

Abstract Submitted  
for the MAR17 Meeting of  
The American Physical Society

**Tuning polymer dynamics by chain-end association** MARTIN TRESS, KUNYUE XING, University of Tennessee Knoxville, PENGFEI CAO, SHIWANG CHENG, TOMONORI SAITO, Oak Ridge National Lab, VLADIMIR NOVIKOV, University of Tennessee Knoxville, ALEXEI SOKOLOV, University of Tennessee Knoxville; Oak Ridge National Lab — Functional end groups in polymers are a molecular tool to reversibly connect and disconnect chains to combine properties of both short polymer and large supramolecular structures. The topology of the latter and in turn the respective properties can be tuned by the choice of the functional group. This is shown in a series of polydimethyl siloxanes (PDMS) of different molecular weight (MW) which are terminated by amino and carboxylic (-COOH) groups, respectively. Differential scanning calorimetry and dielectric spectroscopy measurements reveal that segmental dynamics are identical for the chains with two different end groups. In contrast, rheology unravels a mechanical reinforcement for PDMS-COOH and a rise in viscosity by 2 decades. This is accompanied by a 2nd Tg and a corresponding dielectric relaxation process which indicates phase separation of the end groups in clusters forming a physically crosslinked network. As a consequence, the viscoelastic properties can be tuned from common short polymer chains at high temperatures to highly entangled or even crosslinked systems at T close and below the 2nd Tg. This suggests a promising route to combine easy processibility of low MW polymers with the desired mechanical performance of high MW polymers or even crosslinked networks.

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Date submitted: 13 Nov 2016

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