

Aryl-substituted Silanediols as Molecular Precursors for Solventless (Poly)Condensation Reactions

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Polysiloxanes are usually prepared by polycondensation reactions from dichloro- or dialkoxysilane precursors, which are typically hydrolyzed in an acid-catalyzed reaction which is followed by an immediate condensation of the commonly unstable silanol intermediates.^[1] From a synthetic point of view, it would be advantageous if the hydrolysis of the precursors could be separated from their condensation. This leads to better control of the properties of the resulting condensation products. Stable organosilanols can therefore serve as precursors for thermal condensation reactions, to produce siloxanes. In the crystalline solid state, they often exhibit distinct networks of hydrogen bonds.^[2-4] This pre-orientation of the molecules in the crystals can lead to preferential stereochemistry of the condensation products.^[5] Step 1:











Conclusion

The condensation kinetics observed by NMR spectroscopy revealed a strong dependence on condensation temperature, time and substitution pattern at the silicon atom. SEC measurements showed an increased chain length with increasing condensation temperature, time and lower steric demand. Thermal analysis showed the same behavior with increasing T_g. The thermally induced aryl cleavage was investigated in terms of the temperatures required (> 150 °C) and the substitution pattern. In the process, larger aryl groups split off more easily than smaller ones. X-Ray single crystal structures of the silanediols could be correlated with structures of the condensed products.

References

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