

## Microstructures in Methylhydrosiloxane Copolymers and Their Impact On The Functionalized Silicone Polymers

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Methylhydrosiloxane [D<sup>H</sup>] containing copolymers serve as a key building block for generating a variety of functional silicone materials due the accessibility and facile reactivity of backbone Si-H toward a variety of organometallic reactions viz. hydrosilylation, dehydrocoupling, dehydroamination, hydroxylation etc. [1,2]. In the methylhydrosiloxane copolymers, however, there are various microstructures possible depending upon the D/D<sup>H</sup> sequence as well as the stereochemistry around the D<sup>H</sup> units. For many of these functionalized silicone polymers, these microstructural differences may play a vital role in controlling the reactivity as well as the final material properties. In this paper, the impact of such microstructural variations were studied in detail by further functionalizing the microstructurally different yet compositionally identical poly methylhydrosiloxane copolymers into comb-like unbranched alkyl side chain siloxane copolymers. Differential scanning calorimetry (DSC) studies of these comb-like polymers have revealed that the dissociation energy of crystal domains formed by the side chain alkyl grafted on a randomly distributed siloxane backbone is much lower compared to that of the alkyl chains grafted on the block rich siloxane backbone. Small-angle X-ray diffraction (SAXD) results proved that these two comb-like polymers follow different crystallization pathways. The random copolymer crystallizes in end-to-end packing mode of the side alkyl chains whereas the block rich copolymer predominantly crystallizes in a highly ordered structure using an interdigitated packing route of the side chains. The concomitant involvement of the main chain siloxanes towards building of such hierarchical packing was also evident from the temperature dependent Fourier-transform infrared spectroscopy (FTIR) studies of the copolymers. The effect of alkyl impurity as well as the variation of alkyl chain length on the packing behaviour are discussed in relation to molecular chain mobility.

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