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ARTICLE

Chelation-assisted CuAAC of star-shaped polymers enables fast self-healing at low temperatures

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The achievement of self-healing (SH) at ambient conditions (low temperature, no external input of energy) still presents a significant area of research, strongly linked to fast and efficient cross-linking reactions. We here investigate fast cross-linking reactions of star-shaped polymers containing copper chelating moieties (picolinazide) at the end of each arm, able to promote a "click"-reaction by chelation of the Cu(I)-catalyst and thus strongly increasing cross-linking rates. The synthetic preparation and cross-linking-kinetics of a low-molecular model-system (*p*-carboxylic-acid-methylester-picolinazide and phenylacetylene) were investigated by utilizing different catalysts (CuBr, $CuBr(PPh_3)_3$, $Cu(MeCN)_4PF_6$ und CuOAc) applying *in situ* NMR experiments. The most efficient catalyst-systems (CuBr, $CuBr(PPh_3)_3$, $CuF(PPH_3)_3$) were used to monitor the cross-linking of three-arm star-polymers bearing the carboxylic-acid-methylester-picolinazide on each arm *via* melt-rheology studies, in turn enabling self-healing. Complete cross-linking of the components can be observed within 71 minutes even at low temperatures (10 °C), thus generating a highly efficient low-temperature SH-system. Self-healing of a polymeric material at room temperature was demonstrated, consisting of a star-shaped picolinazido-telechelic PIB, an encapsulated multivalent alkyne embedded within a high molecular-weight PIB matrix together with $CuBr(PPh_3)_3$ and a fluorogenic dye, the latter acting as sensing tool for the proceeding click network formation. A damage-induced increase in the fluorescence intensity due to the click activation of the fluorogenic dye at room-temperature and the formation of a polymer network was thus proven. We envision that this highly enhanced speed of cross-linking will facilitate applications of self-healing polymers at low temperature conditions.

1.) Introduction

The concept of self-healing polymers envisions the imagination of everlasting materials able to repair damage autonomously[1]. For the successful development of self-healing (SH) polymers diffusion and reaction of the reactants is critical, in turn filling a crack by a newly formed network, either *via* purely physical ("supramolecular") forces,[2-4] or by action of chemical forces, in both cases requiring partially reversible[5-7] or stable[8, 9] covalent bonds. Prominent examples of such chemical healing-processes include Diels-Alder reactions,[5, 10, 11] epoxide chemistry,[12-22] "click-based" chemistries,[8, 23-30] isocyanate-chemistry,[31] olefin-metathesis[9, 32-34] and thiol chemistry[35, 36]. Although the topic of SH is investigated since more than one decade, there are still major drawbacks preventing crack-formation by SH-concepts, especially at low temperatures. Among the many reported SH-systems a significant number is working at relatively high temperatures (e.g. recent examples working at 100 °C[37] or even 160 °C[38]), so that in these cases SH seems to be more a mending-process *via* thermoplastic shape-reformation rather than a self-healing process acting autonomously. Additionally, often external stimuli such as photochemical activation are required to increase the kinetics of healing[39, 40]. Therefore many of the few fast self-healing systems are directed towards click-reactions, especially the most prominent (CuAAC)[23]is used to create SH-polymers working at room-temperature. Thus, especially the copper-catalyzed azide/alkyne-"click"-reaction (CuAAC)[41-44] is a potentially useful chemical cross-linking reaction, as a high thermodynamic gain tends to drive the reaction to completion, related to complete and dense network formation. By use of copper[44] in the oxidation state +I as catalyst, the 1,3-dipolar-Huisgen-reaction fulfills all criteria for a click[41] candidate. Thus, the CuAAC is accelerated by a factor of 10^7 resulting in high yields (< 99 %) within short time-scales[26, 27, 42, 45, 46]. Consequently, CuAAC is an excellent candidate for self-healing-systems and therefore already used widely: Namely, bis-azides, bis-alkynes[30, 47] and azido-star-shaped polymers or monomers and oligomers[8, 28, 29, 48, 49] have been demonstrated to generate self-healing-systems being highly efficient at room-temperature within hours down to even minutes. Further investigations improved the efficiency of such systems by modifying the catalyst[8,49], increasing the density of

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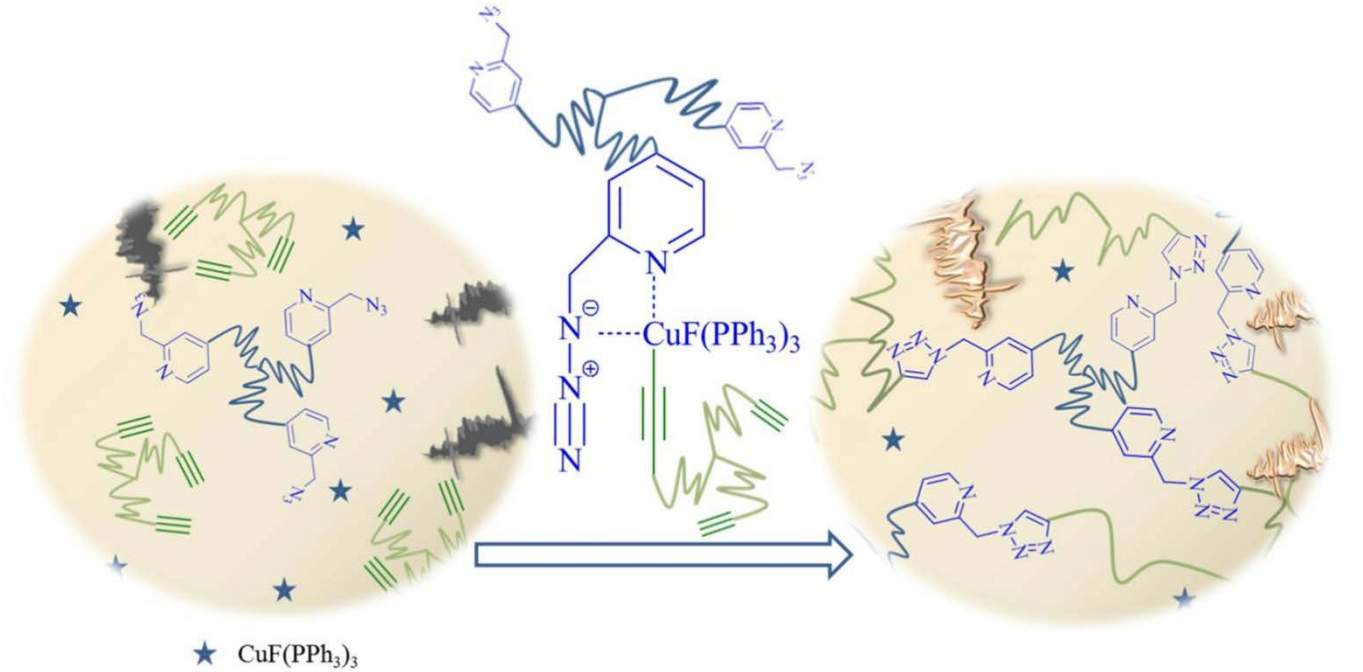

Fig. 1 Proposed healing mechanism: Using star-shaped polymers functionalized with copper chelating azides suitable for chelation-assisted CuAAC enables fast network-formation even at lower temperatures.

