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

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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 $20^{\circ} \mathrm{C}$ 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

[^0]like the azide/alkyne-"click"-reaction (CuAAC) [7], where the former reactions are exceptionally well-suited for tuning the timescale of the crosslinking reaction $[2 a, 8]$. 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]
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 2-ureido- $4[1 \mathrm{H}]$-pyrimidinones [21] provide a good basis for the commercially available self-healing material SupraB ${ }^{\text {TM }}$ [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 $27^{\circ} \mathrm{C}$. Deuterated chloroform $\left(\mathrm{CDCl}_{3}\right)$ 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 ${ }^{\mathrm{TM}}$ using a $\mathrm{H}_{\mathrm{HR}} \mathrm{H}$ Guard-17369 and a $\mathrm{GMH}_{\mathrm{HR}}-\mathrm{N}-18055$ column in THF at $40^{\circ} \mathrm{C}$ and via detection of the refractive index with a VE 3580 RI detector of Viscotek ${ }^{\mathrm{TM}}$. For external calibration PIB-standards ( $320 \mathrm{~g} / \mathrm{mol}$ to $578,000 \mathrm{~g} / \mathrm{mol}$ ) from Viscotek ${ }^{\mathrm{TM}}$ were used. In case of PIBs functionalized with supramolecular moieties GPC spectra were recorded on a GPCmax VE 2001 from Viscotek ${ }^{\mathrm{TM}}$ equipped with a column set of a $\mathrm{H}_{\mathrm{HR}}-\mathrm{H}$ Guard- 17369 column, a CLM30111 column and a G2500H $\mathrm{HR}^{-17354}$ column in THF ( $1 \mathrm{~mL} /$ min ) at $35^{\circ} \mathrm{C}$. For determination of absolute molecular weights a triple detection array (light scattering, viscosity, refractive index) was applied. Calibration was performed using PS-standards (1000 $\mathrm{g} / \mathrm{mol}$ to $115,000 \mathrm{~g} / \mathrm{mol}$ ). For evaluation of data OmniSEC software (V 4.5.6) was used. The concentration of all samples was $3 \mathrm{mg} / \mathrm{mL}$ and the flow rate was $1 \mathrm{~mL} / \mathrm{min}$. 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 $-90^{\circ} \mathrm{C}$ and then heated up to $160^{\circ} \mathrm{C}$ with a heating rate of $10 \mathrm{~K} \mathrm{~min}^{-1} . T_{g}$ '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 $25^{\circ} \mathrm{C}$ up to $800^{\circ} \mathrm{C}$ with a heating rate of $10^{\circ} \mathrm{C} \mathrm{min}^{-1}$. 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 $1064 \pm 6.5 \mathrm{~nm}$; 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 $20 \mathrm{mg} \mathrm{mL}^{-1}$. 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 (文 $\equiv \mathrm{Cu}(\mathrm{I})-\mathrm{catalyst}$, $\equiv \operatorname{supramolecular~moiety).~}$
arm star PIB with azide and thymine endgroups as well as lithium trifluoroacetate (LiTFA) were dissolved in THF at a concentration of $20 \mathrm{mg} \mathrm{mL}^{-1}$. 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-Golay 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 $\mathrm{Cu}-\mathrm{K}_{\alpha}$ 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 $\left(23^{\circ} \mathrm{C}\right)$ in a $q$-range of $0.2-2.8 \mathrm{~nm}^{-1}$ 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-1H-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 $\mathrm{CaCl}_{2}$ and freshly distilled over $\mathrm{CaH}_{2}$ 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 trimethylsilylprotected 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 $\operatorname{DCM}(v / v=40 / 60)$ was added to