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# A dual crosslinked self-healing system: Supramolecular and covalent network formation of four-arm star polymers



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Diana Döhler<sup>a</sup>, Herwig Peterlik<sup>b</sup>, Wolfgang H. Binder<sup>a,\*</sup>

<sup>a</sup> Chair of Macromolecular Chemistry, Institute of Chemistry, Division of Technical and Macromolecular Chemistry, Faculty of Natural Science II (Chemistry, Physics and Mathematics), Martin-Luther-University Halle-Wittenberg, Von-Danckelmann-Platz 4, Halle D-06120, Germany
 <sup>b</sup> Faculty of Physics, Dynamics of Condensed Systems, University of Vienna, Strudlhofgasse 4, Vienna 1090, Austria

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#### ABSTRACT

Restoration of large volume damage together with mechanical stability of self-healing polymers requires fast and efficient reversible crosslinking processes together with the presence of a static network. We investigate four-arm star polymers as a dual self-healing material, equipped with hydrogen bonding moieties and azide endgroups applicable for crosslinking based on "click" cycloaddition reaction (CuAAC). The concepts takes advantage of additional supramolecular network formation due to supramolecular cluster formation. To this effect four-arm star poly(isobutylene)s were prepared via living carbocationic polymerization (LCCP) in combination with simple endgroup transformation steps and microwave-assisted click-chemistry to introduce thymine moieties as supramolecular tie points. Fourarm star thymine-telechelic PIB was obtained as a tough rubbery material as proven via meltrheology and SAXS measurements with clusters of  $\approx 10$  hydrogen bonding moieties resulting in a selfhealing response at room temperature. To enable the design of a doubly crosslinked self-healing system, four-arm star PIBs bearing an average of 1.7 azide groups and 2.3 thymine endgroups/polymer were crosslinked with a three-arm star alkyne-telechelic PIB. A weakly crosslinked covalent network reinforced by supramolecular hydrogen bonding interactions was obtained in which "click"-crosslinking reduces the number of clustered hydrogen bonds from  $\approx 10$  to  $\approx 8$ . Macroscopic self-healing studies of the double covalent and supramolecular network structure revealed fast and multiple self-healing at 20 °C within 24 h. The now designable four-arm star polymers enabled the design of a highly efficient self-healing system based on double network formation due to "click"-crosslinking and supramolecular cluster formation.

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## 1. Introduction

The development and further improvement of self-healing polymers to effect faster self-healing systems operating at ambient conditions is attracting the interest of many materials scientists [1]. Therefore, fast and efficient crosslinking reactions leading to subsequent network formation to generate complex architectures play a key role in order to impart mechanical stability within a material after the self-healing event [2]. Network formation can be realized via chemical crosslinking based on Diels—Alder (DA) chemistry [3], disulfide exchange reactions [4], curing of epoxides [5], ROMP [1c,d,5a,6] or "click"-type-reactions like the azide/alkyne-"click"-reaction (CuAAC) [7], where the former reactions are exceptionally well-suited for tuning the timescale of the crosslinking reaction [2a,8]. The CuAAC in particular opens suitable pathways for crosslinking approaches not only for the design of self-healing materials [9] but also for the preparation of polymer nanoparticles [10], particle-like structures [11] or cellulose nanoplatelet gels [12]. While using chemical crosslinking concepts often reactive components are applied, which require encapsulation [8a,13] or are stored in an appropriate container within a (polymer) matrix in order to prevent their reaction or degradation before a damage event occurs [14]. However, the aforementioned systems are often just either working at elevated temperatures [15] or can be applied for healing of a single damage event only.

Another self-healing concept not showing these drawbacks is based on dynamic supramolecular network formation [16]



<sup>\*</sup> Corresponding author. Tel.: +49 (0) 345 55 25930. *E-mail address: wolfgang.binder@chemie.uni-halle.de* (W.H. Binder).

applying supramolecular interactions such as hydrogen bonds [16a,b,17], ionomers [18],  $\pi$ - $\pi$ -stacking interactions [19] or metalligand interactions [20] where a multiple self-healing response can be realized via rebonding of supramolecular moieties. One of the first concepts based on hydrogen bonding was reported by Lehn [16b], who introduced the term "dynamers" (dynamic polymers) allowing reversible formation and exchange reactions within a polymeric material. The well known hydrogen bonds based on 2ureido-4[1H]-pyrimidinones [21] provide a good basis for the commercially available self-healing material SupraB<sup>™</sup> [21,22]. Although already several supramolecular polymers find application in self-healing materials, the final supramolecular networks are often soft and not shape-persistent. Therefore the generation of sufficient mechanical stability within such a polymeric material is still challenging. In order to reinforce the mechanical stability either multiphase systems with hard-soft-segments analogous to the creation of thermoplastic elastomers (TPEs) [23] or nanoparticles [24] can be introduced into the polymer. Other strategies rely on the formation of rubber-like self-healing materials [16a,25], where the building blocks themselves show sufficient high mobility and dynamics. We in the past [2c] have investigated bivalent barbiturate-functionalized PIBs resulting in tough rubbery materials with increased thermal stability and self-healing abilities at room temperature due to dynamic supramolecular cluster formation [2b,c,26]. Overall, the generation of newly formed covalent or supramolecular bonds and thus network formation represents a key requirement for a successful healing response and for the restoration of mechanical properties, e.g. based on amphiphilic conetworks (APCN) [27].

To overcome the aforementioned disadvantages of covalent and supramolecular self-healing concepts, we have designed a self-healing system based on double network formation by combining a covalent network together with a supramolecular and therefore multiple self-healing concept based on hydrogen bonding moieties forming supramolecular clusters (see Fig. 1). If now a damage event is occurring the already existing supramolecular aggregates, formed via phase separation effects between the nonpolar polymer backbone and the polar supramolecular moiety will break, resulting in two newly generated surfaces with sticky supramolecular tie points. The now via an additional covalent network crosslinked polymer is reinforced and thus structurally stable, enabling self-healing via reformation of the supramolecular aggregates between the covalent tie points.

To enable a realization of this concept, star polymers functionalized with azide-endgroups and hydrogen bonding moieties simultaneously were prepared in order to introduce both, the covalent tie points (via CuAAC) and the hydrogen bonding moieties acting as the supramolecular (reversible) network. Covalent crosslinking was effected by subsequent mixing with a second component, (a three-arm star alkyne-telechelic polymer) and a copper(I)-catalyst, in turn effecting subsequent covalent network formation via CuAAC.

#### 1.1. Instrumentation

NMR spectra were recorded on a Varian Gemini 2000 (400 MHz) at 27 °C. Deuterated chloroform (CDCl<sub>3</sub>) was used as solvent. All chemical shifts were given in ppm. MestRec-C software (version 4.9.9.6) was used for interpretation of the NMR-spectra. ATR-IR spectra were performed on a Bruker Tensor VERTEX 70 equipped with a Golden Gate Heated Diamond ATR Top-plate. Opus 6.5 was used for analyzing data. Gel permeation chromatography (GPC) measurements were performed on a Viscotek GPCmax VE 2002 from Viscotek™ using a H<sub>HR</sub>H Guard-17369 and a GMH<sub>HR</sub>-N-18055 column in THF at 40 °C and via detection of the refractive index with a VE 3580 RI detector of Viscotek<sup>™</sup>. For external calibration PIB-standards (320 g/mol to 578,000 g/mol) from Viscotek<sup>™</sup> were used. In case of PIBs functionalized with supramolecular moieties GPC spectra were recorded on a GPCmax VE 2001 from Viscotek™ equipped with a column set of a  $H_{HR}$ -H Guard-17369 column, a CLM30111 column and a G2500H<sub>HR</sub>-17354 column in THF (1 mL/ min) at 35 °C. For determination of absolute molecular weights a triple detection array (light scattering, viscosity, refractive index) was applied. Calibration was performed using PS-standards (1000 g/mol to 115,000 g/mol). For evaluation of data OmniSEC software (V 4.5.6) was used. The concentration of all samples was 3 mg/mL and the flow rate was 1 mL/min. Differential scanning calorimetry (DSC) experiments were performed using a DSC 204 F1 Phoenix provided from NETZSCH. In order to investigate the glass transition temperature  $(T_g)$  polymers were first cooled to - 90 °C and then heated up to 160 °C with a heating rate of 10 K min<sup>-1</sup>.  $T_g$ 's were determined upon heating from the amorphous glass state of the polymers to the liquid state as midpoint of a small change within the heat capacity. For analyzing of data Proteus-Thermal Analysis (V 5.2.1) from NETZSCH was applied. Thermogravimetric analysis (TGA) was performed on a NETZSCH TG tarsus 209 instrument. Under a nitrogen atmosphere the sample was heated in a Pt pan over a temperature range of 25 °C up to 800 °C with a heating rate of 10 °C min<sup>-1</sup>. For analyzing of data OriginPro7 was used. Matrixassisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF-MS) experiments were performed on a Bruker Autoflex III system operating in linear mode. For data evaluation flexAnalysis software (version 3.0) was used. Ions were formed by laser desorption (smart beam laser at 355, 532, 808, and  $1064 \pm 6.5$  nm; 3 ns pulse width; up to 2500 Hz repetition rate), accelerated by a voltage of 20 kV, and detected as positive ions. As matrix trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was used dissolved in THF at a concentration of 20 mg mL<sup>-1</sup>. Four-arm star thymine-functionalized PIB and four-



