Dynamics and Welding Behavior of Metallosupramolecular Polymer Films

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Supramolecular polymers that bear a reversible and dynamic linkage between individual macromonomers possess intriguing materials' properties including scratch healing and welding of films.^{1,2} Comparing the macroscopic mechanical properties of healed or welded samples to those of their pristine counterparts allows one to quantify the healing or welding progress, respectively.³ However, a better understanding of the underlying mechanisms is necessary to allow for a precise engineering of such materials. In order to elucidate the role of molecular mixing and interphase generation during the welding process, we combined bulk mechanical investigations with an analysis of the network relaxation and microscopically explored the reshuffling at the interface. This approach allowed us to gain a deeper understanding of the rearrangements that restore the original materials' properties of metallosupramolecular polymers (MSPs).



Figure 1: Schematic of the formation of Eu^{3+} and Tb^{3+} -based metallosupramolecular polymers and a mixed interphase upon welding films of the two materials at elevated temperature.

Flexible MSP films were prepared by coordination of either Eu³⁺ or Tb³⁺ ions to telechelic poly(ethylene-*co*-butylene) end-capped with methylbenzimidazolyl pyridine ligands and subsequent compression-molding. These films can be healed or welded upon exposure to elevated temperatures or UV-light.⁴ Accordingly, the progress of the welding process of films on the macroscopic level was evaluated by mechanical testing. Moreover, films that each featured a different metal ion were welded to analyze the diffusion of metal ions and the growth of an interphase on a microscopic scale by scanning transmission electron microscopy with energy dispersive X-ray spectroscopy. In combination with rheological measurements, the molecular processes can be directly correlated with the macroscopic welding efficiency. The results establish an improved understanding of these dynamic processes, which is a prerequisite in developing materials with tailored properties.

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