

View Article Online View Journal

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. Kaupp, K. Hiltebrandt, V. Trouillet, P. Mueller, A. S. Quick, M. Wegener and C. Barner-Kowollik, *Chem. Commun.*, 2015, DOI: 10.1039/C5CC09444E.



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 <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> 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/chemcomm

ChemComm



Wavelength Selective Polymer Network Formation of End-Functional Star-Polymers

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Michael Kaupp,^a Kai Hiltebrandt,^a Vanessa Trouillet,^b Patrick Mueller,^c Alexander S. Quick,^{a, c} Martin Wegener^c and Christopher Barner-Kowollik^{*a}

www.rsc.org/

A wavelength selective technique for light-induced network formation based on two photo-active moieties, namely *ortho*methylbenzaldehyde and tetrazole is introduced. The network forming species are photo-reactive star polymers generated via reversible activation fragmentation chain transfer (RAFT) polymerization, allowing the network to be based on almost any vinylic monomer. Direct laser writing (DLW) allows to form any complex three-dimensional structure based on the photo-reactive star-polymers.

Polymer networks¹ find widespread applications in areas such as biomedicine, drug delivery, separation processes, hydrogels, and gas storage.² Light induced reactions benefit from environmentally friendly conditions, spatial and temporal control as well as overcoming large activation barriers in relatively short periods of time.³ Photo-chemical processes have already been shown to be a highly efficient tool in general⁴ and in particular for the formation of complex macromolecular structures such as block copolymers⁵ or telechelic precursors for gels.⁶ The facile spatial control over the reaction enables the synthesis of structured materials for example by employing photo-lithographic processes.^{4c, 7}

In principle, networks are formed via common polymerization techniques leading to crosslinking of multifunctional monomer units.⁸ The current contribution describes the first light-induced network formation which is selective towards the employed wavelength and can further be employed to fabricate three-dimensional structures via direct laser writing



Figure 1 Schematic overview of the employed combination of wavelength selection photo-induced reactions with RAFT-polymerization for network formation. DLW alloc for the formation of close to arbitrary three-dimensional structures.

(DLW). DLW is a highly versatile lithographic technique employing two-photon absorption and allows for the fabrication of micrometer scale structures with a tight y focused laser.9 Figure 1 shows a schematic overview of the synthetic steps leading to a macroscopic and microscop of network formation. To the best of the authors' knowledge, the current work also entails the first description of photo-reactive reversible activation fragmentation chain transfer (RAFT) sta polymers. Kuriara and coworkers described RAFT star polyme, able to photo-isomerize based on azo-benzene groups.¹⁰ Other reports describe photo-isomerizing (azo-benzene group ;)¹¹ and photo-degradable (nitrobenzene groups) star polymers that were synthesized via atom transfer radical polymerizatic (ATRP) as well as photo-linkable star polymers (due anthracene groups) fabricated via anionic polymerization.¹³ In the current publication the wavelength required for the network formation is only dependent on the photo-activ species attached to the RAFT-agent and can thereby b matched to other light sensitive groups in the system or the

^{a.} Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstaße 18, 76128 Karlsruhe, Germany and Institut für Biologische Grenzflächen, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Karlsruhe, Germany. E-mail: christopher.barner-kowollik@kit.edu

^{b.} Institute for Applied Materials (IAM) and Karlsruhe Nano Micro Facility (KMNF), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

^c Institut für Angewandte Physik, Institut für Nanotechnologie, Karlsruhe Institute of Technology (KIT), Wolfgang-Gaede-Straße 1, 76131 Karlsruhe, Germany.

Electronic Supplementary Information (ESI) available: Comprehensive experimental and analytical information. See DOI: 10.1039/x0xx00000x



Figure 2 Structure of the 4-arm RAFT agent TetraPE-RAFT and formation of the *ortho*quinodimethane structure upon irradiation.

envisaged application, for example in biological systems, where certain wavelengths may be harmful. RAFT has been employed numerous times for the formation of star polymers¹⁴ with up to twelve arms¹⁵ and there also exist several RAFT agents containing photo-active groups, such as the here employed *ortho*-methylbenzaldehyde (photo-enol)¹⁶ and tetrazole (nitrile imine mediated tetrazole ene coupling; NITEC)¹⁷ as well as phenacyl sulfide¹⁸ moiety. Previous studies revealed that RAFT polymers can be utilized under DLW conditions.¹⁸ The previously published photo-active RAFT agents have two properties in common: First, they are based on trithiocarbonates which are known to be stable under irradiation with UV-light;¹⁹ second, the photo-active group is tethered to the so-called R-group of the RAFT agent.