Fig. 1. Concept of a doubly crosslinked self-healing system based on supramolecular and covalent network formation via CuAAC ( $\star \equiv$  Cu(1)-catalyst,  $\bullet \equiv$  supramolecular moiety).

arm star PIB with azide and thymine endgroups as well as lithium trifluoroacetate (LiTFA) were dissolved in THF at a concentration of  $20 \text{ mg mL}^{-1}$ . Solutions of the applied matrix, the polymer, and the salt were mixed in a volume ratio of 25:5:1. Smoothing and baseline subtraction of the recorded MALDI-ToF-MS spectrum was performed using a three point Savitzky–Golav algorithm. *Rheological measurements* were performed on an oscillatory plate rheometer MCR 101 from Anton Paar (Physica). For all measurements a PP08 measuring system (parallel plated, diameter 8 mm) was used. For regulating the sample temperature thermoelectric cooling/heating in a Peltier chamber under dry oxygen was applied. Frequency measurements were performed within the LVE. For evaluation of data the RheoPlus/32 software (V 3.40) and OriginPro7 was used. Small-angle X-ray scattering (SAXS) experiments were performed with Cu-K<sub> $\alpha$ </sub> radiation (wavelength 0.1542 nm) from a microfocus source (Incoatec High Brilliance) using a pinhole camera system (Nanostar, Bruker AXS, equipped with a 2D position sensitive detector, Vantec 2000). SAXS investigations were performed at room temperature (23 °C) in a *q*-range of 0.2–2.8 nm<sup>-1</sup> and the samples were placed between commercial aluminum foils.

#### 1.2. Abbreviations

Living carbocationic polymerization (LCCP), 2,6-di-*tert*-butylpyridine (DtBP), *N*,*N*-dimethylacetamid (DMA), biphenyl tetracumyl chloride (BPTCC), 3-(bromopropoxy)benzene (BPB), isobutylene (IB), poly(isobutylene) (PIB), dichloromethane (DCM), copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC), *N*,*N*-diisopropylethylamine (DIPEA), tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl) methyl]amine (TBTA), small-angle X-ray scattering (SAXS).

### 1.3. Materials

All materials were obtained from Sigma–Aldrich and used without further purification if not mentioned otherwise. *N*-hexane was predried over KOH and freshly distilled over sodium and KOH under a nitrogen atmosphere prior to use. DCM was predried over CaCl<sub>2</sub> and freshly distilled over CaH<sub>2</sub> under nitrogen atmosphere prior to use.

#### 1.4. Synthesis

The synthesis of biphenyl tetracumyl chloride (tetravalent initiator for LCCP) was carried out according to literature [28]. Synthesis of TBTA was done according to Lee et al. [29] Three-arm star alkyne-telechelic PIB was prepared out of trimethylsilyl-protected alkyne-telechelic PIB which was synthesized via LCCP [2a].

# 1.5. General polymerization procedure - synthesis of four-arm star bromide-telechelic PIB (1)

For the polymerization of isobutylene living carbocationic polymerization (LCCP) was used. The synthesis was carried out under a dry atmosphere of argon. A three-necked round-bottom flask equipped with rubber septum, stop cock and mechanical stirrer was heated under vacuo and flushed with argon several times. Dry *n*-hexane and dry DCM (v/v = 40/60) was added to the flask and the solution was started to cool down to  $-70 \,^{\circ}$ C with a methanol cooling bath and liquid nitrogen. During cooling DtBP (0.005 mol L<sup>-1</sup>), DMA (0.005 mol L<sup>-1</sup>) and BPTCC (0.006 mol L<sup>-1</sup>, 80% activity) as initiator dissolved in dry DCM was added at the final temperature. The reaction mixture was stirred at  $-70 \,^{\circ}$ C for 10 minutes before the polymerization was started by the addition

of TiCl<sub>4</sub> (0.100 mol L<sup>-1</sup>). Polymerizations were run for 90 minutes. As quenching agent 3-(bromopropoxy)benzene (BPB, 10 equ. of BPTCC) and a second portion of TiCl<sub>4</sub> (0.112 mol L<sup>-1</sup>) was used to introduce bromine endgroups. Quenching proceeded for 5 h in order to achieve complete functionalization of living chain ends. Therefore isopropyl alcohol and dry ice was used as cooling agent. After warming up to room temperature the solvent was removed in vacuo. The crude polymer was dissolved in *n*-hexane and was precipitated into a ten to fifteen excess of MeOH for three times and dried at high vacuo. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.26 (d, 8H, Ar–*H* of quenching agent, <sup>3</sup>J<sub>H,H</sub> = 8.6 Hz), 7.10–6.88 (m, 6H, Ar–*H* of initiator), 6.82 (d, 8H, Ar–*H* of quenching agent, <sup>3</sup>J<sub>H,H</sub> = 6.4 Hz), 3.59 (t, 8H, CH<sub>2</sub>–Br, <sup>3</sup>J<sub>H,H</sub> = 5.9 Hz), 2.32 (q, 8H, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.1 Hz), 1.42 (s, CH<sub>2</sub> of repetitive unit), 1.11 (s, CH<sub>3</sub> of repetitive unit), 0.80 (s, 24H, CH<sub>3</sub> of initiator part).

#### 1.6. Synthesis of four-arm star azide-telechelic PIB (2)

The synthesis was carried out under a dry atmosphere of nitrogen. In a two-necked flask equipped with magnetic stirring bar, septum, reflux condenser and stop cock PIB 1 (1 equ., 200.0 mg, 24.7 µmol) was dissolved in a 1: 1 mixture of *n*-heptane (10.0 mL) and DMF (10.0 mL). To the reaction mixture sodium azide (40 equ., 64.3 mg, 987.6 µmol) was added and heated up to 90 °C for 65 h. After the reaction mixture cooled down, the *n*-heptane-layer was separated and washed with water (five times 25.0 mL). The organic laver was separated and dried over Na<sub>2</sub>SO<sub>4</sub> and after filtration the solvent was removed in vacuo. The crude polymer was dissolved in *n*-hexane and was precipitated into a ten to fifteen excess of MeOH for three times and dried at high vacuo. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.26 (d, 8H, Ar–H of quenching agent,  ${}^{3}J_{H,H} = 8.6$  Hz), 7.10–6.88 (m, 6H, Ar-H of initiator), 6.81 (d, 8H, Ar-H of quenching agent,  ${}^{3}J_{\text{H.H}} = 8.7$  Hz), 4.03 (t, 8H, O–CH<sub>2</sub>,  ${}^{3}J_{\text{H,H}} = 5.9$  Hz), 3.51 (t, 8H,  $CH_2-N_3$ ,  ${}^{3}J_{H,H} = 6.6 \text{ Hz}$ ), 2.04 (q, 8H,  $CH_2-CH_2-CH_2$ ,  ${}^{3}J_{H,H} = 6.2 \text{ Hz}$ ), 1.42 (s,  $CH_2$  of repetitive unit), 1.11 (s,  $CH_3$  of repetitive unit), 0.80 (s, 24H,  $CH_3$  of initiator part).

