, 1052–1103.

[2] a) D. Gust, T. A. Moore, *Science* **1989**, *244*, 35–41; b) T. J. Meyer, *Acc. Chem. Res.* **1989**, *22*, 163–170; c) D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **1993**, *26*, 198–205.

[3] a) K. Kalyanasundaram, *Coord. Chem. Rev.* **1982**, *46*, 159–244; b) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85–277; c) B. P. Fors, C. J. Hawker, *Angew. Chem. Int. Ed.* **2012**, *51*, 8850–8853; *Angew. Chem.* **2012**, *124*, 8980–8983; d) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322–5363.

[4] a) M. L. Marin, L. Santos-Juanes, A. Arques, A. M. Amat, M. A. Miranda, *Chem. Rev.* **2012**, *112*, 1710–1750; b) M. Neumann, S. Füldner, B. König, K. Zeitler, *Angew. Chem. Int. Ed.* **2011**, *50*, 951–954; *Angew. Chem.* **2011**, *123*, 981–985; c) H. J. Liu, W. Feng, C. W. Kee, Y. J. Zhao, D. Leow, Y. H. Pan, C. H. Tan, *Green Chem.* **2010**, *12*, 953–956.

[5] a) X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* **2009**, *8*, 76–80; b) Y. Wang, J. Zhang, X. Wang, M. Antonietti, H. Li, *Angew. Chem. Int. Ed.* **2010**, *49*, 3356–3359; *Angew. Chem.* **2010**, *122*, 3428–3431; c) X. Wang, S. Blechert, M. Antonietti, *ACS Catal.* **2012**, *2*, 1596–1606; d) Y. Wang, X. Wang, M. Antonietti, *Angew. Chem. Int. Ed.* **2012**, *51*, 68–89; *Angew. Chem.* **2012**, *124*, 70–92; e) M. Shalom, S. Inal, C. Fettkenhauer, D. Neher, M. Antonietti, *J. Am. Chem. Soc.* **2013**, *135*, 7118–7121; f) Y. Zheng, L. Lin, X. Ye, F. Guo, X. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 11926–11930; *Angew. Chem.* **2014**, *126*, 12120–12124; g) J. Zhang, Y. Chen, X. Wang, *Energy Environ. Sci.* **2015**, DOI: 10.1039/C1035EE01895A; h) J. Zhang, X. Wang, *Angew. Chem. Int. Ed.* **2015**, *54*, 7230–7232; *Angew. Chem.* **2015**, *127*, 7336–7338; i) Z. Lin, X. Wang, *Angew. Chem. Int. Ed.* **2013**, *52*, 1735–1738; *Angew. Chem.* **2013**, *125*, 1779–1782; j) G. Zhang, M. Zhang, X. Ye, X. Qiu, S. Lin, X. Wang, *Adv. Mater.* **2014**, *26*, 805–809; k) D. J. Martin, K. Qiu, S. A. Shevlin, A. D. Handoko, X. Chen, Z. Guo, J. Tang, *Angew. Chem. Int. Ed.* **2014**, *53*, 9240–9245; *Angew. Chem.* **2014**, *126*, 9394–9399; l) D. Zheng, C. Pang, Y. Liu, X. Wang, *Chem. Commun.* **2015**, *51*, 9706–9709; m) P. Niu, L. Zhang, G. Liu, H.-M. Cheng, *Adv. Funct. Mater.* **2012**, *22*, 4763–4770.

[6] a) L. Chen, Y. Honsho, S. Seki, D. Jiang, *J. Am. Chem. Soc.* **2010**, *132*, 6742–6748; b) A. I. Cooper, *Adv. Mater.* **2009**, *21*, 1291–1295; c) Y. Chen, J. Zhang, M. Zhang, X. Wang, *Chem. Sci.* **2013**, *4*, 3244–3248; d) see Ref. [5a]; e) F. Vilela, K. Zhang, M. Antonietti, *Energy Environ. Sci.* **2012**, *5*, 7819–7832; f) K. Zhang, D. Kopetzki, P. H. Seeberger, M. Antonietti, F. Vilela, *Angew. Chem. Int. Ed.* **2013**, *52*, 1432–1436; *Angew. Chem.* **2013**, *125*, 1472–1476.

[7] a) K. Zhang, Z. Vobecka, K. Tauer, M. Antonietti, F. Vilela, *Chem. Commun.* **2013**, *49*, 11158–11160; b) Z. J. Wang, S. Ghasimi, K. Landfester, K. A. I. Zhang, *Chem. Commun.* **2014**, *50*, 8177–8180.

[8] J. Luo, X. Zhang, J. Zhang, *ACS Catal.* **2015**, *5*, 2250–2254.

[9] Z. J. Wang, S. Ghasimi, K. Landfester, K. A. I. Zhang, *J. Mater. Chem. A* **2014**, *2*, 18720–18724.

[10] Z. J. Wang, K. Landfester, K. A. I. Zhang, *Polym. Chem.* **2014**, *5*, 3559–3562.

