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Aminophenyl double-decker shaped silsesquioxanes: Physical, thermal characterization and applications

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A recently developed class of nano-structured, cage-like silsesquioxanes, formally known as double-decker shaped silsesquioxanes (DDSQ), offers the opportunity to form hybrid polymers with silsesquioxane cages as a part of the polymer backbone. Unlike functionalization of trisilanol silsesquioxanes, functionalized DDSQs generate *cis* and *trans* isomers with respect to the Si-O core. Therefore, it is logical to characterize physical and thermal properties of mixtures with different ratios of *cis* and *trans* isomers. Moreover, these characteristics are also relevant when reacting or incorporating these isomers, or mixtures thereof, with other molecules to form novel materials. In this study, three aminophenyl DDSQs were synthesized. More specifically, two meta-aminophenyl DDSQs, which were differentiated according to the moiety attached to the D-Si (methyl or cyclohexyl), and one para-aminophenyl DDSQ with a methyl moiety were used. Chemical, physical, and thermal characteristics were evaluated for individual isomers as well as binary mixtures of different *cis*/*trans* ratios. Phase diagrams representing solid-liquid melt equilibria of the binary *cis*/*trans* mixtures were developed. Single crystal X-ray diffraction data of isolated isomers helped to interpret the phase behavior. A specific application was chosen to demonstrate advantages of using these DDSQ in high performance thermosetting oligoimides over their organic counterparts. Specifically, they exhibited advantages in areas of liquid to solid *trans*ition and viscosity, which greatly expand the processing window. Additionally, they improve oxidative stability and reduce moisture uptake which provided a significant enhancement for service reliability.

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