A STUDY OF THE TEMPERATURE DEPENDENT HEALING CAPABILITIES OF NEW POLYMERS BASED ON DIELS-ALDER CYCLOADDITION

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ABSTRACT

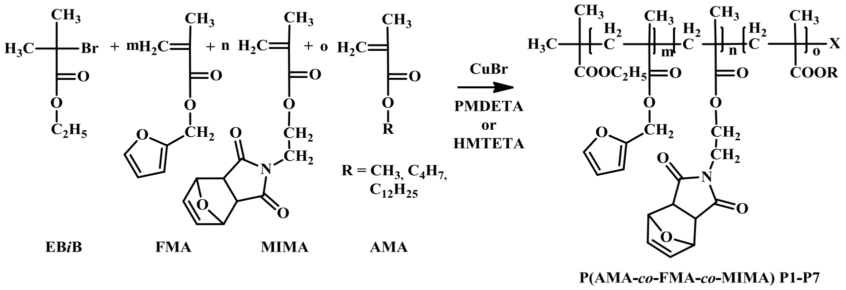
Because of its thermal reversibility, the retro-Diels-Alder (RDA) reaction represents an appealing possibility to produce self-healing polymers with well-defined architectures and tunable properties [1]. However, the polymer architecture for which the Diels-Alder (DA) reaction can best be used to contribute to the healing process is still not well-defined. Therefore, new terpolymers containing moieties for the reversible crosslinking by the DA reaction have been synthesized. These linear polymers are based on a methacrylate backbone containing both functionalities in the side chains and represent a one component self-healing system. As a desirable consequence no separate (low molar mass) crosslinker is necessary to obtain the desired self-healing properties. A protected maleimide is used as functional co-monomer which can be activated after polymerization. Upon the occurrence of local damage the crosslinked material can be heated to a certain temperature, where the retro-Diels-Alder reaction takes place and the material obtains the necessary local mobility for damage closure. Upon cooling to room temperature, the coupling of the two reactive functional groups takes place and the strength of the material is restored. The synthesis of these terpolymers with maleimide methacrylate (MIMA) and furfuryl methacrylate (FMA) as functional units for the DA cycloadditon and different co-monomers in different ratios were achieved by applying the atom transfer radical polymerization (ATRP). Besides the characterization of the obtained polymers by ^{1}H NMR spectroscopy, SEC, and MALDI-TOF MS, the thermal properties were investigated by TGA and DSC. The damage healing was studied by AFM and SEM. To obtain further details on the healing mechanism at the nanoscale additional temperature dependent FTIR measurements during and after shear flow were made.

1. INTRODUCTION

Self-healing materials are currently in the focus of intensive research. Due to their remarkable ability to heal local mechanical damage such as cracks and scratches, they represent promising candidates for a wide range of applications. The ability for self-healing offers the opportunity to increase the life time of the applied materials which is also associated with less repair events as well as less total replacement of these materials [2]. Therefore, in this project, we synthesized new terpolymers containing functional moieties for the reversible crosslinking by the Diels-Alder reaction which have the ability to heal cracks autonomously after reaching a certain temperature.

2. MATERIALS

The new terpolymers contain MIMA and FMA as functional units for Diels-Alder reactions and different co-monomers in different ratios. As co-monomers methyl methacrylate (MMA, **P1**-**P3**), butyl methacrylate (BMA, **P4**-**P6**) and lauryl methacrylate (LMA, **P7**) were used (Scheme 1). The polymers were prepared via ATRP and characterization was carried out using ^{1}H NMR spectroscopy, SEC, MALDI-TOF MS, TGA and DSC measurements [3].



Scheme 1. Schematic representation of the copolymerization of alkyl methacrylates (AMA), FMA and MIMA by ATRP polymerization.