functional groups[28,48], decreasing the starting viscosity of the polymer-mixture and using different molecular-weight polymers[28]. To further accelerate CuAAC mediated SH, often the addition of bases (mainly amine-bases) and external ligands such as tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA), 2-[4-({bis[(1-tert-butyl-1*H*-1,2,3-triazol-4-yl)methyl]amino}methyl)-1*H*-1,2,3-triazol-1-yl]ethyl hydrogen sulfate (BTTES) or 3-[4-({bis[(1-tert-butyl-1*H*-1,2,3-triazol-4-yl)methyl]amino}methyl)-1*H*-1,2,3-triazol-1-yl]propyl hydrogen sulfate (BTTPS) have been investigated[50-53]. It is generally assumed that amine-bases promote the formation of the copper-acetylide and protect copper(I) from oxidation and disproportionation, further avoiding the formation of toxic reactive oxygen species (ROS-species) of Cu(I) in the presence of oxygen and simultaneously keeping the amount of catalytic potent species at a high level for a longer period of time. Thus, a combination of a click-based SH-system with an internal ligand[54, 55], able to accelerate the "click" reaction without the need of an added amine represents a simplified concept, where the number of required components is reduced. We here report for the first time a self-healing system containing star-shaped picolinazido- and alkyne-telechelic polymers based on poly(isobutylene) (PIB), able to form a network with the aid of chelation-assisted CuAAC working within minutes at low temperatures (10 °C) (see Fig. 1).

As the click-based ligand is now designed to effect chelation of the Cu(I)-catalyst prior to cross-linking *via* the CuAAC, we do expect a significantly enhanced cross-linking rate at lower temperature, thus approaching a low temperature SH-system in the absence of externally added components. We explore the synthesis of the star-shaped polymers, together with the optimization of the catalyst as well as the final cross-linking in the melt-state. Furthermore, we investigate a fluorogenic dye as a sensing tool being activated via the chelation-assisted click reaction, in turn visualizing the cross-linking reaction within a bulk material after physical damage.

2.) Experimental section

2.1 Materials

2,4-Pyridinecarboxylic acid hydrate was purchased from TCI and used without further purification. Calcium chloride (ultra dry 99.9 %) was purchased from Alfa Aesar, lithium hydroxide from Lachema, oxalyl chloride from Merck, high molecular weight poly(isobutylene) (250 000 g/mol) from BASF and 4-(dimethylamino)pyridine from Fluka and used without further purification. Copper(I)bromide was obtained by Sigma Aldrich and washed with glacial acetic acid followed by ethanol and finally by diethylether, before it was dried in high vacuum prior

to use. Copper(I)acetate, copper in charcoal (3 wt%), bromotris(triphenylphosphine)copper(I), fluorotris(triphenylphosphine)copper(I) and tetrakis(acetonitrile)copper(I)hexafluorophosphate were purchased from Sigma Aldrich and used without further purification. All other materials were obtained from Sigma-Aldrich and used as received if not mentioned otherwise. *N,N,N*-Triethylamine and methanol were freshly distilled over CaH_2 under a nitrogen atmosphere prior to use. *n*-Hexane was predried over KOH and freshly distilled over sodium and KOH under a nitrogen atmosphere prior to use. Tetrahydrofuran was predried over KOH and CuCl and freshly distilled over sodium and benzophenone under a nitrogen atmosphere prior to use. Dichloromethane was predried over $CaCl_2$ and freshly distilled over CaH_2 under a nitrogen atmosphere prior to use.
The synthesis and encapsulation of (2,2-bis(prop-2-2-ynyloxymethyl)-1-(prop-2-ynyloxy)butane (**4**) in urea-formaldehyde microcapsules (6 – 8 µm) using an oil in water emulsion technique was done according to literature.[8, 29, 56, 57] 3-azido-7-hydroxy-coumarin was synthesized according to known procedures.[58]

2.2 Measurements

NMR spectra were recorded on a Varian Gemini 2000 (400 MHz) or on a Varian Unity Inova 500 (500 MHz) at 27 °C. Deuterated chloroform ($CDCl_3$) or deuterated Tetrahydrofuran (THF-d_8) were used as solvents. All chemical shifts were given in ppm. MestReNova software (version 6.0.2-5475) was used for interpretation of the NMR-spectra. For kinetic investigations 2-(6-azidomethyl)-pyridine-4-carboxylic acid methyl ester (15 mg, 1.0 equivalent) was dissolved in THF-d_8 (0.35 mL), while phenylacetylene (10.3 µL, 1.2 eq.), the catalyst (0.05 or 0.1 eq.) and DIPEA (0.01, 0.1 or 1.2 eq.) (Table 1, entries 5 – 8) were separately dissolved in THF-d_8 (0.40 mL). For using 0.01 eq. of DIPEA a stock solution in THF-d_8 was prepared. Mixing the azide containing solution and the alkyne containing solution represents the starting point for the *in situ* NMR experiments. The first NMR-experiment was recorded directly after mixing the solutions. Further experiments were conducted at different defined periods of time while the corresponding conversion was calculated for each NMR-experiment by comparing the integrals of the CH_2-moiety attached to the azide (educt) and the CH_2-moiety attached to triazol-ring (product) (for detailed information see ESI).
For inline FTIR-measurements a Bruker Vertex 70 MIR spectrometer equipped with an ATR-FTIR diamond probe was used. Opus 6.5 was used for analyzing data.
Rheology experiments were performed on an Anton Paar (Physica) MCR 101/SN 80753612 at 20 °C or either 10 °C. For regulating the sample temperature thermoelectric cooling/heating in a Peltier chamber under a dry oxygen atmosphere was applied. For all measurements parallel plates with a diameter of 8 mm were used. Frequency measurements were performed within the LVE. For cross-linking experiments a picolin-azide-functionalized star-shaped PIB (30.0 mg) and an alkyne-functionalized star-shaped PIB (26.0 mg) were put in a vial and dissolved in $CHCl_3$. After mixing both solutions and evaporating of the solvent the obtained polymer mixture was dried in high vacuo. The catalyst (CuBr, $CuBr(PPh_3)_3$ or $CuF(PPh_3)_3$) (0.1 eq. per functional group) was dissolved in $CHCl_3$ (20 µL) and added as a stock solution to the polymer blend. In case of CuBr and $CuBr(PPh_3)_3$, *N,N*-Diisopropylethylamine (DIPEA) (0.01 or 0.1 equivalents per functional group) was additionally added as a stock solution. Subsequently, the reaction mixture was mixed with a spatula and was immediately put on the rheometer plate. Cross-linking experiments were performed with a strain γ of 0.1 % and with an angular frequency ω ranging from 100 to 1 rad s^{-1}. Gelation times[28, 48, 59] were determined as crossover of the storage (G') and loss modulus (G'') at 10 rad s^{-1}. Each measurement was stopped when the values of loss and storage modulus stayed constant (second decimal place) for at least one hour. This time is considered as the total time. The determined plateau moduli correspond to the storage moduli measured at this total time at 100 Hz. For evaluation of data the RheoPlus/32 software (V 3.40) and OriginPro8 were used.
Gel permeation chromatography (GPC) measurements were performed on a Viscotek GPCmax VE 2002 using a HH_{RH} Guard-17369 and a GMH_{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. The concentration of all samples was 3 mg/mL and the flow rate was 1 mL/min.
Fluorescence measurements were performed on a Cary Eclipse Fluorescence Spectrophotometer from Agilent Technologies. The excitation wavelength was set to 330 nm while detecting the fluorescence emission from 350 to 650 nm. Therefore, solid samples were fixed with quartz glass plates and measured within a solid sample holder. A measurement was performed every 5 minutes over a course of 24 hours. In case of control experiments (unscratched specimen, scratched specimen without $CuBr(PPh_3)_3$) measurements were performed every 5 minutes over a course of 4 hours. For evaluation of data the Cary Eclipse Scan Applications Software (v. 1.2 (147)) and Origin Pro8G (v. 8.0951) was used.

