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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(PPh₃)₃, Cu(MeCN)₄PF₆ und CuOAc) applying in situ NMR experiments. The most efficient catalyst-systems (CuBr, CuBr(PPh₃)₃, CuF(PPh₃)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(PPh₃)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. 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, or by action of chemical forces, in both cases requiring partially reversible or stable covalent bonds. Prominent examples of such chemical healing-processes include Diels-Alder reactions, epoxide chemistry, “click-based” chemistries, isocyanate-chemistry, olefin-metathesis and thiol chemistry. 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 or even 160 °C), 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. Therefore many of the few fast self-healing systems are directed towards click-reactions, especially the most prominent (CuAAC) is used to create SH-polymers working at room-temperature. Thus, especially the copper-catalyzed azide/alkyne-“click”-reaction (CuAAC) 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 in the oxidation state +1 as catalyst, the 1,3-dipolar-Huisgen-reaction fulfills all criteria for a click candidate. Thus, the CuAAC is accelerated by a factor of 10⁷ resulting in high yields (< 99 %) within short timescales. Consequently, CuAAC is an excellent candidate for self-healing-systems and therefore already used widely: Namely, bis-azides, bis-alkynes and azido-star-shaped polymers or monomers and oligomers 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, increasing the density of...
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function groups\textsuperscript{28,48}, decreasing the starting viscosity of the polymer-mixture and using different molecular-weight polymers\textsuperscript{28}. To further accelerate CuAAC mediated SH, often the addition of bases (mainly amine-bases) and external ligands such as tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA), 2-[4-(bis[(1-tert-butyl-1H-1,2,3-triazol-4-yl)methyl]amino)methyl]-1H-1,2,3-triazol-1-yl]ethyl hydrogen sulfate (BTTES) or 3-[4-(bis[(1-tert-butyl-1H-1,2,3-triazol-4-yl)methyl]amino)methyl]-1H-1,2,3-triazol-1-yl]propyl hydrogen sulfate (BTTPS) have been investigated\textsuperscript{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\textsuperscript{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(II)acetate, copper in charcoal (3 wt%), bromotris(triphenylphosphine)copper(1), fluorotris(triphenylphosphine)copper(1) 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 CaH₂ under a nitrogen atmosphere prior to use. Benzophenone was predried over KOH and CuCl and freshly distilled over sodium and KOH under a nitrogen atmosphere prior to use. Tetrahydrofuran was predried over KOH and freshly distilled over sodium and KOH and was immediately put on the rheometer plate. Cross-linking experiments were performed with a strain \( \gamma \) of 0.1 % and with an angular frequency \( \omega \) ranging from 100 to 1 rad s\(^{-1}\). Gelation times 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_RH-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(PPh₃)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)

The synthetic-route to obtain 2-(6-azidomethyl)-pyridine-4-carboxylic acid (1a) was done according to literature with only slight changes: 2,4-pyridinedicarboxylic acid monohydrate (12.0 mmol, 2.0 g) was suspended in methanol (12.0 mL) and subsequently concentrated sulphuric acid (12.0 mmol, 640 \( \mu \)L) 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. \( R_1 (\text{EtOAc}) = 0.61 \). ¹H-NMR (CDCl₃, 400 MHz): \( \delta = 8.90 (dd, 1H, \ J_{HH} = 4.9 Hz, \ J_{HL} = 0.8 Hz, \ CH), 8.65 (dd, 1H, \ J_{HL} = 1.5 Hz, \ J_{HH} = 0.8 Hz, \ CH) \) after which the residue was dissolved in dichloromethane (30.0 mL) and water (30.0 mL). After stirring for two hours the solvent was removed under reduced pressure to provide the crude product, which was purified by dissolving in chloroform (3.3 mL) and sodium chloride (30.0 mL). The obtained solution was filtered and the organic layer was washed with a saturated solution of sodium chloride and dried over magnesium sulphate. The crude product was purified by dissolving in anhydrous tetrahydrofuran (3.3 mL) and sodium chloride (30.0 mL). The obtained solution was filtered and the organic layer was washed with 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 carried out for five hours and then allowed to cool to room temperature, after which it was dissolved in anhydrous methanol (12.0 mL). The solution was acidified with 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). ¹H-NMR (DMSO-\( d_6 \), 400 MHz): \( \delta = 8.51 (d, 1H, \ J_{HH} = 4.9 Hz, \ CH), 7.74 (s, 1H, CH), 7.66 (dd, 1H, \ J_{HH} = 4.9 Hz, \ J_{HL} = 1.1 Hz, \ CH), 4.48 (s, 2H, CH₂) ppm; ¹³C-NMR (DMSO-\( d_6 \), 100 MHz): \( \delta = 167.2, 155.7, 149.5, 149.2, 123.1, 122.4, 55.1 ppm. \)