the flask and the solution was started to cool down to $-70^{\circ} \mathrm{C}$ with a methanol cooling bath and liquid nitrogen. During cooling DtBP ( $0.005 \mathrm{~mol} \mathrm{~L}^{-1}$ ), DMA ( $0.005 \mathrm{~mol} \mathrm{~L}^{-1}$ ) and BPTCC ( $0.006 \mathrm{~mol} \mathrm{~L}^{-1}$, $80 \%$ activity) as initiator dissolved in dry DCM was added and condensed and dried isobutylene ( $1.000 \mathrm{~mol} \mathrm{~L}^{-1}$ ) was added at the final temperature. The reaction mixture was stirred at $-70^{\circ} \mathrm{C}$ for 10 minutes before the polymerization was started by the addition
of $\mathrm{TiCl}_{4}\left(0.100 \mathrm{~mol} \mathrm{~L}^{-1}\right)$. Polymerizations were run for 90 minutes. As quenching agent 3-(bromopropoxy)benzene (BPB, 10 equ. of BPTCC) and a second portion of $\mathrm{TiCl}_{4}\left(0.112 \mathrm{~mol} \mathrm{~L}^{-1}\right)$ 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. ${ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right): \delta 7.26(\mathrm{~d}, 8 \mathrm{H}, \mathrm{Ar}-\mathrm{H}$ of quenching agent, $\left.{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.6 \mathrm{~Hz}\right), 7.10-6.88(\mathrm{~m}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{H}$ of initiator), $6.82\left(\mathrm{~d}, 8 \mathrm{H}, \mathrm{Ar}-\mathrm{H}\right.$ of quenching agent, $\left.{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.6 \mathrm{~Hz}\right), 4.09$ $\left(\mathrm{t}, 8 \mathrm{H}, \mathrm{O}-\mathrm{CH}_{2},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=6.4 \mathrm{~Hz}\right), 3.59\left(\mathrm{t}, 8 \mathrm{H}, \mathrm{CH}_{2}-\mathrm{Br},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=5.9 \mathrm{~Hz}\right)$, $2.32\left(\mathrm{q}, 8 \mathrm{H}, \mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{CH}_{2},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=6.1 \mathrm{~Hz}\right), 1.42\left(\mathrm{~s}, \mathrm{CH}_{2}\right.$ of repetitive unit), $1.11\left(\mathrm{~s}, \mathrm{CH}_{3}\right.$ of repetitive unit), $0.80\left(\mathrm{~s}, 24 \mathrm{H}, \mathrm{CH}_{3}\right.$ 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 , $24.7 \mu \mathrm{~mol})$ 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., $64.3 \mathrm{mg}, 987.6 \mu \mathrm{~mol}$ ) was added and heated up to $90^{\circ} \mathrm{C}$ 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 layer was separated and dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ 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. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right)$ : $\delta 7.26\left(\mathrm{~d}, 8 \mathrm{H}, \mathrm{Ar}-\mathrm{H}\right.$ of quenching agent, $\left.{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.6 \mathrm{~Hz}\right), 7.10-6.88$ $(\mathrm{m}, 6 \mathrm{H}, \mathrm{Ar}-H$ of initiator), $6.81(\mathrm{~d}, 8 \mathrm{H}, \mathrm{Ar}-H$ of quenching agent, $\left.{ }^{3} J_{\mathrm{H}, \mathrm{H}}=8.7 \mathrm{~Hz}\right), 4.03\left(\mathrm{t}, 8 \mathrm{H}, \mathrm{O}-\mathrm{CH}_{2},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=5.9 \mathrm{~Hz}\right), 3.51(\mathrm{t}, 8 \mathrm{H}$, $\left.