2.3 Synthesis

2.3.1 Synthetic-route to obtain 2-(6-azidomethyl)-pyridine-4-carboxylic acid (1a)[55, 60, 61]

The synthetic-route to obtain 2-(6-azidomethyl)-pyridine-4-carboxylic acid (**1a**) was done according to literature[55, 60, 61] with only slight changes: 2,4-pyridinedicarboxylic acid monohydrate (10.9 mmol, 2.0 g) was suspended in methanol (12.0 mL) and subsequently concentrated sulphuric acid (12.0 mmol, 640 µL) was added. The solution was refluxed for 48 hours and then allowed to cool down to room temperature. To accomplish the reaction the mixture was treated with

saturated aqueous sodium bicarbonate solution until it was neutral (pH = 7). The solvent was removed under reduced pressure, after which the residue was dissolved in chloroform (30.0 mL). The obtained solution was filtered and the organic layer was washed with a saturated solution of sodium chloride for several times until the water layer was neutral (pH = 7). The organic layer was dried over magnesium sulphate and concentrated under reduced pressure to provide 2,4-pyridinedicarboxylic acid dimethyl ester. R_f (EtOAc) = 0.61. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.90 (*dd*, 1H, $^3J_{H,H}$ = 4.9 Hz, $^5J_{H,H}$ = 0.6 Hz, C*H*), 8.65 (*dd*, 1H, $^4J_{H,H}$ = 1.5 Hz, $^5J_{H,H}$ = 0.8 Hz, C*H*), 8.03 (*dd*, 1H, $^3J_{H,H}$ = 4.9 Hz, $^4J_{H,H}$ = 1.6 Hz, C*H*), 4.03 (*s*, 3H, CH_3), 3.98 (*s*, 3H, CH_3) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 165.1, 164.8, 150.8, 149.1, 138.8, 126.4, 124.4, 53.2, 53.0 ppm.

2,4-pyridinedicarboxylic acid dimethyl ester (3.8 mmol, 750 mg) and ultra dry calcium chloride (99.99 %, 17.1 mmol, 1.9 g) were dissolved in anhydrous tetrahydrofuran (6.0 mL) and anhydrous methanol (12.0 mL). The solution was cooled to – 5 °C and subsequently sodium borohydride was added in small portions (5.6 mmol, 225 mg, (3 x 75 mg)). The reaction was accomplished after ~ 2 hours 40 minutes and quenched with ice-cold water (15.0 mL). The solution was extracted with chloroform (3 x 40.0 mL) and the combined organic layers were dried over magnesium sulphate. The solvent was removed under reduced pressure to afford 2-(6-hydroxymethyl)-pyridine-4-carboxylic acid methyl ester. R_f (EtOAc) = 0.41. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.70 (*d*, 1H, $^3J_{H,H}$ = 5.1 Hz, C*H*), 7.83 (*s*, 1H, C*H*), 7.75 (*dd*, 1H, $^3J_{H,H}$ = 5.1 Hz, $^4J_{H,H}$ = 0.7 Hz, C*H*), 4.83 (*s*, 2H, CH_2), 3.96 (*s*, 3H, CH_3) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 165.5, 160.4, 149.4, 138.1, 121.6, 119.8, 64.2, 52.7 ppm.

2-(6-hydroxymethyl)-pyridine-4-carboxylic acid methyl ester (0.3 mmol, 50 mg) was dissolved in anhydrous dichloromethane (6.6 mL), followed by the addition of *N,N,N*-triethylamine (1.5 mmol, 207 µL) and *para*-toluenesulfonyl chloride (0.5 mmol, 87 mg). After stirring for two hours the solvent was removed under reduced pressure. The residue was dissolved in anhydrous tetrahydrofuran (3.3 mL) and sodium azide (3.0 mmol, 193 mg) was added. The reaction was stirred for further 24 hours at room temperature, after which it was diluted with ethyl acetate (30.0 mL) and water (30.0 mL). After extraction of the aqueous layer with ethyl acetate (three times 30.0 mL), the combined organic layers were washed with a saturated solution of sodium chloride and dried over magnesium sulphate. The crude product was purified by silica chromatography (*n*-Hex:EtOAc, 4:1, R_f = 0.65 in *n*-Hex:EtOAc, 1:1) providing 2-(6-azidomethyl)-pyridine-4-carboxylic acid methyl ester. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.74 (*d*, 1H, $^3J_{H,H}$ = 5.0 Hz, C*H*), 7.89 (*s*, 1H, C*H*), 7.79 (*dd*, 1H, $^3J_{H,H}$ = 5.0 Hz, $^4J_{H,H}$ = 1.4 Hz, C*H*), 4.56 (*s*, 2H, CH_2), 3.96 (*s*, 3H, CH_3) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 165.3, 157.0, 150.5, 138.4, 122.1, 121.1, 55.4, 52.8 ppm.

2-(6-azidomethyl)-pyridine-4-carboxylic acid methyl ester (2.6 mmol, 500 mg) was dissolved in methanol (10.0 mL), followed by the addition of a 1.0 M aqueous solution of lithium hydroxide (7.8 mmol, 7.8 mL). The reaction was stirred for 25 minutes at room temperature. Neutralization was done by the addition of a 1.0 M solution of hydrogen chloride. The solvent was removed under reduced pressure and the product was dried in high vacuum until constant weight to obtain 2-(6-azidomethyl)-pyridine-4-carboxylic acid (**1a**). ^{1}H-NMR (DMSO-d_6, 400 MHz): δ = 8.51 (*d*, 1H, $^3J_{H,H}$ = 4.9 Hz, C*H*), 7.74 (*s*, 1H, C*H*), 7.66 (*dd*, 1H, $^3J_{H,H}$ = 4.9 Hz, $^4J_{H,H}$ = 1.1 Hz, C*H*), 4.48 (*s*, 2H, CH_2) ppm; ^{13}C-NMR (DMSO-d_6, 100 MHz): δ = 167.2, 155.7, 149.5, 149.2, 123.1, 122.4, 55.1 ppm.

To provide 2-(6-azidomethyl)-pyridine-5-carboxylic acid (**1b**) the same protocol was used, beginning with step II and using 2,5-pyridinedicarboxylic acid dimethyl ester as starting material. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ = 8.99 (*s*, 1H, C*H*), 8.18 (*dd*, 1H, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 2.0 Hz, C*H*), 7.34 (*d*, 1H, $^3J_{H,H}$ = 7.9 Hz, C*H*), 4.49 (*s*, 2H, CH_2) ppm; ^{13}C-NMR (DMSO-d_6, 100 MHz): δ = 167.6, 156.0, 151.0, 137.9, 134.7, 121.7, 54.8 ppm.