The two herein employed photo-active RAFT agents share the aforementioned properties. Thereby, the star conformation does not undergo cleavage reactions while being polymerized (Z-group approach),²⁰ and the photo-active groups remains on the more accessible periphery of the stars. The design of the RAFT agents is based on four symmetric arms attached to a pentaerythritol center (see Figure 2 and Figure 3).

The syntheses of the 4-arm RAFT agents as well as the conditions for the RAFT polymerization are described in the ESI. As a proof-of-concept, two styrene derivatives containing different heteroatoms were selected (4-chloromethyl-styrene and 4-bromostyrene), so they can readily be differentiated in X-ray photoelectron spectroscopy (XPS) measurements. In principal, a large range of monomers can be employed. Trithiocarbonate-based RAFT agents are able to mediate the polymerization of different monomer classes such as acrylate, acrylamide and styrene derivatives.^{14b} As the main part of the network consists of the polymeric chains, the chemical (functionality, polarity...) and physical (toughness, rigidity...) properties of the network can be easily adjusted via the choice of monomer and chain length. Since polymerization and network formation are independent, the free choice of monomer and arm length leads to further versatility of the presented system.

The conversion was kept relatively low (*DP* around 6 per arm, approximately 30 % conversion) to avoid side reactions such as arm-arm coupling and loss of end-group functionality. Low dispersities, lack of multimodalities in the gel permeation chromatogram (GPC) traces as well as the signals in the NMR spectra indicate an excellent control over polymerization with



Figure 3 Structure of the 4-arm RAFT agent TetraTet-RAFT and formation of the nitrile imine upon irradiation.

high end-group functionalization (see Figure S 13 to S 16 in th. ESI).

As a suitable counterpart for both photo-functional group maleimide derivatives were selected, based on their high reactivity towards *ortho*-quinodimethane and nitrile imine intermediates, enabling a rapid network formation. For the macroscopic network formation a small trifunctional maleimide was employed (refer to the ESI). In the DLY / process, a polymer containing maleimide side groups was used, as it leads to crosslinking at lower conversions ar 1 therefore allows for a faster writing speed.^{9e}

the small trifunctional maleimide is facile and non-demanding The two components are dissolved in a stoichiometric ratio with regard to the reactive end-group concentrations in small volume of solvent (refer to Table S 1 in the ESI). For the macroscopic networks dichloromethane (DCM) was employed yet the only demand the solvent has to fulfil is to dissolve the components and not absorb in the employed UV-light (implying that the network formation is independent of the solvent). Only in the case of the photo-enol functional star the solution has to be subsequently freed from oxygen via purgir. with nitrogen to ensure a rapid reaction. Network formation proceeds via irradiation with a suitable light source, in the current case simple low pressure compact lamps and LEDs, until solidification can be observed (2.5 h - 23.5 h; see Figu 2.4 and Figure 5 top). Subsequently, the network is freed free unreacted starting material via washing several times wit' DCM. Since the tetrazole moiety is profluorescent, fluorescent network (see Figure S 22) is formed from nor fluorescent starting material, giving a simple indication of successful reaction.

The formed networks were analyzed via XPS in order to ga specific chemical information and to detect bromine or

Journal Name

Journal Name

Please do not adjust margins

COMMUNICATION



Figure 4 Network formation employing the photo-enol functional RAFT star polymer. Top: Via a fluorescent lamp (λ_{max} = 355 nm). Bottom: Via LEDs (λ_{max} = 375 nm).

chlorine signals from the polymer corresponding to one network species, respectively. The results can be found in the ESI (Figure S 24 to S 31) and can be summarized as follows: The UV-induced network formation does not change the chemical constitution of the precursor materials, as they are incorporated into the network. Only in the case of the tetrazole based network one side reaction can be identified, namely the oxidation of the trithiocarbonate, which does not alter the integrity of the network. The oxidation leads to a new peak at around 168.6 eV binding energy, which has been found in XP spectra of RAFT polymers before.²¹

After establishing the network forming ability of the individual networks it is important to show the wavelength selectivity. Therefore, the behaviour of the tetrazole-functional star (mixed with the maleimide linker) when irradiated with the wavelength corresponding to the photo-enol activation (LEDs at 375 nm) is investigated. Hereby, the network formation as well as the photo-triggered NITEC reaction is suppressed, evidenced by unaltered GPC traces and NMR spectra (see Figure 6). Thus, the formation of photo-enol and tetrazole networks is wavelength selective. The difference in the GPC



Figure 5 Top: Network formation employing the tetrazole functional RAFT star polymer ((λ_{max} = 320 nm).