\mathrm{CH}_{2}-\mathrm{N}_{3},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=6.6 \mathrm{~Hz}\right), 2.04\left(\mathrm{q}, 8 \mathrm{H}, \mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{CH}_{2},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=6.2 \mathrm{~Hz}\right)$, 1.42 ( $\mathrm{s}, \mathrm{CH}_{2}$ of repetitive unit), 1.11 ( $\mathrm{s}, \mathrm{CH}_{3}$ of repetitive unit), 0.80 ( s , $24 \mathrm{H}, \mathrm{CH}_{3}$ 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., $300.0 \mathrm{mg}, 38.5 \mu \mathrm{~mol}$ ) was dissolved in toluene ( 5.0 mL ). Isopropanol ( 2.0 mL ), water ( 2.0 mL ), DIPEA ( 8.0 equ., $55.1 \mu \mathrm{~L}$, $308.0 \mu \mathrm{~mol}$ ) and TBTA ( 0.2 equ., $4.1 \mathrm{mg}, 7.7 \mu \mathrm{~mol}$ ) were added and the reaction mixture was purged with argon for 40 minutes. $\mathrm{CuBr}\left(\mathrm{PPh}_{3}\right)_{3}(0.2$ equ., $7.1 \mathrm{mg}, 7.7 \mu \mathrm{~mol})$ was added followed by purging with argon for 5 minutes and then alkyne-functionalized thymine ( 8.0 equ., $51.0 \mathrm{mg}, 308.0 \mu \mathrm{~mol}$ ) 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: $100 \mathrm{~W}, 90^{\circ} \mathrm{C}, \Delta T=10^{\circ} \mathrm{C}$, SPS method ("pulse - no pulse - pulse"), 32 h . After the reaction was finished $\left(\mathrm{R}_{\mathrm{f}}\left(\mathrm{CHCl}_{3}\right)=0.05\right)$ the crude reaction mixture was diluted with chloroform ( 50.0 mL ). The organic layer was washed with saturated $\mathrm{NH}_{4} \mathrm{Cl}$-solution (two times 50.0 mL ) and with water ( 50.0 mL ). The organic layer was separated and dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and after filtration the solvent was removed in vacuo. The crude polymer was purified via column chromatography $\left(\mathrm{SiO}_{2}, n\right.$-hexane $/ \mathrm{CHCl}_{3}$ ( $\mathrm{v}: \mathrm{v}=1: 2$ ) followed by $\mathrm{CHCl}_{3}, \mathrm{CHCl}_{3} / \mathrm{MeOH}(\mathrm{v}: \mathrm{v}=100: 2$ ) and $\mathrm{CHCl}_{3} / \mathrm{MeOH}(\mathrm{v}: \mathrm{v}=100: 3)$ ). The so obtained polymer was finally purified via dialysis in THF and dried at high vacuo. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right.$, 400 MHz ): $\delta 8.15(\mathrm{~s}, 4 \mathrm{H}, \mathrm{N}-H), 7.69(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}$ of thymine endgroup), 7.33 (s, 4H, CH of triazole ring), 7.26 ( $\mathrm{d}, 8 \mathrm{H}, \mathrm{Ar}-\mathrm{H}$ of quenching agent, $\left.{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.6 \mathrm{~Hz}\right), 7.10-6.87(\mathrm{~m}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{H}$ of
initiator), $6.78\left(\mathrm{~d}, 8 \mathrm{H}, \mathrm{Ar}-\mathrm{H}\right.$ of quenching agent, $\left.{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.7 \mathrm{~Hz}\right), 4.94$ $\left(\mathrm{s}, 8 \mathrm{H}, \mathrm{C}-\mathrm{CH}_{2}-\mathrm{N}\right), 4.57\left(\mathrm{t}, 8 \mathrm{H}, \mathrm{O}-\mathrm{CH}_{2},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=7.0 \mathrm{~Hz}\right), 3.97(\mathrm{t}, 8 \mathrm{H}$, $\left.\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{N},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=5.6 \mathrm{~Hz}\right), 2.38\left(\mathrm{q}, 8 \mathrm{H}, \mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{CH}_{2}\right.$, $\left.{ }^{3} J_{\mathrm{H}, \mathrm{H}}=6.3 \mathrm{~Hz}\right), 1.41\left(\mathrm{~s}, \mathrm{CH}_{2}\right.$ of repetitive unit), $1.11\left(\mathrm{~s}, \mathrm{CH}_{3}\right.$ of repetitive unit), 0.79 (s, 24H, $\mathrm{CH}_{3}$ 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., $300.0 \mathrm{mg}, 38.5 \mu \mathrm{~mol}$ ) was dissolved in toluene ( 5.0 mL ). Isopropanol ( 2.0 mL ), water ( 2.0 mL ), DIPEA ( 8.0 equ., $55.1 \mu \mathrm{~L}$, $308.0 \mu \mathrm{~mol}$ ) and TBTA ( 0.2 equ., $4.1 \mathrm{mg}, 7.7 \mu \mathrm{~mol}$ ) were added and the reaction mixture was purged with argon for 40 minutes. $\mathrm{CuBr}\left(\mathrm{PPh}_{3}\right)_{3}(0.2$ equ., $7.1 \mathrm{mg}, 7.7 \mu \mathrm{~mol})$ was added