2.3.2 Synthesis of star-shaped azido-telechelic PIBs (2a, 2b)

Synthesis of star-shaped azido-telechelic PIBs (**2a**, **2b**) was done using 1,3,5-tris(2-hydroxy-2-propyl)-benzene[62] as initiator in living carbocationic polymerization (LCCP) of isobutylene according to literature[63-65] followed by quenching with allyltrimethylsilane (ATMS) and further endgroup-transformation to the corresponding alcohol according to known procedures[66, 67].

2-(6-azidomethyl)-pyridine-4-carboxylic acid (**1a**) (674 µmol, 120 mg, 11.6 equiv.) was dissolved in anhydrous dichloromethane (5.0 mL), followed by the addition of oxalyl chloride (674 µmol, 56 µL, 11.6 equiv.). The reaction was heated under reflux for five hours and then allowed to cool down to room temperature. Subsequently star-shaped PIB-OH (58 µmol, 350 mg, 1 equiv.) and 4-(dimethylamino)-pyridine (88 µmol, 11 mg, 1.5 equiv.) which were dissolved in dichloromethane (5.0 mL) were added to the solution. Finally *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (263 µmol, 50 mg, 4.5 equiv.) was added to the ice-cooled reaction mixture, which was then heated under reflux for three days. In the next step the solution was diluted with dichloromethane (30.0 mL) and filtered. The organic layer was washed with a saturated solution of ammonium chloride and dried over sodium sulphate. The solvent was evaporated under reduced pressure to afford the crude product, which was purified by dissolving in *n*-hexane and precipitation into an excess of methanol. The final polymer was dried at high vacuum until constant weight to provide star-shaped azido-telechelic PIB (**2a**). (M_n(GPC) = 6520 g· mol^{-1}, M_w/M_n = 1.3). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 8.76 (*d*, 3H, $^3J_{H,H}$ = 5.0 Hz, C*H*), 7.90 (*s*, 3H, C*H*), 7.80 (*dd*, 3H, $^3J_{H,H}$ = 5.0 Hz, $^4J_{H,H}$ = 1.1 Hz, C*H*), 7.13 (*s*, 3H, C*H* of initiator), 4.57 (*s*, 6H, CH_2), 4.33 (*t*, 6H, $^3J_{H,H}$ = 6.8 Hz, CH_2), 1.85 (*s*, 6H, CH_2), 1.41 (*s*, CH_2 of repetitive unit), 1.11 (*s*, CH_3 of repetitive unit), 0.80 (*s*, 18H, CH_3 of initiator) ppm.

The synthetic route to obtain **2b** was the same as described for

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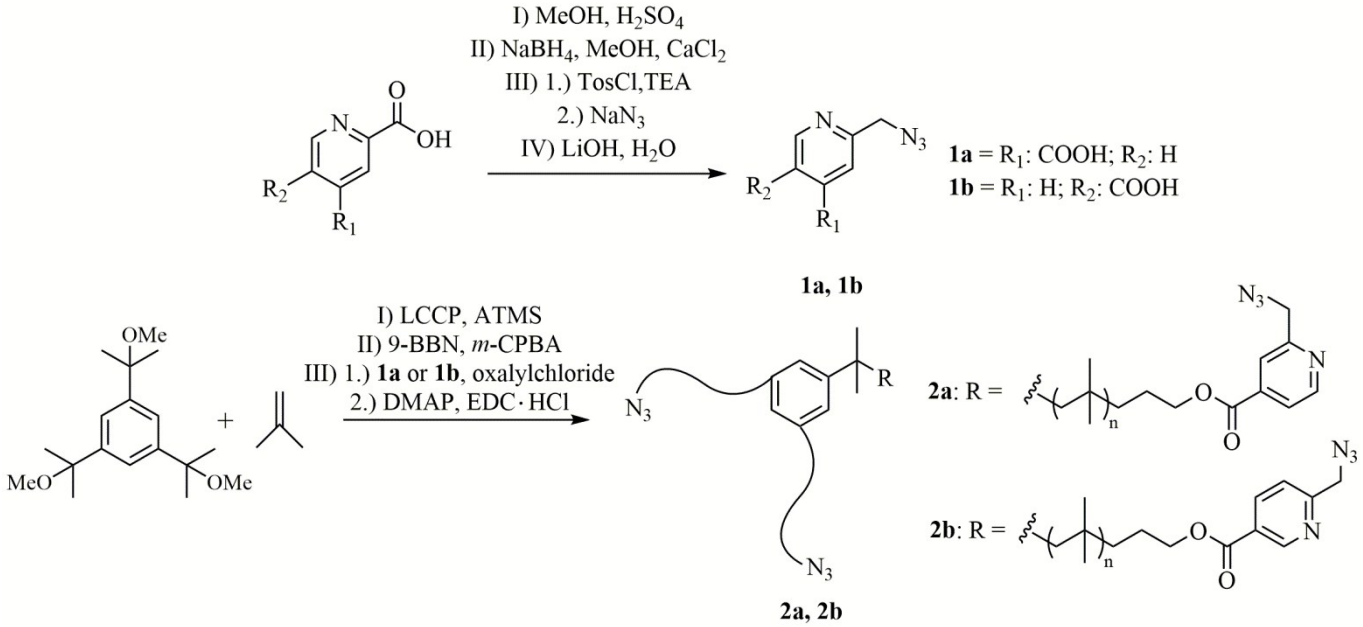

Fig. 2 Synthetic-route to obtain star-shaped azido-telechelic PIBs (**2a**, **2b**) with picolin-azide moiety suitable for the chelation-assisted CuAAC.

2a, with the only exception that instead of using the esterification agent **1a** it had been used its stereo-analogue **1b**. (M_n(GPC) = 5780 g · mol^{-1}, M_w/M_n = 1.3). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 9.20 (*s*, 3H, C*H*), 8.34 (*dd*, 3H, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,H}$ = 2.1 Hz, C*H*), 7.46 (*d*, 3H, $^3J_{H,H}$ = 8.1 Hz, C*H*), 7.14 (*s*, 3H, C*H* of initiator), 4.58 (*s*, 6H, CH_2), 4.34 (*t*, 6H, $^3J_{H,H}$ = 6.7 Hz, CH_2), 1.86 (*s*, 6H, CH_2), 1.43 (*s*, CH_2 of repetitive unit), 1.12 (*s*, CH_3 of repetitive unit), 0.81 (*s*, 18H, CH_3 of initiator) ppm.

2.3.3 Synthesis of star-shaped PIB-Alkyne (3)

Synthesis of trivalent PIB-Alkyne (**3**) was done according to known procedures[29]. (M_n(GPC) = 6560 g · mol^{-1}, M_w/M_n = 1.4). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.28 (*d*, 6H, $^3J_{H,H}$ = 8.9 Hz, C*H* of quenching agent), 7.13 (*s*, 3H, C*H* of initiator), 6.89 (*d*, 6H, $^3J_{H,H}$ = 8.8 Hz, C*H* of quenching agent), 4.66 (*d*, 6H, $^4J_{H,H}$ = 2.4 Hz, O–CH_2), 2.50 (*t*, 3H, $^4J_{H,H}$ = 2.4 Hz, C–C*H*), 1.41 (*s*, CH_2 of repetitive unit), 1.11 (*s*, CH_3 of repetitive unit), 0.79 (*s*, 18H, CH_3 of initiator) ppm.