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. ¹H-NMR (DMSO-\( d_6 \), 400 MHz): \( \delta = 8.99 (s, 1H, CH), 8.18 (dd, 1H, \ J_{HH} = 7.9 Hz, \ J_{HL} = 2.0 Hz, \ CH), 7.34 (d, 1H, \ J_{HH} = 7.9 Hz, \ CH), 4.49 (s, 2H, CH₂) ppm; ¹³C-NMR (DMSO-\( d_6 \), 100 MHz): \( \delta = 165.7, 156.0, 151.0, 137.9, 134.7, 121.7, 54.8 ppm. \)

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-hydroxymethyl)-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 excess of methanol. The final polymer was dried at high vacuum until constant weight to obtain 2,4-hexafunctional polyisobutylene (Mₙ(GPC) = 6520 g·mol⁻¹, \( M_w/M_n = 1.3 \). ¹H-NMR (CDCl₃, 500 MHz): \( \delta = 8.76 (d, 3H, \ J_{HH} = 5.0 Hz, \ CH), 7.90 (s, 3H, CH), 7.80 (dd, 3H, \ J_{HH} = 5.0 Hz, \ J_{HL} = 1.1 Hz, CH), 7.13 (s, 3H, CH of initiator) ppm, 13C-NMR (CDCl₃, 100 MHz): \( \delta = 157.0, 150.5, 138.4, 122.1, 121.1, 55.4, 52.8 ppm. \)

The synthetic route to obtain 2b was the same as described for...
2a, with the only exception that instead of using the esterification agent 1a it had been used its stereo-analogue 1b. (M$_d$(GPC) = 5780 g mol$^{-1}$, M$_w$/M$_n$ = 1.3). 1H-NMR (CDCl$_3$, 400 MHz): δ = 9.20 (s, 3H, CH$_3$), 8.34 (dd, 3H, $^3$J$_{H,H}$ = 8.1 Hz, $^4$J$_{H,H}$ = 2.1 Hz, CH$_3$), 7.46 (d, 3H, $^3$J$_{H,H}$ = 8.1 Hz, CH$_3$), 7.14 (s, 3H, CH$_3$ of initiator), 4.58 (s, 6H, CH$_2$), 4.34 (t, 6H, $^3$J$_{H,H}$ = 6.7 Hz, CH$_2$), 1.86 (s, 6H, 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$_d$(GPC) = 6560 g mol$^{-1}$, M$_w$/M$_n$ = 1.4). 1H-NMR (CDCl$_3$, 400 MHz): δ = 7.28 (d, 6H, $^3$J$_{H,H}$ = 8.9 Hz, CH of quenching agent), 7.13 (s, 3H, CH of initiator), 6.89 (d, 6H, $^3$J$_{H,H}$ = 8.8 Hz, CH of quenching agent), 4.66 (d, 6H, $^4$J$_{H,H}$ = 2.4 Hz, O–CH$_2$), 2.50 (t, 3H, $^3$J$_{H,H}$ = 2.4 Hz, C–CH$_2$), 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 substitution (III) of the corresponding alcohol to the azide -carboxylic acid methyl ester and phenylacetylene.

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(Table 1, entry 1). Changing the catalyst to [Cu(CH3CN)4]PF6 tested, resulting in an only poor conversion within nine hours.