#### 1.7. Synthesis of four-arm star thymine-functionalized PIB (3)

The synthesis was carried out under a dry atmosphere of argon. In a one-necked flask equipped with magnetic stirring bar PIB 2 (1.0 equ., 300.0 mg, 38.5 µmol) was dissolved in toluene (5.0 mL). Isopropanol (2.0 mL), water (2.0 mL), DIPEA (8.0 equ., 55.1 µL, 308.0 µmol) and TBTA (0.2 equ., 4.1 mg, 7.7 µmol) were added and the reaction mixture was purged with argon for 40 minutes. CuBr(PPh<sub>3</sub>)<sub>3</sub> (0.2 equ., 7.1 mg, 7.7 µmol) was added followed by purging with argon for 5 minutes and then alkyne-functionalized thymine (8.0 equ., 51.0 mg, 308.0 µmol) was added to the reaction mixture. After a final purging with argon for 5 minutes the flask was sealed with a rubber septum and placed in a microwave oven. Irradiation conditions: 100 W, 90 °C,  $\Delta T = 10$  °C, SPS method ("pulse - no pulse - pulse"), 32 h. After the reaction was finished  $(R_f (CHCl_3) = 0.05)$  the crude reaction mixture was diluted with chloroform (50.0 mL). The organic layer was washed with saturated NH<sub>4</sub>Cl-solution (two times 50.0 mL) and with water (50.0 mL). The organic layer was separated and dried over Na<sub>2</sub>SO<sub>4</sub> and after filtration the solvent was removed in vacuo. The crude polymer was purified via column chromatography (SiO<sub>2</sub>, *n*-hexane/CHCl<sub>3</sub> (v:v = 1:2) followed by CHCl<sub>3</sub>, CHCl<sub>3</sub>/MeOH (v:v = 100:2) and  $CHCl_3/MeOH$  (v:v = 100:3)). The so obtained polymer was finally purified via dialysis in THF and dried at high vacuo. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.15 (s, 4H, N-H), 7.69 (s, 4H, CH of thymine endgroup), 7.33 (s, 4H, CH of triazole ring),7.26 (d, 8H, Ar-H of quenching agent,  ${}^{3}J_{H,H} = 8.6 \text{ Hz}$ ), 7.10–6.87 (m, 6H, Ar–H of initiator), 6.78 (d, 8H, Ar–*H* of quenching agent,  ${}^{3}J_{H,H} = 8.7$  Hz), 4.94 (s, 8H, C–CH<sub>2</sub>–N), 4.57 (t, 8H, O–CH<sub>2</sub>,  ${}^{3}J_{H,H} = 7.0$  Hz), 3.97 (t, 8H, CH<sub>2</sub>–CH<sub>2</sub>–N,  ${}^{3}J_{H,H} = 5.6$  Hz), 2.38 (q, 8H, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>,  ${}^{3}J_{H,H} = 6.3$  Hz), 1.41 (s, CH<sub>2</sub> of repetitive unit), 1.11 (s, CH<sub>3</sub> of repetitive unit), 0.79 (s, 24H, CH<sub>3</sub> of initiator part).

# 1.8. Synthesis of four-arm star PIBs with azide and thymine endgroups (4a, 4b)

The synthesis was carried out under a dry atmosphere of argon. In a one-necked flask equipped with magnetic stirring bar PIB 2 (1.0 equ., 300.0 mg, 38.5 µmol) was dissolved in toluene (5.0 mL). Isopropanol (2.0 mL), water (2.0 mL), DIPEA (8.0 equ., 55.1 µL, 308.0 µmol) and TBTA (0.2 equ., 4.1 mg, 7.7 µmol) were added and the reaction mixture was purged with argon for 40 minutes. CuBr(PPh<sub>3</sub>)<sub>3</sub> (0.2 equ., 7.1 mg, 7.7 µmol) was added followed by purging with argon for 5 min and then alkyne-functionalized thymine (1.1 equ., 7.0 mg, 42.4 µmol) was added to the reaction mixture. After a final purging with argon for 5 minutes the flask was sealed with a rubber septum and placed in a microwave oven. Irradiation conditions: 100 W, 90 °C,  $\Delta T = 10$  °C, SPS method ("pulse – no pulse – pulse"), 17 h. After irradiation the crude reaction mixture was diluted with chloroform (20.0 mL). The organic layer was washed with saturated NH<sub>4</sub>Cl-solution (two times 25.0 mL) and with water (25.0 mL). The organic layer was separated and dried over Na<sub>2</sub>SO<sub>4</sub> and after filtration the solvent was removed in vacuo. The crude polymer was purified via column chromatography (SiO<sub>2</sub>, solvent gradient: n-hexane/CHCl<sub>3</sub> (v:v = 1:1), CHCl<sub>3</sub>,  $CHCl_3/MeOH (v:v = 100:1), CHCl_3/MeOH (v:v = 100:2) and CHCl_3/$ MeOH (v:v = 100:5)). Thus, two polymer fractions ( $R_{f1} = 0.08 - 0.36$ ,  $R_{f2} = 0.03 - 0.13$ ) were obtained and were finally purified separately via dialysis in THF and dried at high vacuo. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.01 (s, N–H), 7.68 (s, CH of thymine endgroup), 7.33 (s, CH of triazole ringe), 7.26 (d, 8H, Ar-H of quenching agent,  ${}^{3}J_{\text{H,H}} = 8.6 \text{ Hz}$ ), 7.09–6.88 (m, 6H, Ar–H of initiator), 6.78 (d, 8H, Ar–*H* of quenching agent,  ${}^{3}J_{H,H} = 8.7$  Hz), 4.94 (s, C–CH<sub>2</sub>–N), 4.57 (t, O-CH<sub>2</sub> of thymine endgroup,  ${}^{3}J_{\text{H,H}} = 7.0 \text{ Hz}$ ), 4.03 (t, O-CH<sub>2</sub> of azide endgroup,  ${}^{3}J_{\text{H,H}} = 6.1 \text{ Hz}$ ), 3.97 (t, CH<sub>2</sub>-CH<sub>2</sub>-N of thymine endgroup,  ${}^{3}J_{\text{H,H}} = 5.7 \text{ Hz}$ ), 3.51 (t, CH<sub>2</sub>-CH<sub>2</sub>-N of azide endgroup,  ${}^{3}J_{\rm H,H} = 6.6 \,\rm{Hz}$ ), 2.38 (q, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub> of thymine endgroup,  ${}^{3}J_{\rm H,H}$  = 6.3 Hz), 2.04 (q, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub> of azide endgroup,  ${}^{3}J_{\rm H,H} = 6.3$  Hz), 1.41 (s, CH<sub>2</sub> of repetitive unit), 1.11 (s, CH<sub>3</sub> of repetitive unit), 0.79 (s, 24H,  $CH_3$  of initiator part).

#### 2. General part

#### 2.1. Synthesis and characterization of four-arm star PIBs

We have planned the self-healing system based on supramolecular and covalent network formation of star polymers based on the preparation of four-arm star polymers (poly(isobutylene)s (PIBs)) bearing thymine- and azide-endgroups, the latter enabling covalent crosslinking via a CuAAC process in combination with a three-arm star alkyne-telechelic polymer (see Fig. 1). The basic architecture is generated via the four-arm star PIB (**2**), able to be subsequently functionalized via "click"-based chemistry. Four-arm star bromide-telechelic PIB **1** was prepared via living carbocationic polymerization (LCCP, see Scheme 1) using biphenyl tetracumyl chloride (BPTCC) as initiator and 3-(bromopropoxy)benzene (BPB) as quencher [28,30].