Figure 6 NMR (in CDCl₃) and GPC comparison of the maleimide trilinker, the 4-arm tetrazole RAFT star polymer and the reaction mixture irradiated for 5 h with the LEDs t 375 nm. No reaction occurs.

trace at higher retention times can be attributed to the addition of the small maleimide-trilinker prior to the irradiation. The selectivity towards a specific wavelength is very useful for systems or applications where only a state wavelength range can be employed due to other photosensible groups or possible side reactions.

To evidence the versatility of the photo-functional RAFT star they further were employed in DLW. The many possibilities of DLW are demonstrated by writing three-dimensional logos of the Karlsruhe Institute of Technology (KIT) with dimensions of 40×15×5 µm. The structures were written at a fundamental center wavelength of 640 nm in order to excite the molecules via two-photon absorption. Scanning electron microscopy (SEM) images of both structures can be found in Figure 7. For both formulations, the fabricated structures are well-defined



Figure 7 Top: SEM image of three-dimensional structure generated via DLW based of photo-enol functional star polymers; Middle: Structure stemming from tetrazole functional star polymers. The spherical impurities most are caused by so call a microexplosions. Bottom: Fluorescence of the three-dimensional structure associate. with the tetrazole functional star polymers irradiated at 405 nm. Bottom right Emission spectrum of the fluorescence. Scale bars: 2 µm.

This journal is © The Royal Society of Chemistry 20xx

Journal Name

COMMUNICATION

and only show moderate post-polymerization shrinkage. The lamellar edges are an artefact from the discretization of the structure. The structure stemming from photo-enol functional star polymers (Figure 7 top) is very clean, whereas the structure employing tetrazole functional star polymers (Figure 7 middle) shows some spherical impurities most probably stemming from microexplosions or contaminations. Similar to the macroscopic networks, the DLW structure

prepared via NITEC also displays fluorescence, which can be seen in Figure 7 bottom. The fluorescence can only be observed for the three-dimensional NITEC structure indicating that the impurities observed in SEM are neither stemming from structure formation nor structure degradation.

In summary, a novel concept for the light-induced network formation is described as a platform technology. Key feature is the wavelength selective network formation, as it is based on two different photo-active moieties, i.e. photo-enol and tetrazole functionalities which are activated at different wavelength. The latter group allows for the synthesis offluorescent networks. The polymeric precursors are produced with the versatile RAFT polymerization process, which allows the network to be based on almost any material from vinylic monomer, and is hence an important lever for adjusting the material properties of the respective networks. The versatility of the entire concept is further demonstrated via the combination with DLW, which allows for the network to be fabricated into any desired three-dimensional structure with micrometer scale resolution.

Acknowledgements

C. B.-K. acknowledges support from the Karlsruhe Institute of Technology (KIT) via the STN program of the Helmholtz association.

References

- 1 E. S. Dragan, Chem. Eng. J., 2014, 243, 572.
- D. Yuan, W. Lu, D. Zhao and H.-C. Zhou, *Adv. Mater.*, 2011, 23, 3723.
- 3 (a) T. Wu, H. Tang, C. Bohne and N. R. Branda, Angew. Chem. Int. Ed., 2012, 51, 2741; (b) T. Muraoka, C.-Y. Koh, H. Cui and S. I. Stupp, Angew. Chem., 2009, 121, 6060.
- 4 (a) M. A. Tasdelen and Y. Yagci, Angew. Chem. Int. Ed., 2013, 52, 5930; (b) A. Emeline, A. Salinaro, V. K. Ryabchuk and N. Serpone, Int. J. Photoenergy, 2001, 3, 1; (c) G. Delaittre, A. S. Goldmann, J. O. Mueller and C. Barner-Kowollik, Angew. Chem. Int. Ed., 2015, 54, 11388.
- K. K. Oehlenschlaeger, J. O. Mueller, N. B. Heine, M. Glassner, N. K. Guimard, G. Delaittre, F. G. Schmidt and C. Barner-Kowollik, *Angew. Chem. Int. Ed.*, 2013, 52, 762.
- 6 H. Zhou and J. A. Johnson, Angew. Chem., 2013, 125, 2291.
- 7 (a) C. Rodriguez-Emmenegger, C. M. Preuss, B. Yameen, O. Pop-Georgievski, M. Bachmann, J. O. Mueller, M. Bruns, A. S.