2.3.4 Embedding procedure

To embed all required components to one SH-specimen (3 g), high molecular weight PIB (~ 250 000 g/mol, 2.49 g) was dissolved in *n*-hexane (40.0 mL) over night. To this highly viscous mixture star-shaped picolinazido-telechelic PIB (**2b**) (5 wt%, 146 mg) dissolved in *n*-hexane (1.0 mL), UF-capsules containing (2,2-bis(prop-2-2-ynyloxymethyl)-1-(prop-2-ynyloxy)butane (**4**) (10 wt%, 300 mg), $CuBr(PPh_3)_3$ (2 wt%, 60 mg) and 3-azido-7-hydroxy-coumarin (2.5 wt% of **2b**,4 mg) were added. Afterwards all components were homogeneously mixed by using a VORTEX-GENIE® touch mixer. To get rid of air-bubbles, the pressure was reduced carefully to 150 mbar and kept at this level for at least ten minutes. Finally, the viscous mixture was poured into a mould and kept at 50 °C over night. Specimen of approximate dimensions of 5 mm x 13 mm x 0.8 mm were cut out with a razor blade.

For control experiments a second specimen was synthesized without any catalyst ($CuBr(PPh_3)_3$), therefore the amount of high molecular weight PIB was increased to 2.55 g.

3.) Results and discussion

Reaction rates within the chelation-assisted mechanism are increased by several orders in comparison to the classical CuAAC, caused by the usage of internal ligands, able to form a complex with copper as previously reported[55]. Due to pre-organization of the corresponding reactants (azide/alkyne) close to each other caused by the copper-chelating moiety the chelation-assisted CuAAC is the fastest version of this click-type reaction so far. To utilize this concept to improve healing-kinetics of polymers, we attached the chelating 2-(6-azidomethyl)-pyridine-4-carboxylic acids (**1a**, **1b**) to star-

shaped hydroxy-telechelic PIB (see Fig. 2) in turn acting as cross-linking reagent for SH.

1a has been synthesized over four steps (I – IV), starting with esterification (I), followed by selective reduction (II) and substitution (III) of the corresponding alcohol to the azide-group. Further hydrolysis (IV) opens the possibility to attach **1a** to the corresponding polymeric alcohol *via* an esterification reaction. For the synthesis of **1b** just three steps (II – IV) are required, due to the commercial availability of 2,5-pyridinedicarboxylic acid dimethyl ester.

The required hydroxy-telechelic PIB has been synthesized starting with living carbocationic polymerization (LCCP) of isobutylene and quenching with ATMS, consequently followed by complete endgroup transformation to the corresponding alcohol[63,64, 65].

Accordingly, we explored the "click"-kinetics of chelation-assisted CuAAC in solution for low molecular structure (3.1) as well as in the melt-state for polymeric structure (3.2).

3.1 *In situ* model NMR-investigations of the chelation-assisted CuAAC of low-molecular 2-(6-azidomethyl)-pyridine-4-carboxylic acid methyl ester and phenylacetylene.

To achieve highly efficient and fast self-healing *via* chelation-assisted CuAAC, different reaction setups including the change of the copper source and the addition of DIPEA as a base were investigated *via in situ* NMR measurements. Therefore, 2-(6-azidomethyl)-pyridine-4-carboxylic acid methyl ester and phenylacetylene served as ideal low-molecular substrates for *in situ* NMR-studies containing the azide, the alkyne, the copper(I) source and *N,N*-Diisopropylethylamine (DIPEA) (Table 1, entries 5 – 8) separately dissolved in deuterated THF. Mixing all components together in a NMR-tube defined the starting-point of every single experiment (see Table 1), in turn allowing to quantify the kinetics of the reaction.

Table 1 – Chelation-assisted CuAAC of 2-(6-azidomethyl)-pyridine-4-carboxylic acid methyl ester (c = 104 mM) and phenylacetylene (c = 125 mM) at 27 °C in deuterated THF investigated *via in situ* NMR-measurements.

ent.	catalyst	time	DIPEA	conv.
1	Cu/Charcoal[a]	9 h	---	< 1 %
2	$[Cu(CH_3CN)_4]PF_6$[a]	24 h	---	32 %
3	Cu(OAc)[a]	16 h	---	82 %
4	CuBr[a]	9 h	---	> 99 %
5	CuBr[a]	< 5 min[c]	1.2 eq.[d]	> 99 %
6	CuBr[a]	< 5 min[c]	0.1 eq.[e]	> 99 %
7	CuBr[a]	17 min	0.01 eq.[f]	> 99 %
8	$CuBr(PPh_3)_3$[b]	2 h	0.01 eq.[f]	10 %

[a] 0.1 equivalents of catalyst were added. [b] 0.05 equivalents of catalyst were added. [c] first NMR-spectrum showed complete conversion. [d] c = 125 mM. [e] c = 10.4 mM. [f] c = 1.04 mM.

First of all a commercially available Cu/charcoal catalyst was tested, resulting in an only poor conversion within nine hours (Table 1, entry 1). Changing the catalyst to $[Cu(CH_3CN)_4]PF_6$ (Table 1, entry 2) and Cu(OAc) (Table 1, entry 3) resulted in enhanced conversions of 32 % and 82 % within one day, turning out to be too slow for fast self-healing applications. Upon testing several Cu(I)-catalysts, CuBr delivered the best results, driving the reaction to completion within nine hours (Table 1, entry 4). Thus, CuBr was chosen to run the reaction in the presence of DIPEA, which can promote the formation of Cu-acetylide-species in the first step and therefore "initially" the "click"-reaction. Already in the first NMR-spectrum, measured five minutes after mixing all components no NMR-resonances of the starting material can be seen (Table 1, entries 5 and 6). Even with just 1 mol % DIPEA the reaction went into completion within 17 minutes (Table 1, entry 7). $CuBr(PPh_3)_3$ was also tested as catalyst due to its increased solubility in THF[47], caused by the attached triphenylphosphin-ligands. Surprisingly, $CuBr(PPh_3)_3$ showed a lower conversion in the presence of 1 mol % DIPEA (Table 1, entry 8) in comparison to pure CuBr. Thus, we claim that DIPEA is not just promoting the formation of the initially required Cu-acetylide by acting as a base, but also further disintegrates unreactive CuBr clusters[42], delivering an ideal catalyst system for fast click-reactions in solution.

3.2 Cross-linking of star-shaped telechelic PIBs (2a + 3 and 2b + 3) *via* chelation-assisted CuAAC monitored *via* melt-rheology.