In order to achieve the desired architecture as well as complete endgroup functionalization the polymerization was conducted for 90 minutes followed by a quenching period of 5 h combined with repeated addition of TiCl<sub>4</sub> to force the equilibrium towards fourarm star bromide-telechelic PIB **1** [28,30]. Complete endgroup functionalization of PIB **1** was proven via <sup>1</sup>H-NMR-analysis as the resonances of the six aromatic protons of the quenching unit and the resonances of the methyl groups of the initiator part (24 protons) are in relation of one to four (see Fig. S1 Supporting Information).

For the preparation of four-arm star azide-telechelic PIB **2** a simple endgroup transformation methodology using sodium azide and heating in a 1: 1 mixture of *n*-heptane and DMF at 90 °C for 65 h was applied (see Scheme 1). In order to synthesize four-arm star thymine-telechelic PIB **3** via a microwave-assisted copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) reaction [26a] (see Scheme 2), polymer **2** was treated with alkyne-functionalized thymine in a solvent mixture of toluene, water and isopropanol. Additionally, *N*,*N*-diisopropylethylamine (DIPEA, 8.0 equ.), tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA, 0.2 equ.) and CuBr(PPh<sub>3</sub>)<sub>3</sub> (0.2 equ.) were added and reacted under microwave irradiation.

The desired polymer **3** was obtained via column chromatography followed by dialysis. In a similar manner four-arm star PIBs with both, azide- and thymine-endgroups 4a and 4b were synthesized (see Scheme 2). The already optimized reaction conditions of the microwave-assisted CuAAC reaction were adapted and the reaction time was decreased from 32 to 17 h with respect to the functional endgroups of polymer 2. Furthermore, the amount of alkyne-functionalized thymine was reduced from 8.0 to 1.1 equivalents. Following the aforementioned work-up strategy two polymers 4a and 4b with different endgroup compositions were separated via column chromatography and further cleaned up via dialysis. The complete endgroup transformation within the fourarm star azide-telechelic PIB 2 and thymine-telechelic PIB 3 after click-reaction as well as the endgroup composition of partially thymine-functionalized PIBs 4a and 4b was investigated and proven via FTIR- and <sup>1</sup>H-NMR-spectroscopy (see Fig. 2a and b).

According to the FTIR-spectra displayed in Fig. 2a the stretching vibration of the azide group is visible at 2097 cm<sup>-1</sup> in case of polymer **3**. Consequently, no azide group was detected in PIB **3** after complete conversion of all azide groups with alkyne-functionalized thymine. Instead, the carbonyl stretching vibration of the attached thymine moiety was observed at 1690 cm<sup>-1</sup>. The <sup>1</sup>H-NMR-analysis of the four-arm star azide-telechelic PIB **2** clearly revealed a shift of the resonances of the CH<sub>2</sub>-groups of the quencher part to higher field in comparison to four-arm star bromide-telechelic PIB **1** (e.g. from 2.32 ppm to 2.04 ppm for CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), followed by an



Scheme 1. Synthetic route towards four-arm star bromide- 1 and azide-telechelic 2 PIBs.



**Scheme 2**. Synthetic route towards four-arm star thymine-telechelic PIB **3** and four-arm star PIBs with azide and thymine endgroups **4a** and **4b** via copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) of four-arm star azide-telechelic PIB **2** with alkyne-functionalized thymine (labeling (a, b, c, ...) refers to the assignments in Fig. 2).

even more prominent low-field shift (e.g. from 2.04 ppm (b') to 2.38 ppm (b) for CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>) for four-arm star thyminetelechelic PIB **3**. Additionally, the resonances of the amine proton (g) and the CH proton of the thymine group (f) as well as the resonance of the click proton (d) were observed indicating a successful click reaction and a complete functionalization with the supramolecular moieties (see Fig. 2b).

The FTIR-spectra of PIBs **4a** and **4b** after partial functionalization with thymine groups after the click reaction show both, the

stretching vibration of the azide group and the carbonyl stretching vibration of the supramolecular moiety proving qualitatively the presence of both desired endgroups. A quantitative analysis of the endgroup composition within polymers **4a** and **4b** was accomplished via NMR-analysis.The resonances of the CH<sub>2</sub>-moieties of the quencher part bearing either the azide group or the thymine endgroup were used for the quantification, obtaining 0.7 azide groups per four-arm star PIB **4a** and 1.7 azide groups per four-arm star polymer **4b** (see Fig. 2b and Table 1).



Fig. 2. a) FTIR-spectra of four-arm star PIBs 2, 3, 4a and 4b, b) <sup>1</sup>H-NMR-spectra of four-arm star PIBs 2, 3, 4a and 4b (for assignment (a, b, c, d, e) see Scheme 2).

Entry	Polymer	M <sub>n, theor.</sub> [g/mol]	$M_{n, NMR}^{a}$ [g/mol]	$M_{n, \text{ GPC}} [g/\text{mol}]$	$M_w/M_n^b$	Amount of azide endgroups <sup>c</sup>	$T_g [^{\circ}C]$	$T_{\text{decay}}^{d} [^{\circ}C]$
1	PIB-Br <sub>4</sub> 1	8000	7400	8500	1.55	_	-58.2	325.0
2	PIB-(N <sub>3</sub> ) <sub>4</sub> <b>2</b>	8000	7500	8400	1.52	4.0	-59.7	301.4
3	PIB-thymine <sub>4</sub> <b>3</b>	8700	8100	9300	1.48	0.0	-59.0	360.3
4	PIB-thymine <sub>3</sub> -(N <sub>3</sub> ) <b>4a</b>	8500	8000	11,300	1.76	0.7	-59.8	350.4
5	PIB-thymine <sub>2</sub> -(N <sub>3</sub> ) <sub>2</sub> 4b	8300	8800	10.500	1.98	1.7	-58.5	295.2

Results for the synthesis of four-arm star PIBs 1–4b, molecular weight data, polydispersities, glass transition temperatures ( $T_g$ ), decomposition temperatures and azide endgroups of four-arm star PIBs 2–4b.

<sup>a</sup> Determined via <sup>1</sup>H-NMR-spectroscopy: integration of resonances of initiator at 0.79 ppm–0.80 ppm and of polymer at 1.11 ppm or at 1.40 ppm – 1.42 ppm.

<sup>b</sup> Determined via GPC.

Table 1

<sup>c</sup> Determined via <sup>1</sup>H-NMR-spectroscopy.

<sup>d</sup> Determined at 5% weight loss.

Furthermore, polymers **3** and **4b** were additionally characterized via MALDI-ToF mass spectrometry (see Figs. S2 and S3 Supporting Information). In case of four-arm star thyminetelechelic PIB **3** one series with a distance of 56.1 Da correlating to one isobutylene unit was observed matching to the sodium adduct of the desired structure, with all four labile hydrogen atoms of the NH groups within the thymine moiety exchanged against sodium-ions. In contrast, for polymer **4b** a sodium and a lithium series were detected whereas both series reflect the structure of the polymer with one labile NH proton exchanged either against sodium- or lithium-ions.

Table 1 summarizes the molecular weight data, polydispersities, glass transition temperatures ( $T_g$ ), and the decomposition temperatures of four-arm star PIBs **1–4b**.

Molecular weights determined via GPC and NMR are in good agreement with the theoretical molecular weight projected to 8000 g/mol, corresponding to 2000 g/mol per polymer arm. The obtained polydispersities indicate the living character of the polymerization. In case of polymers **4a** and **4b** containing the different endgroups a slight increase in the molecular weight as well as in the polydispersity was observed, which can be attributed to the superposition of several molecular weight distributions. The glass transition temperature of all prepared polymers is in the range of -58.0 °C to -60.0 °C, thus contributing to their high diffusion mobility under ambient conditions; with thermogravimetric analysis proving their thermal stability up to 295 °C (see Table 1).

#### 2.2. Macroscopic self-healing studies

The dynamics and the self-healing ability of four-arm star thymine-telechelic PIB **3** were investigated via melt rheology [2a,2c], performing frequency sweep measurements at 20 °C and 40 °C over a broad frequency range (see Fig. 3a and b).

