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Molecular Dynamics in Vitrimers: Effects of Molecular Weight and Crosslinking in PnBMA

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The thermal, viscoelastic, and dynamic properties of poly(n-butyl methacrylate) (PnBMA) vitrimer samples were investigated as a function of molar mass and crosslink density. The sample set includes a high molar mass series comprising the homopolymer, vitrimer precursor, and vitrimers with 1% and 5% crosslinking. Additionally, a low molar mass set was provided, in which the vitrimer contains 3% crosslinking. Thermal properties were investigated with Temperature-Modulated DSC, which revealed an increasing T_g with vitrimer content. The local and segmental dynamics were investigated by DS. A failure of tTs for the local dynamics, as measured by DS, was due to the merging of α- and β-process.

Chain dynamics were examined through rheology. Vitrimers exhibited an extended elastic plateau (phase angle, $\delta \sim 1°$) with an asymmetric shape, indicating an inhomogeneous distribution of crosslinks. The analysis of the T-dependent shift factors $a_T(T)$ revealed a change from Williams-Landel-Ferry (WLF) to an Arrhenius T-dependence at a crossover temperature T_x. It was shown that $T_x/T_g \sim 1.3 - 1.4$. These findings emphasize the role of dynamic crosslinks in governing vitrimer relaxation and the difference in length and timescales.

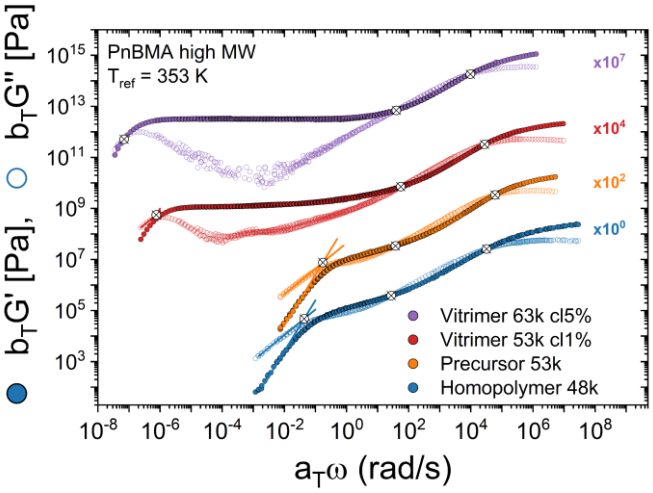

Figure 1. Master curves of the frequency-dependent storage (G'-filled symbols) and loss (G''-open symbols) moduli of homopolymer (blue), vitrimer precursor (orange), vitrimer with 1% crosslinks (red), and vitrimer with 5% crosslinks (purple), for the high molar mass PnBMA all at the same reference temperature. Lines with respective slopes of 2 and 1, are used to obtain the terminal (flow) characteristic frequency. Crossed circles are used to indicate characteristic frequencies.

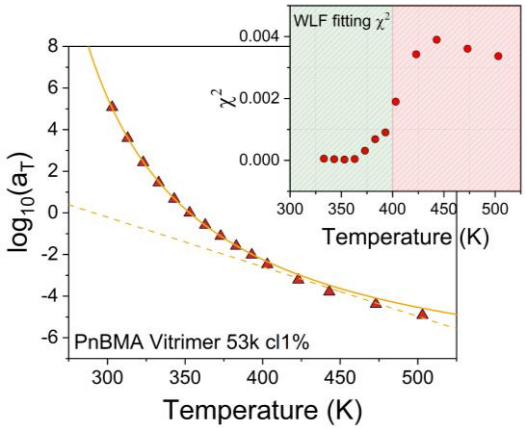

Figure 2. Horizontal shift factors, a_T, from the master curve in Figure 1 plotted against T for the PnBMA vitrimer ($53\ kg \cdot mol^{-1}$, 1% crosslink). The transition from WLF to Arrhenius behavior is identified by analyzing the χ^2 parameter (inset). The WLF fit (solid line) includes data in the green-shaded region, while the pronounced deviations are within the red-shaded region.