To adapt the concept of chelation-assisted CuAAC in order to facilitate fast cross-linking even at lower temperatures, it is necessary to use multivalent polymers, ensuring network formation. Thus, we have functionalized three arm-star poly(isobutylene) with 2-(6-azidomethyl)-pyridine-(4 or 5)-carboxylic acid (**1a**, **1b**) *via* esterification. The so obtained polymers (**2a**, **2b**) have been consequently analyzed by GPC, NMR- and IR-spectroscopy, showing the successful introduction of the chelation-assisted capable endgroup (see Supporting Information). We further investigated the cross-linking behaviour at different conditions (change of catalyst, temperature) by reacting azido-telechelic PIBs (**2a**, **2b**)with the star-shaped PIB-alkyne (**3**), monitored by melt rheology-measurements (see Table 2) similar to conventional CuAAC based systems[28, 29, 48, 68]. As the use of CuBr in solution delivered full conversion in the shortest period of time it was firstly tested in a melt-rheology experiment. Although 1 mol % of DIPEA was added, network formation took 870 minutes (gelation-time, see Table 2, entry 1) which is mainly attributed to oxidation during the rheology experiment. Thus, we decided to test $CuBr(PPh_3)_3$ as an alternative catalyst despite its relatively poor performance in the initial low molecular weight compound-tests[8, 28, 29, 48]. Consequently, this system showed significantly shorter gelation-times (Table 2, entries 2 and 3); changing the counterion of the catalyst to fluoride, thus additionally improved the observed gelation-times tremendously. Accordingly, cross-linking took place within just 15 minutes at room-temperature (Table 2, entry 5). Thus, this system is even faster than cross-linking hyperbranched PIB-

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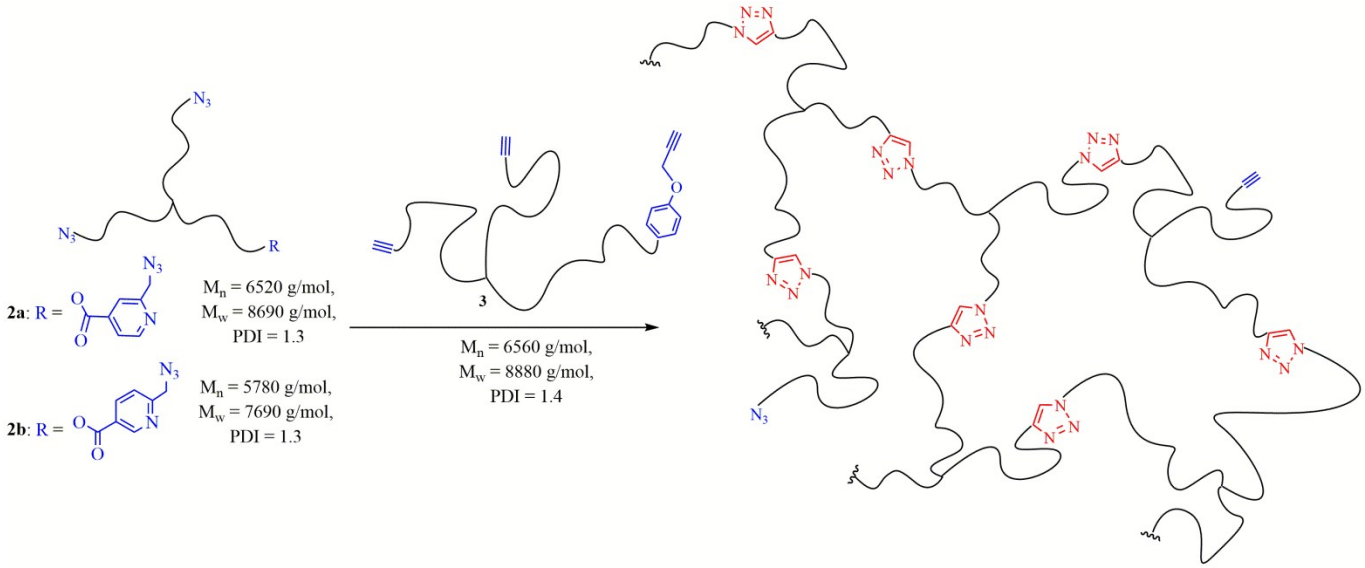
Table 2 – Network formation of star-shaped azido-telechelic PIBs (**2a** or **2b**) and PIB-alkyne (**3**) using the chelation-assisted CuAAC to enable fast self-healing at low temperatures (10 °C) monitored by applying melt-rheology measurements.



ent.	mixture	catalyst[c]	T [°C]	Gel_t[d] [min]	c_M [M]	c_{Cu} [M] (10^{-2})	k_0 [$M^{-3}\cdot min^{-1}$]	$k_{crossover}$ [$M^{-3}\cdot min^{-1}$]	r_0 [$M\cdot min^{-1}$]
1	**2a** + **3**[a]	CuBr	20	870	0.254	2.54	---	---	---
2	**2a** + **3**[a]	$CuBr(PPh_3)_3$	20	255	0.254.	2.54	2200	7300	0.092
3	**2a** + **3**[b]	$CuBr(PPh_3)_3$	20	266	0.254	2.54	400	1000	0.017
4‘	[29]	$CuBr(PPh_3)_3$	20	290	0.238	2.38	700	2700	0.023
5	**2a** + **3**	$CuF(PPh_3)_3$	20	15	0.254	2.54	---[e]	---[e]	---[e]
6	**2b** + **3**	$CuF(PPh_3)_3$	20	29	0.200	2.00	3100	9100	0.050
7	**2b** + **3**	$CuF(PPh_3)_3$	10	71	0.200	2.00	2500	7500	0.041

‘ Values are reprinted with permission of [29]. [a] = 0.01 eq. of DIPEA were added. [b] = 0.1 eq. of DIPEA were added. [c] = 0.1 eq. of catalyst were added. [d] Determined *via* melt-rheology, $G'' = G'$ at ω = 10 Hz. [e] Reaction is too fast for determination.

polymers (20 °C, 33 minutes) *via* conventional CuAAC. By changing from the 2,4- (**2a**) to the 2,5-isomer (**2b**) the cross-linking time is nearly doubled to 29 minutes at 20 °C (Table 2, entry 6). Although lowering the temperature beyond room-temperature is slowing down the click-kinetics, cross-linking is still fast – even at 10 °C the gel point was reached within 71 minutes (Table 2, entry 7).

Referring to Ampudia[69] and Barton[70] the rate-constants near the gel point have been calculated according to equation 1:

$$k = \frac{e^{(k'\cdot t)} - 1}{t\cdot [A]_o\cdot [Cu]^2} \qquad (1)$$

Thus, for all performed cross-linking reactions an acceleration of the reaction rates by progressing time can be observed (see Fig. 3).