followed by purging with argon for 5 min and then alkyne-functionalized thymine ( 1.1 equ., $7.0 \mathrm{mg}, 42.4 \mu \mathrm{~mol}$ ) 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: $100 \mathrm{~W}, 90^{\circ} \mathrm{C}, \Delta T=10^{\circ} \mathrm{C}$, 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 $\mathrm{NH}_{4} \mathrm{Cl}$-solution (two times 25.0 mL ) and with water ( 25.0 mL ). The organic layer was separated and dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and after filtration the solvent was removed in vacuo. The crude polymer was purified via column chromatography $\left(\mathrm{SiO}_{2}\right.$, solvent gradient: $n$-hexane/ $\mathrm{CHCl}_{3}(\mathrm{v}: \mathrm{v}=1: 1), \mathrm{CHCl}_{3}$, $\mathrm{CHCl}_{3} / \mathrm{MeOH}(\mathrm{v}: \mathrm{v}=100: 1), \mathrm{CHCl}_{3} / \mathrm{MeOH}\left(\mathrm{v}: \mathrm{v}=100: 2\right.$ ) and $\mathrm{CHCl}_{3} /$ $\mathrm{MeOH}(\mathrm{v}: \mathrm{v}=100: 5)$ ). Thus, two polymer fractions ( $\mathrm{R}_{\mathrm{f} 1}=0.08-0.36$, $\mathrm{R}_{\mathrm{f} 2}=0.03-0.13$ ) were obtained and were finally purified separately via dialysis in THF and dried at high vacuo. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right.$, 400 MHz ): $\delta 8.01$ (s, N-H), 7.68 ( $\mathrm{s}, \mathrm{CH}$ of thymine endgroup), 7.33 (s, CH of triazole ringe), 7.26 ( $\mathrm{d}, 8 \mathrm{H}, \mathrm{Ar}-\mathrm{H}$ of quenching agent, $\left.{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.6 \mathrm{~Hz}\right), 7.09-6.88(\mathrm{~m}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{H}$ of initiator), $6.78(\mathrm{~d}, 8 \mathrm{H}$, $\mathrm{Ar}-\mathrm{H}$ of quenching agent, $\left.{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.7 \mathrm{~Hz}\right), 4.94\left(\mathrm{~s}, \mathrm{C}-\mathrm{CH}_{2}-\mathrm{N}\right), 4.57(\mathrm{t}$, $\mathrm{O}-\mathrm{CH}_{2}$ of thymine endgroup, $\left.{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=7.0 \mathrm{~Hz}\right), 4.03\left(\mathrm{t}, \mathrm{O}-\mathrm{CH}_{2}\right.$ of azide endgroup, ${ }^{3}{ }_{\mathrm{J}, \mathrm{H}}=6.1 \mathrm{~Hz}$ ), $3.97\left(\mathrm{t}, \mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{N}\right.$ of thymine endgroup, $\left.{ }^{3} J_{\mathrm{H}, \mathrm{H}}=5.7 \mathrm{~Hz}\right)$, $3.51\left(\mathrm{t}, \mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{N}\right.$ of azide endgroup, $\left.{ }^{3} J_{\mathrm{H}, \mathrm{H}}=6.6 \mathrm{~Hz}\right), 2.38\left(\mathrm{q}, \mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{CH}_{2}\right.$ of thymine endgroup, $\left.{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=6.3 \mathrm{~Hz}\right), 2.04\left(\mathrm{q}, \mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{CH}_{2}\right.$ of azide endgroup, $\left.{ }^{3} J_{\mathrm{H}, \mathrm{H}}=6.3 \mathrm{~Hz}\right), 1.41\left(\mathrm{~s}, \mathrm{CH}_{2}\right.$ of repetitive unit), $1.11\left(\mathrm{~s}, \mathrm{CH}_{3}\right.$ of repetitive unit), 0.79 ( $\mathrm{s}, 24 \mathrm{H}, \mathrm{CH}_{3}$ 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 $\mathrm{TiCl}_{4}$ to force the equilibrium towards fourarm star bromide-telechelic PIB 1 [28,30]. Complete endgroup functionalization of PIB 1 was proven via ${ }^{1} \mathrm{H}$-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 $90^{\circ} \mathrm{C}$ 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-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA, 0.2 equ.) and $\mathrm{CuBr}\left(\mathrm{PPh}_{3}\right)_{3}$ ( 0.2 equ.) were added and reacted under microwave irradiation.