At 20 °C a prominent rubbery plateau with a plateau modulus  $G_N^0$  of 1.1 E6 Pa at high frequencies as well as an extremely high viscosity n of 5.6 E7 Pa·s at low frequency was observed (see Fig. 3a). Both phenomena can only be explained by the presence of a supramolecular network due to the formation of supramolecular junction points built up by thymine moieties. The approximate lifetime of the supramolecular aggregates was estimated via the crossover time of G' and G'' according to Feldman et al. [31] Thus, a bond lifetime of around 67 s was calculated indicating open supramolecular aggregates due to the dissociation of hydrogen bonds at low frequencies and a closed state of supramolecular clusters at higher frequencies, explaining the rubber-like behavior of the fourarm star thymine-telechelic PIB 3 at room temperature. Similar observations were reported by Herbst et al. [2c] who investigated bivalent barbiturate-functionalized PIBs showing self-healing due to the ability of rearrangement within the dynamic supramolecular aggregates.

In contrast, the bond lifetime of the junction points within polymer **3** decreased from 67 s at 20 °C to approximately 1 s at 40 °C. Terminal flow at low frequencies was observed by the determined slopes of *G'* and *G''* in this frequency range (see Fig. 3b). Nevertheless, even at this moderately increased temperature, higher values for the plateau modulus ( $G_N^0 = 9.8$  E5 Pa) and for the viscosity ( $\eta = 1.2$  E6 Pa·s) were recorded than ever reported for linear high molecular weight PIB [32].

All results obtained by frequency and thus time dependent oscillatory rheology measurements support the presence of a supramolecular network due to phase separation effects between the non-polar polymer backbone and the polar thymine moieties, resulting in supramolecular cluster formation as already described



Fig. 3. Frequency sweeps of four-arm star thymine-telechelic PIB 3 a) at 20 °C, b) at 40 °C and c) macroscopic self-healing experiments of a cut specimen at 20 °C (upper part) and 40 °C (lower part).



**Fig. 4.** a) Frequency sweep of four-arm star PIB **4b** at 40 °C. Rheological investigation of an equimolar polymer mixture with respect to the azide-/alkyne-ratio composed of threearm star alkyne-telechelic PIB and four-arm star PIB **4b**: b)development of the loss factor *tan*(δ) during the progress of the CuAAC at 40 °C, c) frequency sweep at 40 °C after CuAAC.

by us previously [2c,26b] for the bivalent polymers. Consequently, macroscopic self-healing studies were performed to investigate the self-healing performance of four-arm star thymine-telechelic PIB **3**. Polymer films with a thickness of around 1 mm were cut with a razor blade. After bringing the freshly generated and sticky surfaces into contact again photos were taken in defined time intervals (see photos in Fig. 3c). At 20 °C complete self-healing was achieved after 72 h whereas the intersection of the former cut is still partially visible. On the contrary, at 40 °C complete closure of the damaged region was observed within 24 h due to the higher mobility at this temperature as evidenced by the frequency sweep measurement.

For the creation of a self-healing system based on double network formation the four-arm star PIB **4b** bearing 1.7 azide groups and 2.3 thymine endgroups per one molecule was cross-linked with a three-arm star alkyne-telechelic PIB (the final product being referred as *crosslinked* **4b**) thus combining a covalent but single-time crosslinking concept with the supramolecular and thus multiple self-healing concept via hydrogen bonding interactions. Therefore, an equimolar polymer mixture with respect to the azide-/alkyne-ratio was prepared by simple mixing and subsequently investigated via melt rheology before adding a Cu(I)-catalyst required for covalent network formation via click reaction (see Fig. 4a).

A frequency sweep measurement of the four-arm star PIB 4b at 40 °C demonstrated the presence of supramolecular aggregation although just 2.3 thymine moieties per molecule are attached (see Fig. 4a). In contrast, the investigation of a neat equimolar polymer mixture (with respect to the endgroups) composed of the four-arm star polymer 4b and the three-arm star alkyne-telechelic PIB before "click"-crosslinking revealed a liquid-like behavior as the loss modulus is larger than the storage modulus over the whole investigated frequency range (see Fig. S4 Supporting Information). "Click"-crosslinking was started by addition of CuBr(PPh<sub>3</sub>)<sub>3</sub> to the polymer mixture at 40 °C. The reaction was monitored over a timeframe of 70 h where every 10 minutes a frequency sweep measurement was performed. During the first 600 minutes the change of the loss factor  $tan(\delta)$  with time at 10 1/s was investigated (see Fig. 4b) showing a decrease from 2.2 to 1.8 whereas the temporal changes became less prominent with increasing time. After 70 h the value of the loss factor  $tan(\delta)$  became less than one indicating the formation of covalent network points. In order to further force the crosslinking process via click chemistry to completeness a temperature sweep measurement from (-10 °C) to 150 °C with a heating rate of 1 °C/min was conducted. Afterwards the frequency measurement at 40 °C was repeated displaying a crossover of G'and G'' at around 10 1/s as well as a rough approximation of the slopes of G' and G'' vs. angular frequency  $\omega$  (see Fig. 4c).

Furthermore, an increase in *G*' of around 190% and in *G*" of around 50% was noticed (see Fig. S4 Supporting Information for comparison). Thus, the formation of a weakly crosslinked covalent network reinforced by supramolecular hydrogen bonding interaction can be proven. In contrast, crosslinking experiments of polymer **4a** bearing only 0.7 azide groups per four-arm star polymer **4a** with a three-arm star alkyne-telechelic PIB was not sufficient to form even a weakly crosslinked covalent network.

Macroscopic self-healing studies of the final covalent and supramolecular network composed of polymer **4b** and three-arm star alkyne-telechelic PIB (crosslinked **4b**) reveal fast selfhealing at room temperature within 24 h, whereas already after 2 h a significant reduction of the depth of the former cut was observed (see Fig. 5). Moreover this self-healing process could be repeated several times due to the presence of supramolecular interactions proving the reliability of our double crosslinked selfhealing system.

#### 2.3. SAXS investigations of supramolecular polymer networks

In order to further confirm supramolecular aggregation providing the basis for the self-healing response of the polymers SAXS measurements were conducted. Therefore, PIB **3** as well as the polymer mixture composed of polymer **4b** and three-arm star alkyne-telechelic PIB were investigated in a q-range of 0.2–2.8 nm<sup>-1</sup> at room temperature (see Fig. 6a) and the so obtained results are summarized in Table 2.

SAXS data were analyzed assuming spheres with a Gaussian size distribution with a structure factor derived from a hard sphere model (Percus–Yevick model as described in literature [2c,26b] and in the Supporting Information). The strongest difference is observed in the hard sphere volume fraction, which decreases from 0.39 for the four-arm star thymine-telechelic PIB **3** to 0.23 for the crosslinked **4b**. As the hard sphere volume fraction is a measure for the probability to find a neighboring supramolecular cluster, crosslinking reduces this probability and thus the



Fig. 5. Macroscopic self-healing experiments of a cut specimen of crosslinked 4b after CuAAC at 20  $^\circ\text{C}$ .



Fig. 6. a) SAXS profiles of four-arm star thymine-telechelic PIB 3 (black dotted curve) and of crosslinked 4b (grey dotted curve) after covalent network formation via CuAAC. Fitting of SAXS data (Gaussian distribution) of four-arm star thymine-telechelic PIB 3 (grey solid curve) and of crosslinked 4b (black solid curve). b) proposed structure of the obtained double network (crosslinked 4b) composed of a weakly crosslinked covalent polymer network reinforced by supramolecular aggregation of thymine moieties.

cluster-cluster aggregation. Additionally, the typical distance of the supramolecular clusters (twice the value of the hard-sphereradius) is  $d = 2 \cdot R_2 = 6.7$  nm for PIB **3** and decreases to d = 6.3 nm for the crosslinked 4b. From the hard sphere radius, the aggregation number N of the respective system (representing the amount of hydrogen bonding moieties within supramolecular clusters) was calculated, which decreases from  $\approx 10$  to  $\approx 8$  from PIB 3 to the crosslinked 4b. Thus, "click" crosslinking reduces the number of clustered hydrogen bonds implying that four four-arm star polymers **4b** are forming one supramolecular cluster, connected to the three-arm star alkyne-telechelic PIB via triazole-ring formation due to click-chemistry (see Fig. 6b). Furthermore, it is proposed that not all alkyne-groups will participate in the CuAAC reaction due to their restricted and additionally decreasing mobility during the progress of the click-reaction as well as due to the presence of supramolecular tie points.