3. METHODS

The self-healing studies were made using AFM and SEM. AFM measurements were performed in tapping mode with a NTegra Aura (NT-MDT, Moscow, Russia) with commercially available non-contact cantilevers (NSC35, MicroMash). The scratches were performed by using the lithographic mode of the AFM software by dragging the AFM tip at high forces along a line/cross over the surface. Further self-healing experiments and the surface topography were measured using a scanning electron microscope LEO-1450 VP (Variable Pressure) from Carl Zeiss SMT. For this purpose, the crosslinked films were scratched with a hollow needle in a controlled manner to prepare larger scratches, annealed for individual timescales to obtain the different healing states at different temperatures and sputtered with a 10 nm thick gold layer before the measurement. Rheology with in situ FTIR was carried out with a ThermoFisher Haake Mars III rheometer coupled to a Nicolet iS10 ATR-FTIR. The rheology with *in situ* FTIR was employed to study the rheology of crosslinking of the polymer followed by reversible heating and cooling cycles to ascertain reversible changes in mechanical properties along with spectroscopic changes in the Diels-Alder adducts in the polymer. These tests allowed following the cyclic and reversibly occurring Diels-Alder and retro-Diels-Alder reactions. The ratio of the peak height of the furan ring breathing at 1065 cm^{-1} and that of the carbonyl stretch at 1724 cm^{-1} was monitored and used to quantify the healing.

4. RESULTS

The DSC measurements provide highly useful insides into the reversibility capabilities of the copolymers. As depicted in Figure 1 an important precondition for the suitability of self-healing properties of a polymer is the presence of different characteristic transitions during the heating cycles of the DSC measurement. An endothermic peak in the 1st heating curve is expected above 120 °C caused by the energy required for the retro-Diels-Alder reaction and the subsequent evaporation of the furan (protecting group). In addition, the glass transition temperatures (T_g) of the non-crosslinked copolymers should be visible. In the 2nd heating curve the endothermic peak at the T_{RDA} should appear again; however, the area below the curve will be smaller because only the energy of the retro-Diels-Alder reaction is visible; the energy of the evaporation process can not be observed. The appearance of this peak in the 2nd heating curve is a precondition for the later healing process. It depends on the properties of the copolymer, like the co-monomer which causes the flexibility/mobility of the chain and the glass transition temperature.

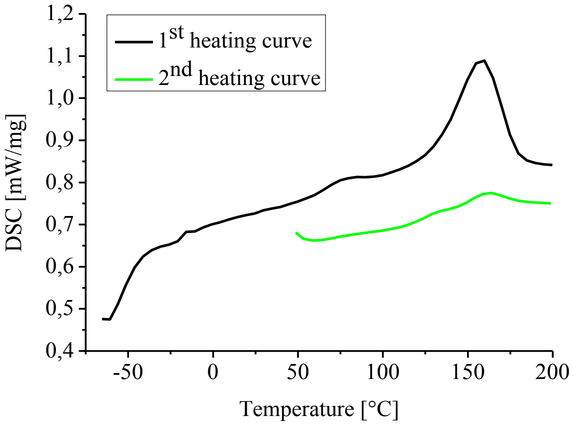


Figure 1: DSC analysis of copolymer **P7**.

The study of the self-healing properties of copolymer **P7** was this time performed by using SEM for visualization (Figure 2). A scratch was created using a hollow needle. Afterwards, the films were annealed for 1 and 3 min at 160 °C, respectively. After only 1 min the scratch was only lightly visible while after 3 min the scratch disappeared completely. Copolymer **P7** has the ability to heal also scratches on a millimeter scale (length).

