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# 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. Four-arm star thymine-telechelic PIB was obtained as a tough rubbery material as proven via melt-rheology and SAXS measurements with clusters of $\approx 10$ hydrogen bonding moieties resulting in a self-healing 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]

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applying supramolecular interactions such as hydrogen bonds [16a,b,17], ionomers [18], $\pi-\pi$-stacking interactions [19] or metal-ligand 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[1H]-pyrimidinones [21] provide a good basis for the commercially available self-healing material SupraB$^{TM}$ [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 °C. Deuterated chloroform ($CDCl_3$) 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 $H_{HR}$H Guard-17369 and a GM$H_{HR}$-N-18055 column in THF at 40 °C and via detection of the refractive index with a VE 3580 RI detector of Viscotek™. For external calibration PIB-standards (320 g/mol to 578,000 g/mol) from Viscotek™ 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 G2500$H_{HR}$-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$^{-1}$. $T_g$*'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 °C up to 800 °C with a heating rate of 10 °C min$^{-1}$. For analyzing of data OriginPro7 was used. Matrix-assisted 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 ± 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$^{-1}$. Four-arm star thymine-functionalized PIB and four-

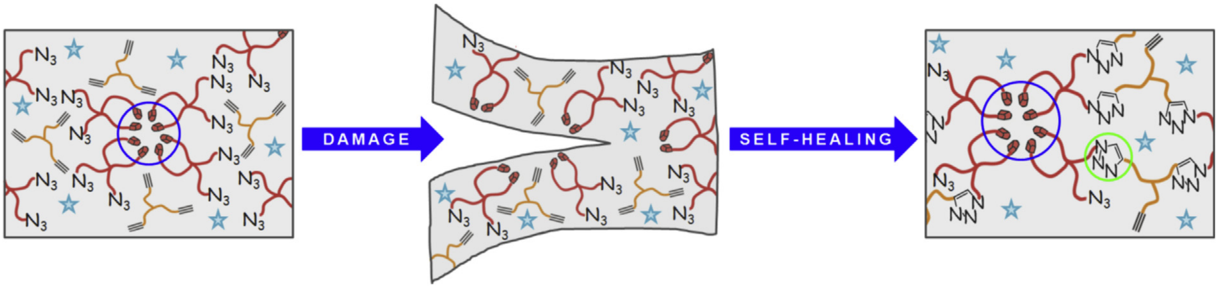

**Fig. 1.** Concept of a doubly crosslinked self-healing system based on supramolecular and covalent network formation via CuAAC (☆ ≡ Cu(I)-catalyst, ● ≡ supramolecular moiety).

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