This autocatalytic-effect is caused by an increasing concentration of the formed triazole-rings during the proceeding cross-linking reactions, as these heterocyclic rings can act as internal ligands, being capable to chelate copper. Further auto-acceleration of the chelation-assisted CuAAC by the newly formed triazole-rings should not be as strong as for the classical CuAAC, due to the presence of the internal pyridinium-ligand already at the very beginning of each reaction. Indeed, the acceleration factors for the chelation-assisted CuAAC vary from 2.9 – 3.3 (Table 2 and Figure 3, entries 2, 6 and 7) and are therefore lower compared to the

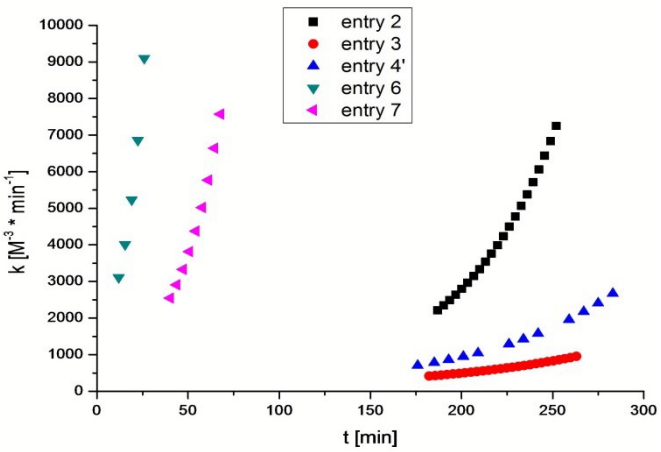


Fig. 3 Development of the rate-constant *k vs.* time *t* for cross-linking of **2a** + **3** and **2b** + **3**.

classical CuAAC approach utilizing polymers with comparable molecular weights (Table 2, entry 4', acceleration factor of 3.4). Although there is only a slight difference in the acceleration of the chelation-assisted CuAAC and the classical CuAAC, there are tremendous differences in the calculated rate-constants. While the classical CuAAC is starting with a rate-constant of k_0 ~ 700 $M^{-3} \cdot min^{-1}$ (Table 2, entry 4'), up to fourfold higher k_0-values (2200 – 3100 $M^{-3} \cdot min^{-1}$) are observed for the cross-linking reactions following the chelation-assisted CuAAC mechanism from the very beginning (Table 2, entries 2, 6 and 7). In entry 3, the rate-constant k_0 is ~ 400 $M^{-3} \cdot min^{-1}$ and is therefore just 1/5 of k_0 in entry 2, which is in contrast to identical gelation times of ~ 260 minutes for both experiments. Nevertheless, for cross-linking **2b** + **3** in the presence of the most active catalyst ($CuF(PPh_3)_3$), k_0-values of ~ 2500 – 3100 $M^{-3} \cdot min^{-1}$ (Table 2, entries 6 and 7) are observed already at the very beginning of the reaction, resulting in strongly reduced gelation-times (29 – 71 minutes) even at 10 °C.

By using equation 2[71, 72] network strand densities ν_x were determined for the finally cross-linked materials:

$$G_N = \nu_x RT = \frac{\rho RT}{M_c}\left(1 - \frac{2M_c}{M_n}\right) \qquad (2)$$

where G_N is the measured plateau-modulus at ω = 100 Hz, ρ is the density of the polymer mixture, M_n is the average molecular weight of the polymer mixture, R is the universal gas constant, R = 8.3145 $J \cdot mol^{-1} \cdot K^{-1}$, T is temperature in K and M_c is the average molecular weight between two network points. By assuming a complete conversion the maximum network strand density $\nu_{x,max}$ was calculated. By using the experimentally determined plateau moduli the experimental network strand density $\nu_{x,exp}$ was calculated. Relating the experimental and the maximum network strand density provide information about the amount of formed network points during the cross-linking and thus the completeness of the reaction (see Table 3).

Table 3 – Calculated network-densities based on eq. 2 for cross-linking **2a** + **3** and **2b** + **3**.

entry	mixture	G_N[e] [Pa]	$\nu_{x,\,max}$ [mol/m^3]	$\nu_{x,\,exp}$ [mol/m^3]	$\nu_{x,\,exp}$/ $\nu_{x,\,max}$
1	**2a** + **3**[a]	$1 \cdot 10^4$	254	4	1.6 %
2	**2a** + **3**[b]	$1.03 \cdot 10^5$	254	43	17.0 %
3	**2a** + **3**[b]	$1.13 \cdot 10^5$	254	46	18.5 %
5	**2a** + **3**[c]	$2.48 \cdot 10^5$	254	91	40.2 %
6	**2b** + **3**[c]	$8.73 \cdot 10^4$	181	36	19.9 %
7	**2b** + **3**[d]	$1.07 \cdot 10^5$	181	45	24.9 %

[a] Applying CuBr at 20 °C. [b] Applying $CuBr(PPh_3)_3$ at 20 °C. [c] Applying $CuF(PPh_3)_3$ at 20 °C. [d] Applying $CuF(PPh_3)_3$ at 10 °C. [e] Constant value at ω = 100 Hz.

Using CuBr as catalyst (Table 3, entry 1), both the plateau-modulus G_N and the calculated network density $\nu_{x,exp}$ are low (1.6 %), which is in agreement with only slight changes in the viscosity during the cross-linking reaction, indicating that this system is not suitable for efficient and fast cross-linking in the melt-state. Applying $CuBr(PPh_3)_3$ as catalyst resulted in increased network densities up to 18.5 % (Table 3, entries 2 and 3). By changing to the most active catalyst, namely $CuF(PPh_3)_3$ the network density is doubled to 40.2 % (Table 3, entry 5), which is in accordance with the observed short gelation time (15 minutes), whereas cross-linking of isomer **2b**, generated decreased network strand densities of about 20 – 25 % (Table 3, entries 6 and 7). IR-measurements of the finally obtained networks showed complete disappearance of the azide-vibration at ν ~ 2100 cm^{-1} (see Supporting Information).

3.3 "Click"-induced self-healing in polymeric materials

Autonomous self-healing within polymer materials composed of high molecular-weight PIB was probed directly by use of a fluorogenic dye, able to measure the damage induced "click"-reaction directly within the material. The specimen contained the star-shaped picolinazido-telechelic PIB (**2b**, 5 wt%), micro-sized UF-capsules filled with a trivalent alkyne (2,2-bis(prop-2-2-ynyloxymethyl)-1-(prop-2-ynyloxy)butane (**4**), 10 wt%), the Cu(I)-source ($CuBr(PPh_3)_3$, 2 wt%) and the fluorogenic azido-coumarin-dye (2.5 wt% of **2b**). To evoke rupture of the capsules, in turn inducing the healing reaction, the specimen has been damaged by several scratches. Subsequently, the fluorescence-emission of the fluorogenic dye, generated in the subsequent "click" reaction has been measured (see Fig. 4). The chelation-assisted fluorogenic click reaction was investigated for 24 hours at room temperature monitoring the *in situ* fluorescence (excitation: 330 nm, emission: 350 – 650 nm) (see Fig. 4). The observed increase in the fluorescence emission is thus related to the fluorogenic click reaction indicative of the healing. In turn, the alkyne (**4**) undergoes click-reactions with both, the star-shaped picolinazido-telechelic PIB **2b** and the azido-coumarin-dye within the PIB-matrix, which is directly visualized by the formed fluorogenic coumarin-triazol product. As a reference experiment the unscratched specimen was measured, showing no increase of the fluorescence as the

