

Spectroscopic Analysis of Phase Separation Behavior in Model Polyurethanes

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Because of their incompatible structural components, segmented polyurethanes mainly exist as phase separated systems. The degree of phase separation as reflected in the size and perfection of the domains is the most important criterion for the determination of overall sample mechanical properties. Although phase separation kinetics of polymer mixtures have been active areas of study, few investigations have been carried out to characterize the phase separation kinetics of polyurethane block copolymers. Not only is the characterization of the phase separated structure present in segmented polyurethanes important from a practical standpoint, but also the mechanism associated with the phase separation is extremely interesting from a fundamental viewpoint as well. The connectivity between the components, the effect of chain stiffness, and the polydispersity of the hard or soft segments are important parameters which need to be examined in greater detail in order to more fully understand the phase separation mechanism.

In this study we have characterized the phase separation behavior of well defined polyurethanes consisting of the reaction product of [(methylene-bis-(para-phenyl-isocyanate)] (MDI) and butanediol (BD) as the hard segments and polypropylene oxide (PPO) as the soft segment. The success in utilizing vibrational spectroscopy for the study of phase separation depends on the existence of bands sensitive to mixed and phase separated states, respectively. We assigned spectroscopic features characteristic of urethane linkages dispersed in the soft segments as compared to interurethane hydrogen bonding confined to hard segment domains. With a specially designed sample cell, we were able to trap a phase mixed structure at a temperature 60°C below the glass transition temperature of the soft segments. When this quenched sample was brought up to a higher temperature, the increase of one spectroscopic component and the corresponding decrease of the other, provided a direct measurement of phase separation kinetics.

The initial findings associated with a well defined model polyurethane are reported. The phase separation behavior has been interpreted to proceed by a nucleation and growth mechanism with a two dimensional growth initially, followed by a diffusion dominated mechanism.