

~~~~ Polymer Physics Seminar ~~~~

**Kevin A. Masser**

Materials Science and Engineering, Penn State University

Advisor: Professor James P. Runt

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301 Steidle Bldg.

**Dynamics of Hydrogen Bonding Polymer Blends  
Exhibiting Minimized Self Associations and Liquid  
Crystalline Polymers of Unique Chemistry**

The dynamics and states of hydrogen bonding in miscible polymer blends which preferentially form intermolecular associations are investigated. A homopolymer and a copolymer based on poly(*p*-(hexafluoro-2-hydroxyl-2-propyl)styrene) (PolyHFS) form strong intermolecular associations, while the two-CF<sub>3</sub> groups on the polymer provide steric shielding around the hydroxyl group, reducing the ability to form hydrogen bonds with other PolyHFS molecules, while maintaining the ability to form intermolecular associations with another polymer. As well as the HFS homopolymer, a copolymer of the HFS monomer with 2,3-dimethylbutadiene (DMB) was synthesized (HFS[14]:DMB[86]). Purified PolyHFS was blended with a variety of proton accepting polymers, including poly(vinyl methyl ether) (PVME), poly(2-vinyl pyridine) (P2VPy), poly(vinyl acetate) (PVAc), poly(ethylene[30]-ran-vinyl acetate[70]) (EVA70), and poly(ethylene[55]-ran-vinyl acetate[45]) (EVA45). The purified HFS[14]:DMB[86] was blended with PVME. The selection of proton accepting polymers allows for a systematic variation of the hydrogen bonding strength: P2VPy >> PVME > vinyl acetate, as well as a systematic variation of the numbers of interacting sites: PVAc > EVA70 > EVA45, and PolyHFS > HFS[14]:DMB[86]. Broadband dielectric relaxation spectroscopy was used to evaluate the relaxation behavior of the blends. Fourier transform infrared spectroscopy was used to quantify the hydrogen bonding types and concentrations. HFS[14]:DMB[86] blends with PVME exhibit a single glass transition temperature, and a single dynamic glass transition ( $\alpha$  relaxation). The glassy state motion of PVME in the copolymer blends is not suppressed, since a relatively small number of HFS segments are present at any composition. In contrast, the local motion of the HFS:DMB copolymer, related to motions of the HFS segment, is completely suppressed by hydrogen bonding in all blends. Glassy state motions are suppressed in the PVME and P2VPy blends with the HFS homopolymer, and the suppression is dependent on the functional group accessibility. Due to the reduced hydrogen bond strength between HFS and the vinyl acetate functionality, local relaxations are not suppressed in these blends. A local relaxation for free functional groups as well as hydrogen bonded functional groups is present, and the magnitude of these processes can be quantified by the predictions of the Painter-Coleman association model. The HFS homopolymer blends all exhibit a single glass transition, and a single  $\alpha$  relaxation. The dynamic fragility can be related to the fraction of intermolecularly associated segments, and the compositions with the highest fragilities can be predicted in the EVA blends. A relaxation related to the breaking and reforming of hydrogen bonds is present in all HFS homopolymer blends, and its relaxation behavior is dependent on the numbers and strengths of intermolecular associations. Finally, the dynamics of main chain liquid crystalline polymers consisting of rigid mesogens and siloxane spacer segments are investigated. These immiscible segments are covalently bound, and the immiscibility gives rise to their unique structures.