### 3. Summary

We have investigated multivalent star-shaped polymers which can form reversible as well as irreversible crosslinking points aiming at the design of a doubly crosslinked self-healing system based on two separate networks: one via supramolecular clustering of hydrogen bonds, the second via covalent "click"-crosslinking,

 Table 2

 SAXS results of PIB 3, and of the crosslinked 4b after covalent "click" crosslinking via CuAAC.

Entry	Sample	Hard sphere radius <i>R</i> 2 <sup>a</sup> [nm]	Hard sphere volume fraction	Aggregation number N <sup>b</sup>
1	PIB-thymine <sub>4</sub> <b>3</b>	3.33	0.39	≈ 10
2	crosslinked <b>4b</b>	3.15	0.23	≈ 8

<sup>a</sup> SAXS-data were fitted and further analyzed assuming spheres with a Gaussian size distribution with a structure factor from a hard sphere model according to Percus–Yevick (PY model, for more information see Supporting Information) [26b,33].

 $^{b}\,$  Calculated according to equation 1: N  $\,=\,(4\pi R_{2}^{3}\rho N_{A})/(3M)$  (eq. 1).

plications acting under ambient conditions. To this effect, we have synthesized four-arm star bromide-telechelic PIBs via living carbocationic polymerization (LCCP), which were further converted to four-arm star azide-telechelic PIBs via simple endgroup transformation. Furthermore, four-arm star thymine-telechelic PIB as well as four-arm star polymers carrying both, azide-moieties (for covalent network formation) and thymine-moieties (acting as supramolecular tie points) were prepared via microwave-assisted CuAAC reaction. All prepared polymers were completely characterized via <sup>1</sup>H-NMR-investigations, FTIR-investigations and MALDI-ToF mass spectrometry in case of four-arm star supramolecular polymers. Four-arm star thymine-telechelic PIB 3 was investigated via melt-rheology showing a prominent rubbery plateau with a plateau modulus  $G_N^0$  of 1.1 E6 Pa as well as an extremely high viscosity  $\eta$  of 5.6 E7 Pa · s at 20 °C which is attributed to supramolecular cluster formation due to phase separation effects between the polar thymine endgroups and the nonpolar polymer backbone. Supramolecular network formation was additionally proven via SAXS investigations revealing a strong scattering peak at 0.97 nm<sup>-1</sup> corresponding to a distance of supramolecular clusters built up by  $\approx$  10 thymine moieties of 6.5 nm in real space. Macroscopic selfhealing studies were performed by simple cutting of polymer films. observing a complete self-healing of the four-arm star thyminetelechelic PIB 3 after 72 h at 20 °C and after 24 h at 40 °C, respectively. For the creation of the dual crosslinked self-healing system the four-arm star PIB 4b bearing 1.7 azide groups and 2.3 thymine endgroups per one molecule, was crosslinked with a three-arm star alkyne-telechelic PIB at 40 °C, catalyzed by Cu(I)-addition. After 70 h a weakly crosslinked covalent network reinforced by supramolecular hydrogen bonding interaction was obtained as proven via melt rheology and SAXS measurements: in rheology the decrease of the loss factor  $tan(\delta)$  as well as an increase in G' of around 190% and in G" of around 50% in comparison to the neat polymer mixture clearly indicates the formation of the covalent network, whereas SAXS proves the presence of supramolecular clusters. Macroscopic self-healing studies of the so obtained double covalent and supramolecular network structure revealed fast and

thus generating polymeric networks for multiple self-healing ap-

multiple self-healing at 20 °C within 24 h, whereas already after 2 h a significant reduction of the depth of the former cut was observed. Thus, the here presented four-arm star polymers bearing hydrogen bonding moieties enabled the design of a doubly crosslinked self-healing system based on two separate networks due to "click" crosslinking and supramolecular cluster formation.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.01.073.

#### References

[1] (a) Binder WH. Self-healing polymers. From principles to applications. Weinheim: Wiley-VCH; 2013. p. 440;

(b) Michael P, Döhler D, Binder WH. Improving autonomous self healing via combined chemical/physical principles. Polymer 2015;69:216–27.

(c) Blaiszik BJ, Kramer SLB, Olugebefola SC, Moore JS, Sottos NR, White SR. Self-healing polymers and composites. Annu Rev Mater Res 2010;40(1): 179–211;

(d) White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, et al. Autonomic healing of polymer composites. Nature 2001;409(6822):794–7 (e) Akbarzadeh J, Puchegger S, Stojanovic A, Kirchner HOK, Binder WH, Bernstorff S, et al. Timescales of self-healing in human bone tissue and polymeric ionic liquids. Bioinspired Biomim Nanobiomat 2014;3(3):123–30.

(a) Döhler D, Michael P, Binder WH. Autocatalysis in the room temperature copper(I)-catalyzed alkyne-azide "click" cycloaddition of multivalent poly(-acrylate)s and poly(isobutylene)s. Macromolecules 2012;45(8):3335-45;
(b) Herbst F, Döhler D, Michael P, Binder WH. Self-healing polymers via supramolecular forces. Macromol Rapid Commun 2013;34(3):203-20;
(c) Herbst F, Seiffert S, Binder WH. Dynamic supramolecular poly(isobutylene) s for self-healing materials. Polym Chem 2012;3(11):3084-92.

(a) Hizal G, Tunca U, Sanyal A. Discrete macromolecular constructs via the Diels-Alder "click" reaction. J Polym Sci Part A Polym Chem 2011;49(19): 4103-20;

(b) Chen X, Dam MA, Ono K, Mal A, Shen H, Nutt SR, et al. A thermally remendable cross-linked polymeric material. Science 2002;295:1698–702;
(c) Chen X, Wudl F, Mal AK, Shen H, Nutt SR. New thermally remendable highly cross-linked polymeric materials. Macromolecules 2003;36(6):

1802–7; (d) Liu Y-L, Chen Y-W. Thermally reversible cross-linked polyamides with high toughness and self-repairing ability from maleimide- and furanfunctionalized aromatic polyamides. Macromol Chem Phys 2007;208(2):

224–32: (e) Murphy EB, Bolanos E, Schaffner-Hamann C, Wudl F, Nutt SR, Auad ML. Synthesis and characterization of a single-component thermally remendable polymer network: staudinger and stille revisited. Macromolecules 2008;41(14):5203–9:

(f) Park JS, Takahashi K, Guo Z, Wang Y, Bolanos E, Hamann-Schaffner C, et al. Towards development of a self-healing composite using a mendable polymer and resistive heating. J Compos Mater 2008;42(26):2869–81.

- [4] Amamoto Y, Kamada J, Otsuka H, Takahara A, Matyjaszewski K. Repeatable photoinduced self-healing of covalently cross-linked polymers through reshuffling of trithiocarbonate units. Angew Chem Int Ed 2011;50(7):1660–3.
- [5] (a) Blaiszik BJ, Caruso MM, McIlroy DA, Moore JS, White SR, Sottos NR. Microcapsules filled with reactive solutions for self-healing materials. Polymer 2009;50(4):990-7;

(b) Guadagno L, Longo P, Raimondo M, Naddeo C, Mariconda A, Sorrentino A, et al. Cure behavior and mechanical properties of structural self-healing epoxy resins. J Polym Sci Part B Polym Phys 2010;48(23):2413–23;

(c) Guadagno L, Raimondo M, Naddeo C, Longo P, Mariconda A. Self-healing materials for structural applications. Polym Eng Sci 2014;54(4):777–84;

(d) McIlroy DA, Blaiszik BJ, Caruso MM, White SR, Moore JS, Sottos NR. Microencapsulation of a reactive liquid-phase amine for self-healing epoxy composites. Macromolecules 2010;43(4):1855–9;

(e) Montarnal D, Tournilhac F, Hidalgo M, Leibler L. Epoxy-based networks combining chemical and supramolecular hydrogen-bonding crosslinks. J Polym Sci Part A Polym Chem 2010;48(5):1133–41;

(f) Yuan L, Liang G, Xie J, Li L, Guo J. Preparation and characterization of poly(urea-formaldehyde) microcapsules filled with epoxy resins. Polymer 2006;47:5338–49;

(g) Yuan YC, Rong MZ, Zhang MQ, Yang GC, Zhao JQ. Self-healing of fatigue

crack in epoxy materials with epoxy/mercaptan system. Express Polym Lett 2011;5(1):47–59.