[11] R. S. Sprick, J.-X. Jiang, B. Bonillo, S. Ren, T. Ratvijitvech, P. Guiglion, M. A. Zwijnenburg, D. J. Adams, A. I. Cooper, *J. Am. Chem. Soc.* **2015**, *137*, 3265–3270.

[12] a) G.-J. t. Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636–1639; b) P. G. Jessop, *Green Chem.* **2011**, *13*, 1391–1398; c) T. Erdmenger, C. Guerrero-Sanchez, J. Vitz, R. Hoogenboom, U. S. Schubert, *Chem. Soc. Rev.* **2010**, *39*, 3317–3333.

[13] a) J. Texter, *Macromol. Rapid Commun.* **2012**, *33*, 1996–2014; b) D. England, N. Tambe, J. Texter, *ACS Macro Lett.* **2012**, *1*, 310–314; c) M. D. Green, T. E. Long, *Polym. Rev.* **2009**, *49*, 291–314; d) J. Yuan, D. Mecerreyes, M. Antonietti, *Prog. Polym. Sci.* **2013**, *38*, 1009–1036; e) P. Zare, A. Stojanovic, F. Herbst, J. Akbarzadeh, H. Peterlik, W. H. Binder, *Macromolecules* **2012**, *45*, 2074–2084; f) X. Feng, X. Sui, M. A. Hempenius, G. J. Vancso, *J. Am. Chem. Soc.* **2014**, *136*, 7865–7868; g) X. Sui, M. A. Hempenius, G. J. Vancso, *J. Am. Chem. Soc.* **2012**, *134*, 4023–4025; h) Y. Men, D. Kuzmicz, J. Yuan, *Curr. Opin. Colloid Interface Sci.* **2014**, *19*, 76–83; i) D. Wilms, J. Klos, A. F. M. Kilbinger, H. Löwe, H. Frey, *Org. Process Res. Dev.* **2009**, *13*, 961–964.

[14] a) M. C. DeRosa, R. J. Crutchley, *Coord. Chem. Rev.* **2002**, *233–234*, 351–371; b) E. Ji, T. S. Corbitt, A. Parthasarathy, K. S. Schanze, D. G. Whitten, *ACS Appl. Mater. Interfaces* **2011**, *3*, 2820–2829; c) S. Chemburu, T. S. Corbitt, L. K. Ista, E. Ji, J. Fulghum, G. P. Lopez, K. Ogawa, K. S. Schanze, D. G. Whitten, *Langmuir* **2008**, *24*, 11053–11062.

[15] a) F. Yan, J. Texter, *Angew. Chem. Int. Ed.* **2007**, *46*, 2440; *Angew. Chem.* **2007**, *119*, 2492; b) J. Y. Yuan, N. ten Brummelhuis, M. Junginger, Z. L. Xie, Y. Lu, A. Taubert, H. Schlaad, *Macromol. Rapid Commun.* **2011**, *32*, 1157.

[16] a) M. S. Silverstein, N. R. Cameron, *Encyclopedia of Polymer Science and Technology*, Wiley, Weinheim, **2002**; b) M. S. Silverstein, *Prog. Polym. Sci.* **2014**, *39*, 199–234; c) N. R. Cameron, *Polymer* **2005**, *46*, 1439–1449.

[17] B. Kiskan, J. S. Zhang, X. C. Wang, M. Antonietti, Y. Yagci, *Acs Macro Lett.* **2012**, *1*, 546–549.

[18] Agency for Toxic Substances and Disease Registry (ATSDR). U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA, **2012**.

[19] X. H. Gao, H. B. Bin Wu, L. X. Zheng, Y. J. Zhong, Y. Hu, X. W. Lou, *Angew. Chem. Int. Ed.* **2014**, *53*, 5917 – 5921; *Angew. Chem.* **2014**, *126*, 6027 – 6031.
[20] Y. C. Zhang, L. Yao, G. Zhang, D. D. Dionysiou, J. Li, X. Du, *Appl. Catal. B* **2014**, *144*, 730 – 738.
[21] a) C. Schweitzer, R. Schmidt, *Chem. Rev.* **2003**, *103*, 1685 – 1758; b) see Ref. [14a].
[22] W. M. Haynes, D. R. Lide, *CRC handbook of chemistry and physics*, 87th ed., CRC, Boca Raton, FL, **2006**.
[23] a) L.-S. Zhang, K.-H. Wong, H.-Y. Yip, C. Hu, J. C. Yu, C.-Y. Chan, P.-K. Wong, *Environ. Sci. Technol.* **2010**, *44*, 1392 – 1398; b) N. Zhang, S. Liu, X. Fu, Y.-J. Xu, *J. Phys. Chem. C* **2011**, *115*, 9136 – 9145; c) H. Li, Y. Liu, X. Gao, C. Fu, X. Wang, *ChemSusChem* **2015**, *8*, 1189 – 1196.

Received: June 10, 2015
Revised: August 24, 2015