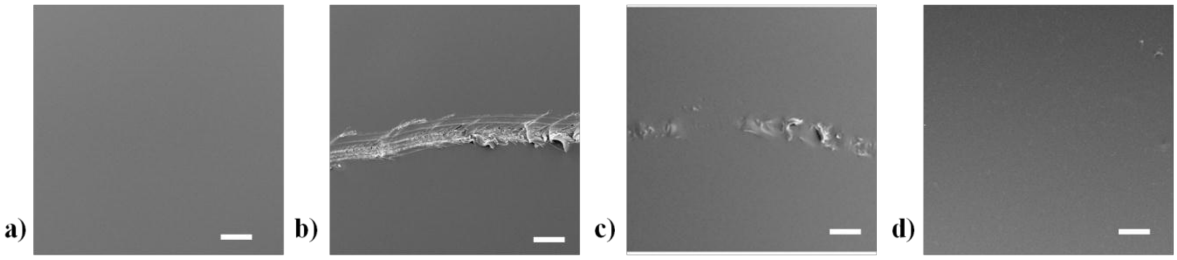


Figure 2: Self-healing experiment of copolymer **P7**. a) Film after crosslinking, b) scratch before annealing, c) scratch after annealing at 160 °C for 1 min and d) scratch after annealing at 160 °C for 3 min (scale bars = 100 µm).

Rheological experiments performed on **P7** at a constant angular strain of 0.1% showed reversible transition of the polymer network indicating flow of the polymer chains which manifest as the healing behavior. Furthermore, quantitative ATR-FTIR showed reversible appearance and disappearance of the furan moiety, as further indication of the Diels-Alder and retro-Diels-Alder reactions as shown in Figure 3.

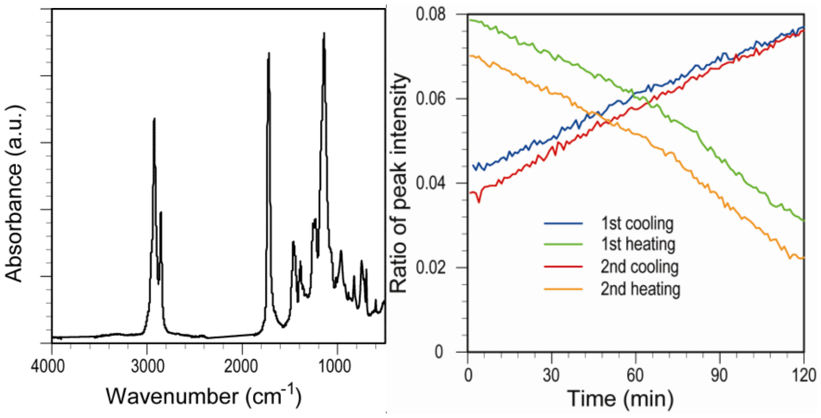


Figure 3: (a) FTIR spectra of the crosslinked polymer prior to the heating and cooling cycles. For quantitative analysis, the peak height ratio of the furan ring breathing at 1065 cm^{-1} to the carbonyl stretch at 1724 cm^{-1} was calculated, and (b) cycling between temperatures of 40 and 160 °C show reversible appearance and disappearance of the furan peak. For each cycle, the temperature was held constant for 120 min.

5. CONCLUSIONS

Well-defined polymers with a methacrylate backbone and the ability to undergo Diels-Alder reactions in the side chain have been produced showing healing behavior at moderate temperatures in the absence of an additional low molar mass crosslinking agent. The copolymer **P7** fulfills all prerequisites for an effective self-healing polymer. Therefore, to the best of our knowledge the described polymers are the first examples for one-component self-healing materials with the complementary Diels-Alder functionalities in the side chain which can reversibly associate and dissociate leading to self-healing behavior.

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REFERENCES

[1] S. D. Bergman, F. Wudl, Mendable polymers, J. Mater. Chem. 18 (2008) 41-62.
[2] S. van der Zwaag in *Self healing materials*. *An alternative approach to 20 centuries of materials science* (Eds.: S. van der Zwaag, A. J. M. Schmets, G. d. van Zaken), Springer, Dordrecht, The Netherlands, (2007) 1-18.
[3] J. Kötteritzsch, S. Stumpf, S. Hoeppener, J. Vitz, M. D. Hager, U. S. Schubert, One-component intrinsic self-healing coatings based on reversible crosslinking by Diels-Alder-cycloadditions, Macromol. Chem. Physic. (2013), DOI: 10.1002/macp.201200712.