[6] (a) Brown EN, Kessler MR, Sottos NR, White SR. In situ poly(ureaformaldehyde) microencapsulation of dicyclopentadiene. J Microencapsul 2003;20(6):719-30;

(b) Jones AS, Rule JD, Moore JS, White SR, Sottos NR. Catalyst morphology and dissolution kinetics of self-healing polymers. Chem Mater 2006;18(5): 1312–7;

(c) Kessler MR, Sottos NR, White SR. Self-healing structural composite materials. Compos Part A Appl S 2003;34(8):743-53;

(d) Toohey KS, Sottos NR, Lewis JA, Moore JS, White SR. Self-healing materials with microvascular networks. Nat Mater 2007;6(8):581-5;

(e) Jackson AC, Bartelt JA, Marczewski K, Sottos NR, Braun PV. Silica-protected micron and sub-micron capsules and particles for self-healing at the micro-scale. Macromol Rapid Commun 2011;32(1):82–7;

(f) Brown EN, White SR, Sottos NR. Microcapsule induces toughening in a selfhealing polymer composite. J Mater Sci 2004;39:1703-10;

(g) Blaiszik BJ, Baginska M, White SR, Sottos NR. Autonomic recovery of fiber/ matrix interfacial bond strength in a model composite. Adv Funct Mater 2010;20(20):3547–54.

[7] (a) Binder WH, Sachsenhofer R. 'Click' chemistry in polymer and materials science. Macromol Rapid Commun 2007;28(1):15–54;

(b) Binder WH, Sachsenhofer R. 'Click' chemistry in polymer and material science: an update. Macromol Rapid Commun 2008;29(12–13):952–81;

(c) Kolb HC, Finn MG, Sharpless KB. Click chemistry: diverse chemical function from a few good reactions. Angew Chem Int Ed 2001;40(11):2004–21;

(d) Tillet G, Boutevin B, Ameduri B. Chemical reactions of polymer crosslinking and post-crosslinking at room and medium temperature. Prog Polym Sci 2011;36(2):191–217.

(e) Vestberg R, Malkoch M, Kade M, Wu P, Fokin VV, Sharpless KB, et al. Role of architecture and molecular weight in the formation of tailor-made ultrathin multilayers using dendritic macromolecules and click chemistry. J Polym Sci Part A Polym Chem 2007;45(14):2835–46;

(f) Iha RK, Wooley KL, Nyström AM, Burke DJ, Kade MJ, Hawker CJ. Applications of orthogonal "click" chemistries in the synthesis of functional soft materials. Chem Rev 2009;109(11):5620-86;

(g) Malkoch M, Schleicher K, Drockenmuller E, Hawker CJ, Russell TP, Wu P, et al. Structurally diverse dendritic libraries: a highly efficient functionalization approach using click chemistry. Macromolecules 2005;38(9):3663–78.

- [8] (a) Gragert M, Schunack M, Binder WH. Azide/alkyne-"click"-Reactions of encapsulated reagents: toward self-healing materials. Macromol Rapid Commun 2011;32(5):419-25;
   (b) Schunack M, Gragert M, Döhler D, Michael P, Binder WH. Low-temperature Cu(1)-catalyzed "click" reactions for self-healing polymers. Macromol Chem Phys 2012;213(2):205-14.
- (a) Sheng X, Mauldin TC, Kessler MR. Kinetics of bulk azide/alkyne "click" polymerization. J Polym Sci Part A Polym Chem 2010;48(18):4093–102;
   (b) Sheng X, Rock DM, Mauldin TC, Kessler MR. Evaluation of different catalyst systems for bulk polymerization through "click" chemistry. Polymer 2011;52(20):4435–41.
- (a) de Luzuriaga AR, Ormategui N, Grande HJ, Odriozola I, Pomposo JA, Loinaz I. Intramolecular click cycloaddition: an efficient room-temperature route towards bioconjugable polymeric nanoparticles. Macromol Rapid Commun 2008;29(12–13):1156–60;
   (b) van der Ende AE, Harrell J, Sathiyakumar V, Meschievitz M, Katz J,

(b) van der Ende AE, Harrell J, Sathiyakumar V, Meschievitz M, Katz J, Adcock K, et al. "Click" reactions: novel chemistries for forming well-defined polyester nanoparticles. Macromolecules 2010;43(13):5665–71.

- [11] Cengiz H, Aydogan B, Ates S, Acikalin E, Yagci Y. Intramolecular cross-linking of polymers using difunctional acetylenes via click chemistry. Des Monomers Polym 2011;14:69–78.
- [12] Filpponen I, Argyropoulos DS. Regular linking of cellulose nanocrystals via click chemistry: synthesis and formation of cellulose nanoplatelet gels. Biomacromolecules 2010;11(4):1060–6.
- [13] Zhao Y, Döhler D, Lv L-P, Binder WH, Landfester K, Crespy D. Facile phaseseparation approach to encapsulate functionalized polymers in core-shell nanoparticles. Macromol Chem Phys 2014;215(2):198–204.
- [14] White SR, Moore JS, Sottos NR, Krull BP, Santa Cruz WA, Gergely RCR. Restoration of large damage volumes in polymers. Science 2014;344(6184): 620–3.

[15] (a) Ossipov DA, Hilborn J. Poly(vinyl alcohol)-based hydrogels formed by "Click chemistry". Macromolecules 2006;39(5):1709–18;
(b) Liu J, Jiang X, Xu L, Wang X, Hennink WE, Zhuo R. Novel reductionresponsive cross-linked polyethylenimine derivatives by click chemistry for nonviral gene delivery. Bioconjug Chem 2010;21(10):1827–35;
(c) Malkoch M, Vestberg R, Gupta N, Mespouille L, Dubois P, Mason AF, et al.

Synthesis of well-defined hydrogel networks using click chemistry. Chem Commun 2006;26:2774–6;

(d) Liu SQ, Ee PLR, Ke CY, Hedrick JL, Yang YY. Biodegradable poly(ethylene glycol)-peptide hydrogels with well-defined structure and properties for cell delivery. Biomaterials 2009;30(8):1453–61

(e) Crescenzi V, Cornelio L, Di Meo C, Nardecchia S, Lamanna R. Novel hydrogels via click chemistry: synthesis and potential biomedical applications. Biomacromolecules 2007;8(6):1844–50;

(f) Huerta-Angeles G, Šmejkalová D, Chládková D, Ehlová T, Buffa R, Velebný V. Synthesis of highly substituted amide hyaluronan derivatives with tailored degree of substitution and their crosslinking via click chemistry. Carbohyd Polym 2011;84(4):1293-300;

(g) Testa G, Di Meo C, Nardecchia S, Capitani D, Mannina L, Lamanna R, et al. Influence of dialkyne structure on the properties of new click-gels based on hyaluronic acid. Int J Pharm 2009;378:86–92;

(h) Díaz DD, Rajagopal K, Strable E, Schneider J, Finn MG. "Click" chemistry in a supramolecular environment: stabilization of organogels by copper(I)catalyzed azide-alkyne [3 + 2] cycloaddition. J Am Chem Soc 2006;128(18): 6056–7.

[16] (a) Cordier P, Tournilhac F, Soulie-Ziakovic C, Leibler L. Self-healing and thermoreversible rubber from supramolecular assembly. Nature 2008;451: 977–80;

(b) Lehn J-M. Dynamers: dynamic molecular and supramolecular polymers. Prog Polym Sci 2005;30:814–31;

(c) Wojtecki RJ, Meador MA, Rowan SJ. Using the dynamic bond to access macroscopically responsive structurally dynamic polymers. Nat Mater 2011;10(1):14–27.

