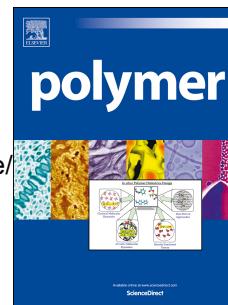


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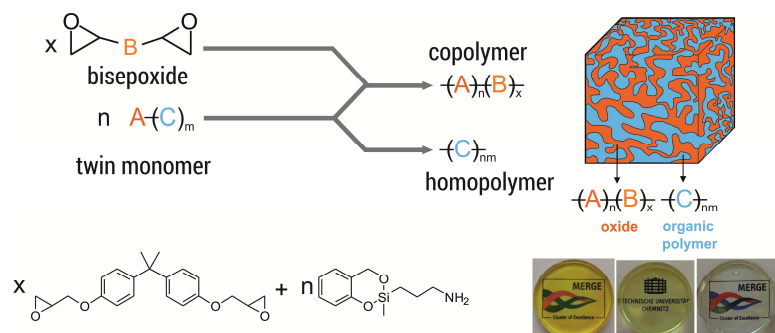
# Ternary hybrid Material Formation by twin polymerization coupled with the bis-epoxide/amine step growth polymerization

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## Graphical Abstract



## Abstract

Homogeneous hybrid materials composed of phenolic resins, crosslinked polydialkylsiloxane moieties with linear epoxide/amine composites have been synthesized by twin polymerization of 2-(3-amino-*n*-propyl)-2-methyl-4*H*-1,3,2-benzodioxasiline (APSI) combined with addition polymerization of bisphenol-A-diglycidylether (BADGE). The ternary formation of three different polymer structures within one procedure in the melt process occurs smoothly as evidenced by solid state <sup>13</sup>C and <sup>29</sup>Si NMR spectroscopy. The formation of *in situ* generated twin monomer moieties with higher functionalities  $f = n \cdot 2$  ( $n > 2$ ,  $n$  is the assumed average degree of polymerization of the linear chain fragments resulting intermediately from APSI and BADGE), compared to the primary reactant APSI ( $f = 2$ ,  $n = 1$ ), triggers the polysiloxane network formation. A novel type of polysiloxane resin is produced by this methodology. Highly thermally stable materials are accessible by appropriate adjustment of reaction conditions and the molar ratio of the reactants. Potential applications are *inter alia* in the field of glue adhesives, veneers, and casting resins.

## Introduction

Epoxy resins are an important class of commercially available compounds used in industrial applications for adhesives and composite materials. Mechanical and physical properties of the target resin can be improved by combination with novolacs, other resin forming components or filler materials.[1–6] The adjustment of the mechanical properties is of great importance to guarantee high hardness without brittleness and good processability during processing.[7–9]

Twin polymerization of monomers derived from salicylic alcohol has been established as an elegant procedure for the synthesis of nanocomposites due to the formation of two different polymers from only one monomer within one process step and without the formation of disturbing byproducts.[10–14] Figure 1 exemplary shows the twin-

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