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Contributions of hard and soft blocks in the self-healing of metal-ligand-containing block copolymers

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ABSTRACT

The main aim of this work is to study the respective contribution of the hard and soft blocks of a metal-ligand containing block copolymer to the self-healing behavior. To this aim, different block copolymers containing terpyridine were synthesized using reversible addition-fragmentation chain transfer (RAFT) polymerization. These block copolymers consisted of polystyrene as the hard block, *n*-butyl acrylate (BA) as soft block and terpyridine units as the ligand moiety placed at different locations in the soft block. These block copolymers were complexed with manganese(II) chloride to introduce transient crosslinks and, thus, self-healing behavior. Homopolymers with the hard and soft block only were also synthesized and tested. A quasi-irreversible crosslinking, *i.e.* by using nickel(II) nitrate, was performed in order to study the dynamics of the permanently (strongly) crosslinked network. Rheological master curves were generated enabling the determination of the terminal flow in these networks and the reversibility of the supramolecular interactions. Additionally, the macroscopic scratch healing behavior and the molecular mobility of the polymer chains in these supramolecular networks were investigated. A kinetic study of the scratch healing was performed to determine the similarities in temperature dependence for rheological relaxations and macroscopic scratch healing. In our previous work, we have explored the effect of strength of the reversible metal-ligand interaction and the effect of changing the ratio of hard to soft block. This work goes further in separating the individual contributions of the hard and soft blocks as well as the reversible interactions and to reveal their relative importance in the complex phenomenon of scratch healing.

1. Introduction

Block copolymers have been widely investigated due to the possibility of obtaining unique combinations of properties resulting from the different blocks not obtainable in random copolymers. For several decades, a number of research groups have reported on microphase separation of block copolymers [1–3]. The tunable synthesis of block copolymers can be used for wide-ranging applications such as stimuli responsive polymers [4–8], controlled drug delivery [9–11], and controlled permeability [12,13]. In recent years, block copolymer networks featuring self-healing ability have been investigated [14–16]. A key challenge in the design of

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intrinsic self-healing polymers is to enable temporary mobility of the polymer network using reversible bond formation while at the same time maintaining the structural integrity of the network. By the incorporation of two distinct polymer blocks with a different viscoelastic behavior, a balance between the two competing properties: mechanical robustness of the glassy block and viscous flow of the soft block can be achieved resulting in an enhancement of the overall material performance.

Intrinsically healable polymers have reversible chemical or physical linkages incorporated within the polymer structure and, consequently, do not require any additional healing agent such as a solvent, catalyst or monomer [17]. Examples of reversible chemical and physical linkages are Diels-Alder reactions [18–23], hydrogen bonding interactions [24–27], ionic clusters in ionomers [28–33], and metal-ligand bonds [26,34–39], which are also used in this contribution. Self-healing behavior is achieved *via* a thermally reversible bond between the metal cation and a terpyridine ligand [40]. These supramolecular interactions can have a range of strengths, directionality as well as a variety of coordination geometries and reversibility [37,41–44]. As reported previously, the dynamics of reversible crosslinks is the primary influencer of the bulk viscosities and, thus, of the resulting healing behavior in supramolecular networks [45].

In this work, we designed a supramolecular block copolymer, in which the soft block bears the reversible moieties. Polystyrene is used as the hard block and the soft block consists of *n*-butyl acrylate (BA) and the ligand moiety (terpyridine). Control experiments were performed by using nickel(II) nitrate resulting in a quasi-irreversible crosslinking as well as by synthesizing homopolymers of the hard or soft block. We used micro-scratch testing and image analysis of the disappearing scratches to quantify self-healing and its kinetics. We performed rheological experiments to study the relaxations of the transient interactions and the polymer backbone. Time-temperature superposition enables us to construct two master curves to analyze the network response over a broad range of time scales. The temperature dependence of the shift factors was used to demonstrate the mechanistic correspondence for rheology and scratch healing. Our previous publications have established the effect of using metal salts of varying complexation strengths [46] as well as the effect of changing the position and ratio of the hard and soft blocks [47]. However in this work we study in detail the individual contribution of the hard and soft blocks as well as the correlation of rheological behavior to macroscopic scratch healing.

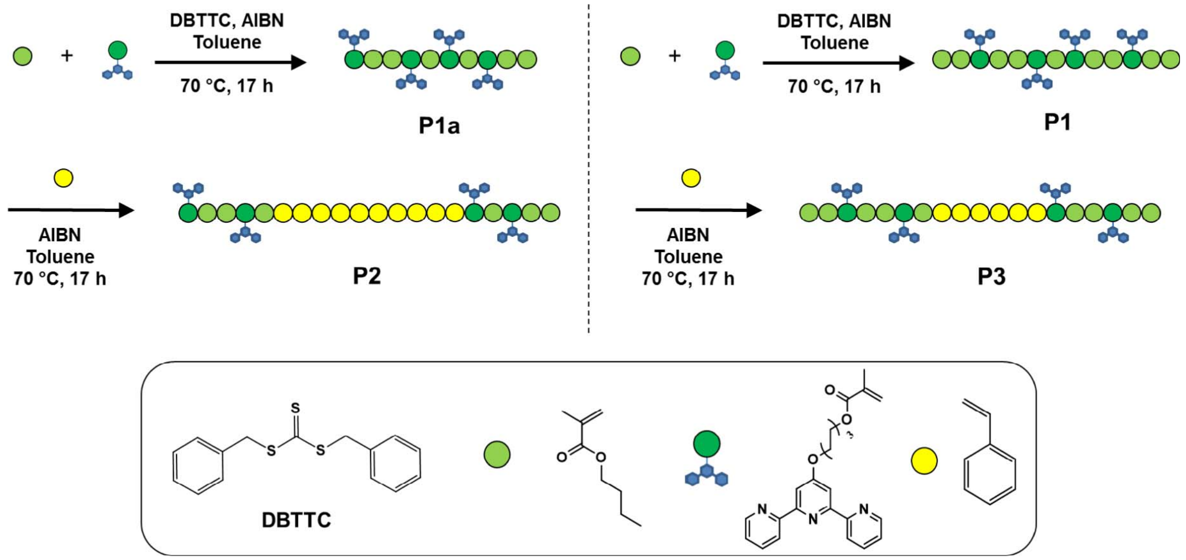
2. Experimental

2.1. Materials

All chemicals used were purchased from Fluka, HetCat, Aldrich, and TCI and used without further purification. 6-(2,2′:6′,2″-Terpyridin-4′-yloxy)-hexyl methacrylate was synthesized according to literature procedures [48]. For ease of reading, the polymers are referred to as **P1** to **P4** and the metallopolymers **MP1** to **MP4**. **P1** to **P4** and **MP2** and **MP3** were prepared according to the literature [47]. *N*-Butyl acrylate and styrene were passed over a short neutral aluminum oxide plug before use. The solvents were dried by refluxing over sodium/benzophenone (toluene) or dried with calcium chloride (chloroform and triethylamine).

2.2. Polymer synthesis

The block copolymers discussed in this study were synthesized by RAFT-polymerization using *S*,*S*-dibenzyl trithiocarbonate (DBTTC) as chain transfer agent [47]. In the first step, *n*-butyl acrylate and the terpyridine monomer were copolymerized resulting in copolymers **P1** and **P1a** (Scheme 1). Subsequently, the copolymers were utilized for the preparation of the block copolymers. For this



Scheme 1. Schematic representation of block copolymer synthesis of **P2** (hard-soft block ratio: 1:1) and **P3** (hard-soft ratio: 1:2).