Goldmann, M. Bastmeyer and C. Barner-Kowollik, Advice Marine 2013, **25**, 6123; (b) T. Pauloehrl, A. Weller K. 1K. 10ehlenschlaege and C. Barner-Kowollik, *Chem. Sci.*, 2013, **4**, 3503.

- 8 (a) J. E. Elliott and C. N. Bowman, *Macromolecules*, 2001, 34 4642; (b) M.-A. Tehfe, F. Dumur, N. Vilà, B. Graff, C. R. Mayer, I. P. Fouassier, D. Gigmes and J. Lalevée, *Macromol. Rap* Commun., 2013, 34, 1104.
- 9 (a) C. N. LaFratta, J. T. Fourkas, T. Baldacchini and R. A. Farre Angew. Chem. Int. Ed., 2007, 46, 6238; (b) S. Maruo and J. T. Fourkas, Laser & Photon. Rev., 2008, 2, 100; (c) T. G. Leong, L. M. Zarafshar and D. H. Gracias, Small, 2010, 6, 792; (d) M. Malinauskas, M. Farsari, A. Piskarskas and S. Juodkazis, Phys. Rep., 2013, 533, 1; (e) A. S. Quick, H. Rothfuss, A. Welle, L. Richter, J. Fischer, M. Wegener and C. Barner-Kowollik, Ad Funct. Mater., 2014, 3571.
- 10 M. Z. Alam, A. Shibahara, T. Ogata and S. Kurihara, *Polymer* 2011, **52**, 3696.
- E. Blasco, B. V. K. J. Schmidt, C. Barner-Kowollik, M. Piñol and L. Oriol, *Macromolecules*, 2014, 47, 3693.
- 12 J. A. Johnson, J. M. Baskin, C. R. Bertozzi, J. T. Koberstein and N. J. Turro, Chem. Commun., 2008, 3064.
- 13 C. Mengel, W. H. Meyer and G. Wegner, *Macromol. Chem. Phys.*, 2001, **202**, 1138.
- 14 (a) C. Barner-Kowollik, T. P. Davis and M. H. Stenzel, Aust. Chem., 2006, 59, 719; (b) G. Moad, E. Rizzardo and S. H. Thang, Aust. J. Chem., 2012, 65, 985.
- X. Hao, C. Nilsson, M. Jesberger, M. H. Stenzel, E. Malmström, T. P. Davis, E. Östmark and C. Barner-Kowollik, J. Polym. Sci., A: Polym. Chem., 2004, 42, 5877.
- 16 M. Kaupp, T. Tischer, A. F. Hirschbiel, A. P. Vogt, U. Geckle, Trouillet, T. Hofe, M. H. Stenzel and C. Barner-Kowollik, *Macromolecules*, 2013, 46, 6858.
- 17 C. J. Dürr, P. Lederhose, L. Hlalele, D. Abt, A. Kaiser, S. Brandau and C. Barner-Kowollik, *Macromolecules*, 2013, 46, 5915.
- 18 M. Kaupp, A. S. Quick, C. Rodriguez-Emmenegger, A. Welle, Trouillet, O. Pop-Georgievski, M. Wegener and C. Barne Kowollik, Adv. Funct. Mater., 2014, 24, 5649.
- 19 T. Gruendling, M. Kaupp, J. P. Blinco and C. Barner-Kowollik, Macromolecules, 2011, 44, 166.
- H. Chaffey-Millar, M. H. Stenzel, T. P. Davis, M. L. Coote and C. Barner-Kowollik, *Macromolecules*, 2006, **39**, 6406.
- 21 A. S. Goldmann, T. Tischer, L. Barner, M. Bruns and C. Barner-Kowollik, *Biomacromolecules*, 2011, **12**, 1137.

This journal is © The Royal Society of Chemistry 20xx

⁴ | *J. Name.*, 2012, **00**, 1-3