

Solid-state polymerization of a novel cyanate ester based on 4- tert -butylcalix[6]arene

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Abstract

© 2020 The Royal Society of Chemistry. A unique cyanate ester based on 4-tert-butylcalix[6]arene has been synthesized. It melts above 400 °C and polymerizes on heating above 300 °C, i.e., in the solid state. The techniques of FTIR, pXRD, NMR, MALDI, TGA, DSC, and fast scanning chip-calorimetry have been used to characterize the monomer and its polymerization. The kinetics of solid-state polymerization has been analyzed by an advanced isoconversional method that has revealed that the process rate is limited by a single step. The activation energy of the process has demonstrated an unusually large value, 380 ± 10 kJ mol⁻¹, which points at cooperative breaking of CN bonds as the rate limiting step. This is in contrast to the regular cyanate esters that polymerize in the liquid-state by consecutive breaking of CN bonds. It has also been found that the polymerization follows zero-order kinetics, which is explained by the topochemical nature of polymerization localized on the surface of the plate-like crystals of the monomer.

<http://dx.doi.org/10.1039/d0py00554a>

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