

The inter and intra-molecular dynamics of polymethylphenylsiloxane under 1-D and 2-D confinement

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Broadband dielectric (BDS) and Fourier transform Infrared (FTIR) spectroscopy are employed to study molecular dynamics of polymethylphenylsiloxane (PMPS) in 1-D and 2-D geometrical constraints. PMPS under the former confinement of thin films down to thickness of 7 nm spin cast on highly conductive silicon wafers in combination with nanostructured counter electrodes are studied by BDS while in the latter case, PMPS infiltrated into porous silica membranes with unidirectional nanopores having diameters down to 4 nm are probed by both BDS and FTIR. The glass transition temperature (T_g) of thin films for all the thickness investigated remained bulk-like but the segmental relaxations of PMPS in nanopores is faster than bulk and changes from VFT to Arrhenius-like temperature dependence for small pores (4 nm). This is attributed to the density inhomogeneity as a consequence of altered molecular packing under confinement in nanopores. Additional slower process observed in native pores is due to attractive interactions of molecules with pores walls. The vibrations of IR active moieties in PMPS follow different temperature dependencies in both the spectral position and the oscillator strength. The phenyl ring and the $\nu_{ar}(C-H)$ stretching vibrations exhibits a kink at T_g and at ca 30 K above T_g . This is attributed to coupling between intra vibrations of phenyl ring and the segmental relaxation.

References

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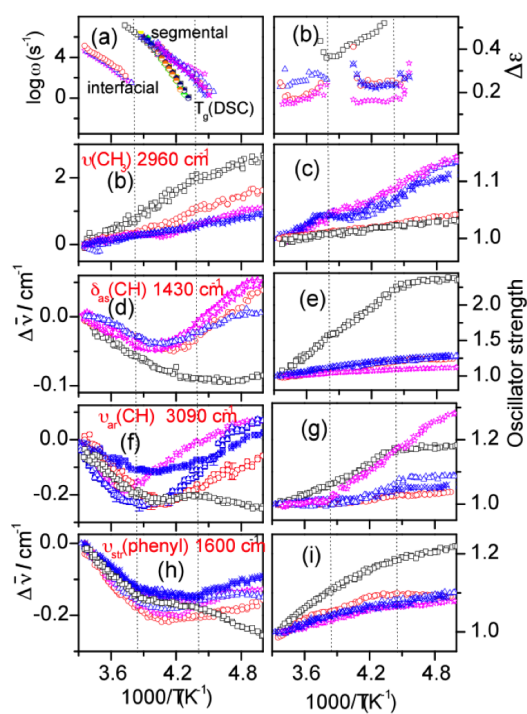


Figure 1: Comparison of inter and intra-molecular dynamics of polyphenylmethylsiloxane in 1- and 2-D dimensional confinement: (a) inter molecular segmental dynamics from BDS; bulk (filled squares), confined in nanoporous silica of pores sizes: -8 nm (circles), 6 nm (triangles) 4 nm (stars). Crossed symbols denote silanized pores. Half filled symbols are dynamics in thin films ranging from 80–7 nm thickness. (b) the corresponding dielectric strength of bulk and confined in pores. (b–i) the temperature dependence of bandshift of the spectral position and oscillator strength of the intra-molecular IR-vibrations in PMPS.