The desired polymer $\mathbf{3}$ was obtained via column chromatography followed by dialysis. In a similar manner four-arm star PIBs with both, azide- and thymine-endgroups $\mathbf{4 a}$ and $\mathbf{4 b}$ 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 $\mathbf{4 a}$ and $\mathbf{4 b}$ was investigated and proven via FTIR- and ${ }^{1} \mathrm{H}$-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 $2097 \mathrm{~cm}^{-1}$ 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 $1690 \mathrm{~cm}^{-1}$. The ${ }^{1} \mathrm{H}-\mathrm{NMR}$-analysis of the four-arm star azide-telechelic PIB 2 clearly revealed a shift of the resonances of the $\mathrm{CH}_{2}$-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 $\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{CH}_{2}$ ), followed by an


Scheme 1. Synthetic route towards four-arm star bromide- $\mathbf{1}$ and azide-telechelic $\mathbf{2}$ PIBs.


Scheme 2. Synthetic route towards four-arm star thymine-telechelic PIB $\mathbf{3}$ and four-arm star PIBs with azide and thymine endgroups $\mathbf{4 a}$ and $\mathbf{4 b}$ via copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) of four-arm star azide-telechelic PIB 2 with alkyne-functionalized thymine (labeling ( $a, b, c, \ldots$ ) refers to the assignments in Fig. 2).
even more prominent low-field shift (e.g. from $2.04 \mathrm{ppm}\left(b^{\prime}\right)$ to $2.38 \mathrm{ppm}(b)$ for $\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{CH}_{2}$ ) 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 $\mathbf{4 a}$ and $\mathbf{4 b}$ 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 $\mathbf{4 a}$ and $\mathbf{4 b}$ was accomplished via NMR-analysis.The resonances of the $\mathrm{CH}_{2}$-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 $\mathbf{4 a}$ and 1.7 azide groups per four-arm star polymer $\mathbf{4 b}$ (see Fig. 2b and Table 1).


Fig. 2. a) FTIR-spectra of four-arm star PIBs $\mathbf{2 , 3}, \mathbf{4 a}$ and $\mathbf{4 b}, \mathbf{b}$ ) ${ }^{1}$ H-NMR-spectra of four-arm star PIBs $\mathbf{2}, \mathbf{3}, \mathbf{4} \mathbf{a}$ and $\mathbf{4 b}$ (for assignment ( $a, b, \mathbf{c}, \mathrm{~d}, \mathrm{e}$ ) see Scheme 2 ).

Table 1
Results for the synthesis of four-arm star PIBs $\mathbf{1 - 4 b}$, molecular weight data, polydispersities, glass transition temperatures ( $T_{g}$ ), decomposition temperatures and azide endgroups of four-arm star PIBs 2-4b.

| Entry | Polymer | $M_{n, \text { theor. }}[\mathrm{g} / \mathrm{mol}]$ | $M_{n, \mathrm{NMR}^{\text {a }}}[\mathrm{g} / \mathrm{mol}]$ | $M_{n, \mathrm{GPC}}[\mathrm{g} / \mathrm{mol}]$ | $\mathrm{M}_{\mathrm{w}} / \mathrm{M}_{\mathrm{n}}{ }^{\text {b }}$ | Amount of azide endgroups ${ }^{\text {c }}$ | $T_{g}\left[{ }^{\circ} \mathrm{C}\right]$ | $T_{\text {decay }}{ }^{\text {d }}\left[{ }^{\circ} \mathrm{C}\right]$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | PIB- $\mathrm{Br}_{4} 1$ | 8000 | 7400 | 8500 | 1.55 | - | -58.2 | 325.0 |
| 2 | PIB-( $\left.\mathrm{N}_{3}\right)_{4} 2$ | 8000 | 7500 | 8400 | 1.52 | 4.0 | -59.7 | 301.4 |
| 3 | PIB-thymine ${ }_{4} 3$ | 8700 | 8100 | 9300 | 1.48 | 0.0 | -59.0 | 360.3 |
| 4 | PIB-thymine ${ }_{3}-\left(\mathrm{N}_{3}\right) \mathbf{4 a}$ | 8500 | 8000 | 11,300 | 1.76 | 0.7 | -59.8 | 350.4 |
| 5 | PIB-thymine ${ }_{2}-\left(\mathrm{N}_{3}\right)_{2} \mathbf{4 b}$ | 8300 | 8800 | 10,500 | 1.98 | 1.7 | -58.5 | 295.2 |