First of all a commercially available Cu/charcoal catalyst was tested, resulting in an only poor conversion 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(PPh3)3 was also tested as catalyst due to its increased solubility in THF, caused by the attached triphenylphosphin-ligands. Surprisingly, CuBr(PPh3)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 clusters42, delivering an ideal catalyst system for fast click-reactions in solution.

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 | 9 h  | ---   | < 1 % |
| 2    | [Cu(CH3CN)4]PF6 | 24 h | ---   | 32 % |
| 3    | Cu(OAc)4 | 16 h | ---   | 82 % |
| 4    | CuBr4 | 9 h  | ---   | > 99 % |
| 5    | CuBr4 | < 5 min | 1.2 eq. | > 99 % |
| 6    | CuBr4 | < 5 min | 0.1 eq. | > 99 % |
| 7    | CuBr4 | 17 min | 0.01 eq. | > 99 % |
| 8    | CuBr(PPh3)3 | 2 h  | 0.01 eq. | 10 % |

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(CH3CN)4]PF6 (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(PPh3)3 was also tested as catalyst due to its increased solubility in THF, caused by the attached triphenylphosphin-ligands. Surprisingly, CuBr(PPh3)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, 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. 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(PPh3)3 as an alternative catalyst despite its relatively poor performance in the initial low molecular weight compound-tests. 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-
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.

| entry | mixture | catalyst | T [°C] | Gel t [min] | cM [M] | cCu [M] (10^{-2}) | k0 [M^{-3}min^{-1}] | k_{crossover} [M^{-3}min^{-1}] | r_0 [M·min^{-1}] |
|-------|---------|----------|--------|------------|--------|------------------|-----------------|-----------------|----------------|
| 1     | 2a + 3a | CuBr     | 20     | 870        | 0.254  | 2.54             | ---             | ---             | ---             |
| 2     | 2a + 3a | CuBr(PPh3)_3 | 20 | 255        | 0.254  | 2.54             | 2200            | 7300            | 0.092          |
| 3     | 2a + 3b | CuBr(PPh3)_3 | 20 | 266        | 0.254  | 2.54             | 400             | 1000            | 0.017          |
| 4     | [29]    | CuBr(PPh3)_3 | 20 | 290        | 0.238  | 2.38             | 700             | 2700            | 0.023          |
| 5     | 2a + 3  | CuF(PPh3)_3 | 20 | 15         | 0.254  | 2.54             | ---             | ---             | ---             |
| 6     | 2b + 3  | CuF(PPh3)_3 | 20 | 29         | 0.200  | 2.00             | 3100            | 9100            | 0.050          |
| 7     | 2b + 3  | CuF(PPh3)_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.

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 $k_0 \approx 700 \text{ M}^{-3} \cdot \text{min}^{-1}$ (Table 2, entry 4'), up to fourfold higher $k_0$-values (2200 – 3100 M$^{-3} \cdot \text{min}^{-1}$) 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 $\approx 400 \text{ M}^{-3} \cdot \text{min}^{-1}$ and is therefore just 1/5 of $k_0$ in entry 2, which is in contrast to identical gelation times of $\approx 260$ 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 $\approx 2500 – 3100 \text{ M}^{-3} \cdot \text{min}^{-1}$ (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 $v_x$ were determined for the finally cross-linked materials:

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

where $G_N$ is the measured plateau-modulus at $\omega = 100 \text{ Hz}$, $\rho$ is the density of the polymer mixture, $M_c$ is the average molecular weight of the polymer mixture, $R$ is the universal gas constant, $R = 8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $T$ 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 $v_{x, \text{max}}$ was calculated. By using the experimentally determined plateau moduli the experimental network strand density $v_{x, \text{exp}}$ 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).

Using CuBr as catalyst (Table 3, entry 1), both the plateau-modulus $G_N$ and the calculated network density $v_{x, \text{exp}}$ 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 $\nu \approx 2100 \text{ cm}^{-1}$ (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-ynylxoxymethyl)-1-(prop-2-ynylxoxy)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
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 \(\alpha\)-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.

![Image](image-url)
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Notes and references

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fast cross-linking at 10 °C