[17] (a) Courtois J, Baroudi I, Nouvel N, Degrandi E, Pensec S, Ducouret G, et al. Supramolecular soft adhesive materials. Adv Funct Mater 2010;20(11): 1803–11;

(b) Müller M, Dardin A, Seidel U, Balsamo V, Iván B, Spiess HW, et al. Junction dynamics in telechelic hydrogen bonded polyisobutylene networks. Macro-molecules 1996;29(7):2577–83;

(c) Sivakova S, Bohnsack DA, Mackay ME, Suwanmala P, Rowan SJ. Utilization of a combination of weak hydrogen-bonding interactions and phase segregation to yield highly thermosensitive supramolecular polymers. J Am Chem Soc 2005;127:18202–11;

(d) Hackethal K, Döhler D, Tanner S, Binder WH. Introducing polar monomers into polyisobutylene by living cationic polymerization: structural and kinetic effects. Macromolecules 2010:43(4):1761–70.

[18] (a) Döhler D, Zare P, Binder WH. Hyperbranched polyisobutylenes for selfhealing polymers. Polym Chem 2014;5(3):992–1000;

(b) Stojanovic A, Appiah C, Döhler D, Akbarzadeh J, Zare P, Peterlik H, et al. Designing melt flow of poly(isobutylene)-based ionic liquids. J Mater Chem A 2013;1:12159–69;

(c) Zare P, Stojanovic A, Herbst F, Akbarzadeh J, Peterlik H, Binder WH. Hierarchically nanostructured polyisobutylene-based ionic liquids. Macromolecules 2012;45(4):2074–84;

(d) Kalista SJ, Pflug JR, Varley RJ. Effect of ionic content on ballistic self-healing in EMAA copolymers and ionomers. Polym Chem 2013;4(18):4910–26;

(e) Rahman MA, Penco M, Peroni I, Ramorino G, Grande AM, Di Landro L. Selfrepairing systems based on ionomers and epoxidized natural rubber blends. ACS Appl Mater Interfaces 2011;3(12):4865–74;

(f) Rahman MA, Spagnoli G, Grande AM, Di Landro L. Role of phase morphology on the damage initiated self-healing behavior of ionomer blends. Macromol Mater Eng 2013;298(12):1350–64.

[19] (a) Burattini S, Colquhoun HM, Greenland BW, Hayes W. A novel self-healing supramolecular polymer system. Faraday Discuss 2009;143:251–64;
(b) Burattini S, Greenland BW, Chappell D, Colquhoun HM, Hayes W. Healable polymeric materials: a tutorial review. Chem Soc Rev 2010;39(6):1973–85;
(c) Burattini S, Greenland BW, Hermida Merino D, Weng W, Seppala J, Colquhoun HM, et al. A healable supramolecular polymer blend based on aromatic *p-p*- stacking and hydrogen-bonding interactions. J Am Chem Soc 2010;132(34):12051–8;
(d) Greenland BW, Bird MB, Burattini S, Cramer R, O'Reilly RK, Patterson JP,

et al. Mutual binding of polymer end-groups by complementary p-p-stacking: a molecular "Roman Handshake". Chem Commun 2013;49(5):454–6.

- [20] Burnworth M, Tang L, Kumpfer JR, Duncan AJ, Beyer FL, Fiore GL, et al. Optically healable supramolecular polymers. Nature 2011;472:334–7.
- [21] Bosman AW, Sijbesma RP, Meijer EW. Supramolecular polymers at work. Mater Today 2004;7(4):34-9.
- [22] www.suprapolix.com.

[23] (a) Chen Y, Kushner AM, Williams GA, Guan Z. Multiphase design of autonomic self-healing thermoplastic elastomers. Nat Chem 2012;4:467–72;
 (b) Holden G, Kricheldorf HR, Quirk RP. In: Thermoplastic elastomers. 3rd ed. Hanser; 2004;

(c) Hentschel J, Kushner AM, Ziller J, Guan Z. Self-healing supramolecular block copolymers. Angew Chem Int Ed 2012;51(42):10561–5.

[24] Chen Y, Guan Z. Self-assembly of core-shell nanoparticles for self-healing materials. Polym Chem 2013;4:4885–9.

 (a) Stukalin EB, Cai L-H, Kumar NA, Leibler L, Rubinstein M. Self-healing of unentangled polymer networks with reversible bonds. Macromolecules 2013;46(18):755-41;
 (b) Tournilhac F, Cordier P, Montarnal D, Soulié-Ziakovic C, Leibler L, Self-

healing supramolecular retworks. Macromol Symp 2010;291–292(1):84–8.
 [26] (a) Herbst F, Schröter K, Gunkel I, Gröger S, Thurn-Albrecht T, Balbach J, et al.

Aggregation and chain dynamics in supramolecular polymers by dynamic rheology: cluster formation and self-aggregation. Macromolecules 2010;43(23):10006–16;

(b) Yan T, Schröter K, Herbst F, Binder WH, Thurn-Albrecht T. Nanostructure and rheology of hydrogen-bonding telechelic polymers in the melt: from micellar liquids and solids to supramolecular gels. Macromolecules 2014;47(6):2122–30.

[27] (a) Kali G, Vavra S, László K, Iván B. Thermally responsive amphiphilic conetworks and gels based on poly(N-isopropylacrylamide) and polyisobutylene. Macromolecules 2013;46(13):5337–44;

(b) Domján A, Mezey P, Varga J. Behavior of the interphase region of an amphiphilic polymer conetwork swollen in polar and nonpolar solvent. Macromolecules 2012;45(2):1037–40;

(c) Kali G, Georgiou TK, Iván B, Patrickios CS. Anionic amphiphilic end-linked conetworks by the combination of quasiliving carbocationic and group transfer polymerizations. J Polym Sci Part A Polym Chem 2009;47(17): 4289–301;

(d) Toman L, Janata M, Spěváček J, Brus J, Sikora A, Horský J, et al. Amphiphilic conetworks. IV. Poly(methacrylic acid)-l-polyisobutylene and poly(acrylic acid)-l-polyisobutylene based hydrogels prepared by two-step polymer procedure. New pH responsive conetworks. J Polym Sci Part A Polym Chem 2009;47(5):1284–91;

(e) Erdodi G, Kennedy JP. Amphiphilic conetworks: definition, synthesis, applications. Prog Polym Sci 2006;31(1):1–18.

- [28] Taylor SJ, Storey RF. Tetrafunctional initiators for cationic polymerization of olefins. J Polym Sci Part A Polym Chem 2004;42(23):5942–53.
- [29] Lee B-Y, Park SR, Jeon HB, Kim KS. A new solvent system for efficient synthesis of 1,2,3-triazoles. Tetrahedron Lett 2006;47(29):5105–9.
- (a) Morgan DL, Martinez-Castro N, Storey RF. End-quenching of TiCl<sub>4</sub>-catalyzed quasiliving polyisobutylene with alkoxybenzenes for direct chain end functionalization. Macromolecules 2010;43(21):8724–40.
  (b) Morgan DL, Storey RF. End-quenching of quasi-living isobutylene polymerizations with alkoxybenzene compounds. Macromolecules 2009;42(18): 6844–7.
- [31] Feldman KE, Kade MJ, Meijer EW, Hawker CJ, Kramer EJ. Model transient networks from strongly hydrogen-bonded polymers. Macromolecules 2009;42(22):9072–81.
- (a) Aharoni SM. Correlations between chain parameters and the plateau modulus of polymers. Macromolecules 1986;19(2):426–34;
   (b) Fetters LJ, Lohse DJ, Richter D, Witten TA, Zirkel A. Connection between polymer molecular weight, density, chain dimensions, and melt viscoelastic properties. Macromolecules 1994;27(17):4639–47.
- [33] (a) Kinning DJ, Thomas EL. Hard-sphere interactions between spherical domains in diblock copolymers. Macromolecules 1984;17(9):1712–8;
  (b) Schwab M, Stühn B. Thermotropic transition from a state of liquid order to a macrolattice in asymmetric diblock copolymers. Phys Rev Lett 1996;76(6): 924–7.