MONITORING KINETICS OF CROSSLINKING AZIDE/ALKYNE-"CLICK"-REACTIONS OF ENCAPSULATED REAGENTS IN SELF-HEALING POLYISOBUTYLENE MATERIALS

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Keywords: self-healing, poly(isobutylene), click-chemistry, kinetics, crosslinking

ABSTRACT

A new concept for self-healing systems based on the copper(I)-catalyzed azide/alkyne-"click"-reaction between liquid multivalent polyisobutylene (PIB)-azides (**1**) and liquid trivalent alkynes (**2-7**) in combination with the microencapsulation approach is reported. In response to applied stress, microcapsules filled with liquid polymers are ruptured and the encapsulated, liquid active materials are released to react under formation of a network via the azide/alkyne-"click"-reaction[1].

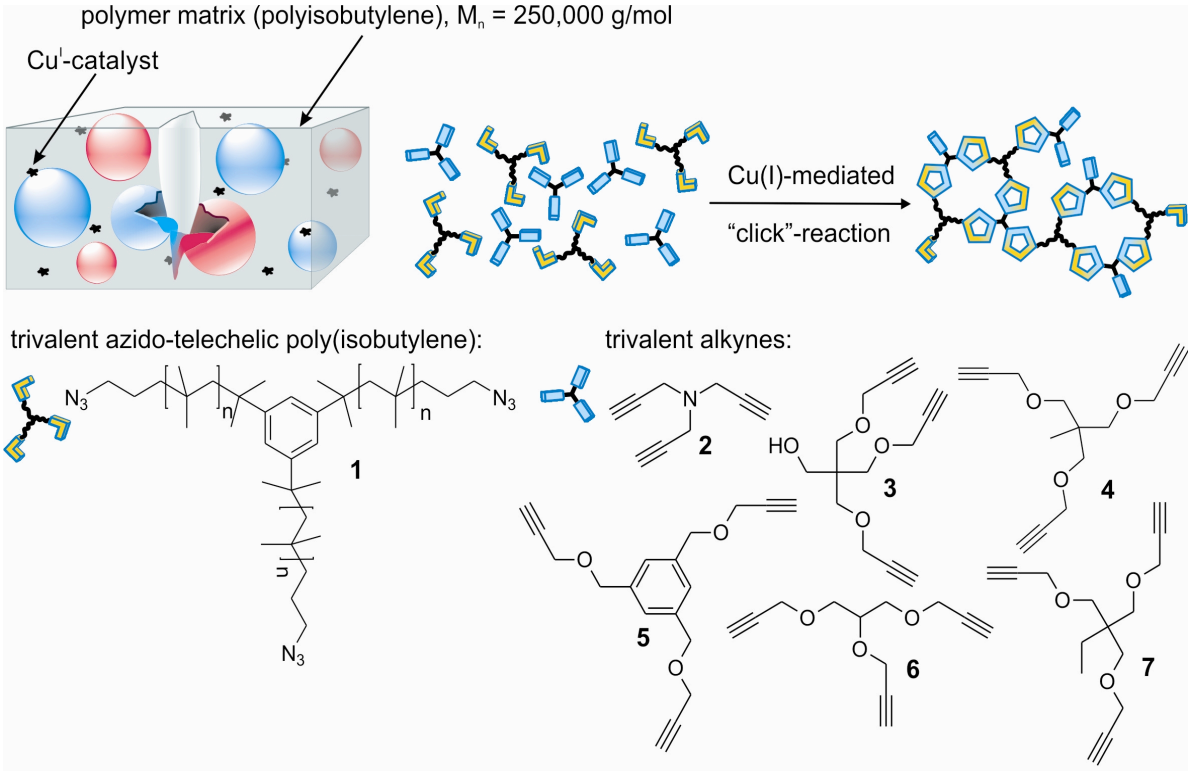

Figure 1: Concept of self-healing systems based on the copper(I)-catalyzed azide/alkyne-"click"-reaction between liquid multivalent polyisobutylene (PIB)-azides (**1**) and liquid trivalent alkynes (**2-7**) in combination with the microencapsulation approach.

Mono-, di- and trivalent azido-telechelic PIBs with low molecular weight (2000-4000 g/mol, prepared via living cationic polymerization) and low molecular weight trivalent alkynes were synthesized, and their crosslinking reaction studied during reaction. The azide/alkyne-"click"-reactions were carried out according to literature by testing a large variety of different Cu(I)-catalysts[2].

In order to obtain information about efficiency and kinetic behavior of the “click”-reactions between monovalent azido-telechelic PIB and trivalent alkynes (such as tripropargyl amine (**2**), tripropargylpentaerythritol (**3**), 3-[2,2-bis(prop-2-ynyloxymethyl)propyloxy]prop-1-yne (**4**), 1,3,5-tris(prop-2-ynyloxymethyl)benzene) (**5**), 1,2,3-tris(prop-2-ynyloxy)propane (**6**) and 2,2-bis(prop-2-ynyloxymethyl)-1-(prop-2-ynyloxy)butane (**7**) investigations in dependency on time, the applied temperature profile and the catalytic system a) directly on an ATR-IR crystal (solvent free state) and b) via ^{1}H-NMR spectroscopy (in THF solution) were conducted. Thereby, the homogeneous catalysts (such as $CuBr(PPh_3)_3$, $CuI{\cdot}P(OEt)_3$, $Cu(MeCN)_4PF_6$, $RuCl_2(PPh_3)_3$) as well as heterogeneous Cu(I)-catalytic systems (such as $CuSO_4{\cdot}5\ H_2O$/sodium ascorbate, CuBr) were tested by determination of the azide's half-life during the reaction. Kinetic investigations in solution showed a step-wise increase of the reaction rate corresponding to the number of the “click”-reactions already conducted on the same substrate due to intramolecular autoacceleration. After defining the most appropriate azide/alkyne/catalyst-system the “click”-reaction of trivalent azido-telechelic PIB with trivalent alkynes was accomplished similar to the previous kinetic experiments in dry THF. The azide/alkyne-“click”-reactions of trivalent azido-telechelic PIB together with the alkynes were monitored *ex-situ* via ATIR spectroscopy leading to the direct observation of the crosslinking “click”-reaction and thus the network-formation.

Subsequently, the trivalent azido-telechelic PIB and trivalent alkynes were successfully encapsulated separately in urea-formaldehyde capsules via an oil-in water-emulsion and then embedded together with the Cu(I)-catalysts into a poly(isobutylene) matrix (M_n = 250 000 g·mol^{-1}). Using $Cu^{I}Br(PPh_3)_3$ as catalyst for the azide/alkyne-“click”-reaction, crosslinking at 40 °C is observed within 380 minutes and at 80 °C within 10 minutes as determined via rheology measurement. Significant recovery of the tensile storage modulus was observed in a material containing 10 wt.-% and accordingly 5 wt.-% capsules including the reactive components within 5 days at room temperature, thus proving a new concept for materials with self-healing properties.

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