${ }^{\text {a }}$ Determined via ${ }^{1} \mathrm{H}$-NMR-spectroscopy: integration of resonances of initiator at $0.79 \mathrm{ppm}-0.80 \mathrm{ppm}$ and of polymer at 1.11 ppm or at $1.40 \mathrm{ppm}-1.42 \mathrm{ppm}$.
${ }^{\mathrm{b}}$ Determined via GPC.
${ }^{\text {c }}$ Determined via ${ }^{1} \mathrm{H}$-NMR-spectroscopy.
${ }^{\text {d }}$ Determined at $5 \%$ weight loss.

Furthermore, polymers $\mathbf{3}$ and $\mathbf{4 b}$ 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 $\mathbf{4} \mathbf{b}$ 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 so-dium- 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 $\mathbf{1 - 4 b}$.

Molecular weights determined via GPC and NMR are in good agreement with the theoretical molecular weight projected to $8000 \mathrm{~g} / \mathrm{mol}$, corresponding to $2000 \mathrm{~g} / \mathrm{mol}$ per polymer arm. The obtained polydispersities indicate the living character of the polymerization. In case of polymers $\mathbf{4 a}$ and $\mathbf{4 b}$ 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 $-58.0^{\circ} \mathrm{C}$ to $-60.0^{\circ} \mathrm{C}$, thus contributing to their high diffusion mobility under ambient conditions; with thermogravimetric analysis proving their thermal stability up to $295^{\circ} \mathrm{C}$ (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 $20^{\circ} \mathrm{C}$ and $40^{\circ} \mathrm{C}$ over a broad frequency range (see Fig. 3 a and b ).

At $20^{\circ} \mathrm{C}$ a prominent rubbery plateau with a plateau modulus $G_{N}^{0}$ of 1.1 E 6 Pa at high frequencies as well as an extremely high viscosity $\eta$ of $5.6 \mathrm{E} 7 \mathrm{~Pa} \cdot \mathrm{~s}$ 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 $G^{\prime}$ and $G^{\prime \prime}$ 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 $\mathbf{3}$ decreased from 67 s at $20^{\circ} \mathrm{C}$ to approximately 1 s at $40^{\circ} \mathrm{C}$. Terminal flow at low frequencies was observed by the determined slopes of $G^{\prime}$ and $G^{\prime \prime}$ in this frequency range (see Fig. 3b). Nevertheless, even at this moderately increased temperature, higher values for the plateau modulus ( $G_{N}^{0}=9.8 \mathrm{E} 5 \mathrm{~Pa}$ ) and for the viscosity ( $\eta=1.2 \mathrm{E} 6 \mathrm{~Pa} \cdot \mathrm{~s}$ ) 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

 $40^{\circ} \mathrm{C}$ (lower part).


Fig. 4. a) Frequency sweep of four-arm star PIB $\mathbf{4 b}$ at $40^{\circ}$. 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 $\mathbf{4 b}$ : b)development of the loss factor $\tan (\delta)$ during the progress of the CuAAC at $40^{\circ} \mathrm{C}$, $\mathbf{c}$ ) frequency sweep at $40^{\circ} \mathrm{C}$ 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 $20^{\circ} \mathrm{C}$ complete self-healing was achieved after 72 h whereas the intersection of the former cut is still partially visible. On the contrary, at $40^{\circ} \mathrm{C}$ 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 $\mathbf{4} \mathbf{b}$ bearing 1.7 azide groups and 2.3 thymine endgroups per one molecule was crosslinked with a three-arm star alkyne-telechelic PIB (the final product being referred as crosslinked $\mathbf{4 b}$ ) 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 $\mathrm{Cu}(\mathrm{I})$ catalyst required for covalent network formation via click reaction (see Fig. 4a).