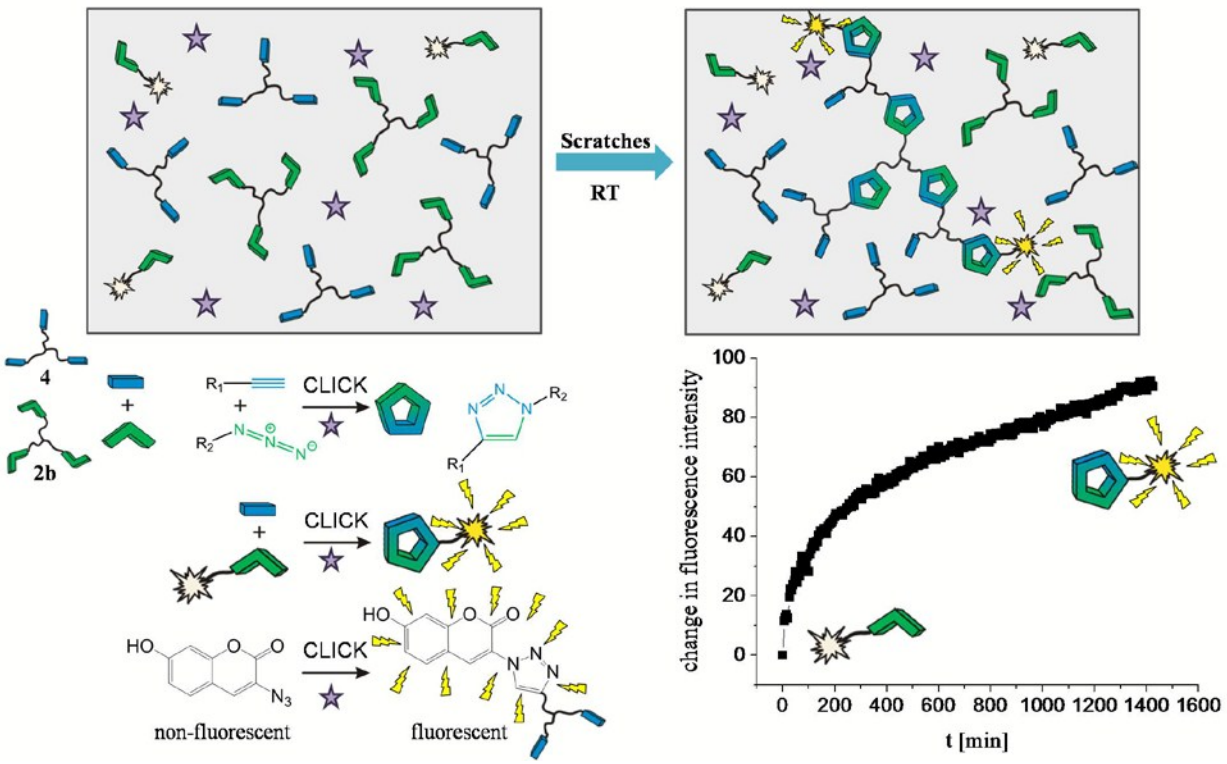


Fig. 4 Fluorogenic click reaction in SH-PIB-specimen. A star-shaped picolinazido-telechelic PIB (**2b**), UF-capsules filled with a trivalent alkyne (the capsules are not pictured in this scheme to keep it clearly-arranged), $CuBr(PPh_3)_3$ and the fluorogenic azido-coumarin-dye are incorporated into a high molecular weight PIB-matrix. Micron-sized capsule breaking was evoked by scratches, in turn increasing the fluorescence intensity of the fluorogenic dye.

incorporated capsules are not broken and therefore no fluorescent click-product can be formed (see ESI, Fig. S25). In a second control experiment a scratched specimen without copper(I)-catalyst was investigated, showing no increase of the fluorescence and thus no triggered click-reactions (see ESI, Fig. S26).

4. Conclusions

We have investigated a synthetic route towards star-shaped picolinazido-telechelic PIBs (**2a**, **2b**) applicable for subsequent cross-linking *via* chelation-assisted CuAAC aiming at the development of low temperature self-healing polymers. Therefore, a model click reaction between 2-(6-azidomethyl)-pyridine-4-carboxylic acid methyl ester and phenylacetylene was investigated *via in situ* NMR measurements in solution varying the catalyst and adding different amounts of a base. For the model click reaction CuBr turned out to be the best catalyst in presence of a catalytical amount of DIPEA, ensuring complete conversion within five minutes at room-temperature.

Due to pre-organization of the copper-acetylide by the donating nitrogen-atom of α-picolin-azide, herein acting as an internal ligand and therefore enabling close proximity of both reactants, the reaction rate of the chelation-assisted CuAAC is increased in contrast to the conventional Cu(I)-promoted "click"-reaction. Thus, while transferring this concept for the first time to self-healing polymers, we functionalized star-shaped PIBs with the corresponding 2-(6-azidomethyl)-pyridine-(4 or 5)-carboxylic acid (**1a**, **1b**) endgroup. Further cross-linking experiments of star-shaped azido-telechelic PIBs (**2a**, **2b**) and PIB-alkyne (**3**) were conducted applying melt-rheology. In contrast to the obtained results in solution, CuBr was not suitable for efficient cross-linking in the melt state, presumably due to its decreased solubility and oxidation stability. Therefore by using it's more stable analogue $CuBr(PPh_3)_3$ network-formation was achieved at room-temperature within 255 minutes. Furthermore, cross-linking was accomplished within 71 minutes even at hampered conditions as lower temperatures (10 °C) utilizing the more active $CuF(PPh_3)_3$ as catalyst. Within this work we have overcome one major drawback of the most self-healing systems known so far – efficient fast healing kinetics especially at temperatures below room-temperature. By applying the concept of the chelation-assisted CuAAC to self-healing star-shaped PIBs we successfully demonstrated a cross-linking system working fast even at low-temperature conditions (10 °C). We successfully demonstrated self-healing of the embedded star-shaped picolinazido-telechelic PIB **2b** with an encapsulated alkyne **4**, using $CuBr(PPh_3)_3$ as catalyst and small amounts of a fluorogenic dye within the polymer-matrix (PIB). Scratch experiments with subsequent fluorescence-measurements of the generated fluorogenic dye have proven the subsequent crosslinking reaction via formation of the highly fluorescent-click-product within the PIB-matrix at room-temperature.

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Notes and references

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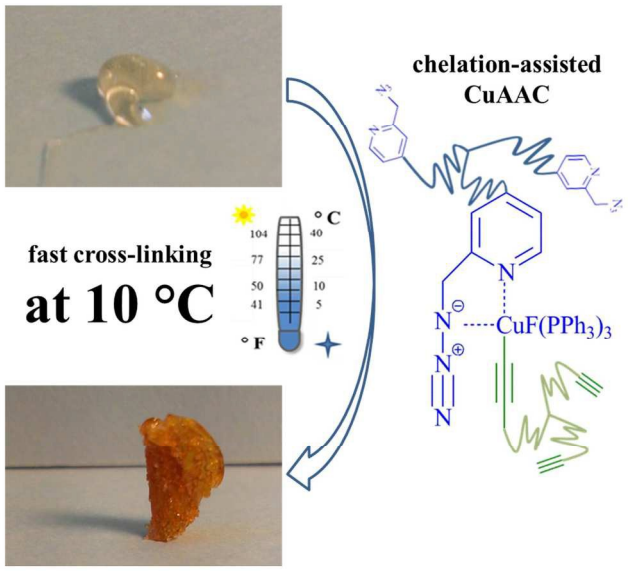

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