MALEIMIDE FUNCTIONALIZED SILOXANE RESINS

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Introduction

Polyorganosiloxanes are a commercially important class of compounds. They exhibit many important properties, including very low glass transition temperatures, making them useful over a wide temperature range. In practice, the polysiloxane polymer is often mixed with a filler material to help improve its mechanical properties. An alternative method for increasing polymer mechanical strength is through the incorporation of certain substituents on the polymer backbone. "Hard" substituents such as carbonates and imides generally result in improved mechanical properties of polysiloxanes.

In this paper, we present the preparation of novel polysiloxane resins modified with "hard" maleimide substituents. Protected ethoxysilyl-substituted propyl-maleimides were prepared. The maleimide substituent was protected with a furanyl group and the monomer polymerized under aqueous acidic conditions. At elevated temperatures ($>120^{\circ}\text{C}$), the polymer undergoes retro Diels-Alder reaction with release of furan (Equation 1). The deprotected polymer can then be selectively crosslinked by a forward Diels-Alder reaction (in the presence of a coreactant having two or more diene functionalities).

The materials were characterized by solution and solid state ^{29}Si and ^{13}C NMR spectroscopy, TGA and DSC.

Results and Discussion

Monomer and Polymer Syntheses. The methyldiethoxysilyl monomer was prepared by the reaction of maleic anhydride with 3-aminopropylmethyldiethoxysilane.³ The maleimide was then protected as an oxonorbornene (Equation 2) against Michael Addition which could occur during the polymerization step.

The exo geometry depicted in Equation 2 for compound 2 was based on an X-ray crystal structure of the triethoxysilyl-substituted version of 2 (Figure 1).

Compound 2 was polymerized by hydrolysis and condensation of the ethoxysilyl- units (4 eq H_2O , 0.1 N HCl). The resultant polymer was a soluble white powder with a glass transition temperature of 30°C . Solution ^{29}Si NMR analysis showed complete consumption of the starting monomer. Two peak massifs were observed in the spectrum (centered at -20.6 and -22.8 ppm) probably corresponding to linear and cyclic components, respectively.^{4,5}

Retro Diels-Alder Reaction. The protecting furanyl group on the maleimide substituent of the polymer can be readily removed at temperatures greater than 120°C . This is observed by TGA (Figure 2) and by ^1H NMR spectroscopy (Figure 3) of the polymer (before and after thermolysis). The TGA reveals a 27 % weight loss beginning at about 120°C corresponding to essentially quantitative loss of the furan (calculated to be 26 % weight loss). The ^1H NMR spectra show disappearance of the peaks centered at 5.7, 5.0 and 2.3 ppm (loss of furan) and appearance of peaks at 5.9 ppm (vinylc hydrogens of the deprotected maleimide).

Figure 1. X-Ray crystal structure showing exo geometry.

Figure 2. TGA of maleimide-siloxane polymer.

Crosslinking of Polymer. The deprotected polymer (Equation 1) was crosslinked to an insoluble resin by forward Diels-Alder reaction with a bis-diene (Equation 3). The initial deprotection step (loss of furan) and subsequent crosslinking was carried out in a one pot process at 140°C . The

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polymer and diene were heated at atmospheric pressure for 30 min. Excess volatiles were then removed at reduced pressure leaving an insoluble clear yellow resin. DSC analysis suggested that the material did not exhibit a glass transition below its retro Diels-Alder temperature (Determined by TGA to be 150 °C).

Figure 3. ¹H NMR spectra of protected (top) and deprotected (bottom) maleimide functionalized siloxane polymers.

Experimental Section

N-(methyldiethoxysilylpropyl)maleimide (1).² Compound 1 was prepared according to Toru's method for preparing other maleimides.³ Because of the hydrolytic instability of the diethoxysilyl groups, workup was modified to avoid the aqueous washing step. 3-aminopropylmethyldiethoxysilane (42 g, 0.22 mol) in benzene (100 mL) was added dropwise to a solution of maleic anhydride (22 g, 0.22 mol) dissolved in benzene (900 mL). The reaction was stirred for 2 h at room temperature. ZnCl₂ (30 g, 0.22 mol) was added in bulk, the mixture stirred for 30 min and then a solution of hexamethyldisilazane (HMDS, 53 g, 0.33 mol) in benzene (100 mL) was added dropwise. After complete addition of the HMDS, the reaction was refluxed for 2 hours, cooled to room temperature and filtered. The volatiles were removed under reduced pressure and the product flash distilled at 112 °C/500 mtorr (yield: 60 g, 78 %). The compound was purified by crystallization from hexanes at 0 °C. ¹H NMR (C₆D₆): δ = 5.77 (s, 2H), 3.60 (q, 4H), 3.59 (t, 2H), 1.68 (m, 2H), 1.09 (t, 6H), 0.51 (m, 2H), 0.04 (s, 3H). ¹³C NMR (C₆D₆): δ = 170.5, 133.3, 58.1, 40.4, 22.6, 18.6, 11.4, -4.8. ²⁹Si NMR (Neat): δ = -6.7.

Diels-Alder Adduct of 1 (2). Compound 1 (9.0 g, 0.033 mol) and furan (6.8 g, 0.099 mol) were placed in a Carrius tube, freeze-pump-thaw degassed, sealed and then heated in an oil bath at 80 °C for 48 hours. The reaction mixture was cooled to room temperature and the excess furan removed *in vacuo*. The desired product formed in quantitative yield (11 g) but contained trace amounts of the starting maleimide (1); probably due to the reversibility of the reaction at the temperature used. ¹H NMR (C₆D₆): δ = 5.60

(d, 2H), 4.89 (d, 2H), 3.61 (q, 4H), 3.59 (t, 2H), 2.06 (s, 2H), 1.71 (m, 2H), 1.09 (t, 6H), 0.60 (m, 2H), 0.06 (s, 3H). (C₆D₆): δ = 175.9, 136.3, 81.0, 58.1, 47.4, 41.5, 21.7, 18.6, 11.2, -4.8. ²⁹Si NMR (Neat): δ = -6.6.

Summary

An oxonorbornyl protected maleimide functionalized siloxane polymer was prepared by aqueous condensation. Thermal analysis of the polymer revealed that retro Diels-Alder reaction begins at 120 °C with quantitative loss of the protecting group. The deprotected polymer was crosslinked to an insoluble resin by reaction with a bis diene.

Future experiments will determine if the insolubility of the crosslinked resin can be reversed by further retro reaction – resulting in formation of the soluble uncrosslinked precursor.

References

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