A frequency sweep measurement of the four-arm star PIB $\mathbf{4 b}$ at $40^{\circ} \mathrm{C}$ 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 $\mathbf{4 b}$ 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 $\mathrm{CuBr}\left(\mathrm{PPh}_{3}\right)_{3}$ to the polymer mixture at $40^{\circ} \mathrm{C}$. 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 $101 / \mathrm{s}$ 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 $\left(-10^{\circ} \mathrm{C}\right)$ to $150^{\circ} \mathrm{C}$ with a heating rate of $1{ }^{\circ} \mathrm{C} / \mathrm{min}$ was conducted. Afterwards the frequency measurement at $40^{\circ} \mathrm{C}$ was repeated displaying a crossover of $G^{\prime}$ and $G^{\prime \prime}$ at around $101 / \mathrm{s}$ as well as a rough approximation of the slopes of $G^{\prime}$ and $G^{\prime \prime}$ vs. angular frequency $\omega$ (see Fig. 4c).

Furthermore, an increase in $G^{\prime}$ of around $190 \%$ and in $G^{\prime \prime}$ 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 $\mathbf{4 a}$ bearing only 0.7 azide groups per four-arm star polymer $4 \mathbf{a}$ with a threearm 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 $\mathbf{4 b}$ 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 $\mathbf{4 b}$ and three-arm star alkyne-telechelic PIB were investigated in a $q$-range of $0.2-2.8 \mathrm{~nm}^{-1}$ 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 $\mathbf{4 b}$. 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 $\mathbf{4 b}$ after CuAAC at $20^{\circ} \mathrm{C}$.
a)
b)



Fig. 6. a) SAXS profiles of four-arm star thymine-telechelic PIB $\mathbf{3}$ (black dotted curve) and of crosslinked $\mathbf{4 b}$ (grey dotted curve) after covalent network formation via CuAAC. Fitting of SAXS data (Gaussian distribution) of four-arm star thymine-telechelic PIB $\mathbf{3}$ (grey solid curve) and of crosslinked $\mathbf{4 b}$ (black solid curve). b) proposed structure of the obtained double network (crosslinked $\mathbf{4 b}$ ) 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 $d=2 \cdot R_{2}=6.7 \mathrm{~nm}$ for PIB 3 and decreases to $d=6.3 \mathrm{~nm}$ for the crosslinked $\mathbf{4 b}$. 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 $\mathbf{4 b}$. Thus, "click" crosslinking reduces the number of clustered hydrogen bonds implying that four four-arm star polymers $\mathbf{4 b}$ 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 $\mathbf{4 b}$ after covalent "click" crosslinking via CuAAC.

| Entry | Sample | Hard sphere <br> radius $R_{2}{ }^{a}[\mathrm{~nm}]$ | Hard sphere <br> volume fraction | Aggregation <br> number $N^{b}$ |
| :--- | :--- | :--- | :--- | :--- |
| 1 | PIB-thymine 43 | 3.33 | 0.39 | $\approx 10$ |
| 2 | crosslinked 4b | 3.15 | 0.23 | $\approx 8$ |

${ }^{\text {a }}$ 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].
${ }^{\mathrm{b}}$ Calculated according to equation $1: \mathrm{N}=\left(4 \pi \mathrm{R}_{2}^{3} \rho \mathrm{~N}_{\mathrm{A}}\right) /(3 \mathrm{M})$ (eq. 1$)$.
thus generating polymeric networks for multiple self-healing applications 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 ${ }^{1} \mathrm{H}$-NMR-investigations, FTIR-investigations and MALDIToF mass spectrometry in case of four-arm star supramolecular polymers. Four-arm star thymine-telechelic PIB $\mathbf{3}$ 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 $5.6 \mathrm{E} 7 \mathrm{~Pa} \cdot \mathrm{~s}$ at $20^{\circ} \mathrm{C}$ 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 $0.97 \mathrm{~nm}^{-1}$ 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 $20^{\circ} \mathrm{C}$ and after 24 h at $40^{\circ} \mathrm{C}$, respectively. For the creation of the dual crosslinked self-healing system the four-arm star PIB $\mathbf{4 b}$ bearing 1.7 azide groups and 2.3 thymine endgroups per one molecule, was crosslinked with a three-arm star alkyne-telechelic PIB at $40^{\circ} \mathrm{C}$, catalyzed by $\mathrm{Cu}(\mathrm{I})$-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 $G^{\prime}$ of around $190 \%$ and in $G^{\prime \prime}$ 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
multiple self-healing at $20^{\circ} \mathrm{C}$ 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 selfhealing 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.

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