SHRINKAGE AND RECYCLABILITY OF POLY(1,2-ETHYLENE-BIS(DIMETHYLSILOXANE))

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Introduction

Non-shrinking polymers are desirable as encapsulants for strain-free packaging for electronics. Ring-opening polymerizations of cyclic monomers such as lactams, cyclic ethers, and cyclic oligosiloxanes have proven an effective strategy for reducing shrinkage.¹ In this report we examined the loss of volume during the ring-opening polymerization of neat 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane **1** to give poly(1,2-ethylene-bis(dimethyl-siloxane)) (Scheme 1). Monomer **1** is under sufficient strain (8-12 kcal/mole) to permit its facile base-catalyzed polymerization to afford high molecular polymer.² Monomer **1** was prepared by hydrolyzing and condensing either 1,2-bis(chlorodimethylsilyl)ethane or 1,2-bis(dimethylethoxysilyl)ethane (Scheme 2) to give a low molecular weight oligomer. Pyrolysis of this oligomer with potassium hydroxide at 280 °C afforded the cyclic monomer in good yield (60-70%). The ease with which the oligomer can be converted to monomer also led us to investigate the potential for recycling the high molecular weight polymer (Scheme 3).³

Scheme 1. Polymerization of neat 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane **1** Scheme 2. Synthesis of monomer **1**. Scheme 3. Recycling monomer **1** from high molecular weight polymer.

Experimental

Materials. Monomer **1** was made using the synthetic strategy described by Piccoli et al.⁴ from either 1,2-bis(chlorodimethylsilyl)ethane (Geleste) or 1,2-bis(dimethylethoxysilyl)ethane. The latter was prepared by chloroplatinic acid-catalyzed hydrosilation of vinyl dimethylethoxysilane. Additional monomer was obtained from Geleste, Inc.. Ring opening polymerizations were initiated with tetrabutylammonium hydroxide (Bu₄NOH) (1 M in methanol; Aldrich).

Polymerizations. Polymerizations were performed in 5 mL graduated cylinders to facilitate measurement of shrinkage. Bu₄NOH (0.5, 0.1, and 0.05 mole %) was added to **1** to give a final volume of 5.00 mL. Volumes were measured immediately after a rapid agitation and again after ~150 hours at which time samples were removed for molecular weight and spectral analysis. A subsequent series of polymerizations was performed in sealed 10 mL

graduated cylinders equipped with ground glass stoppers to prevent monomer evaporation.

Pyrolyses. Polymers (4 g) and potassium hydroxide (0.3 g) were placed in 50 mL round bottom flasks and heated to 280 °C under argon. The resulting distillate from 110-120 °C was collected and characterized by ¹H NMR and gas chromatography.

Characterization. The presence and relative purity of monomer were analyzed with a Hewlett Packard 5890 Series II GC, and 5973 Series Mass Selective Detector. Molecular weights were determined with a Millipore Waters 150-C ALC/GPC using polystyrene standards. Further characterization was achieved using a Perkin Elmer 1750 Infrared Fourier Transform Spectrometer and 300 and 400 MHz Bruker NMR Spectrometers (¹H, ¹³C and ²⁹Si).

Results and Discussion

Polymer Synthesis. Ring-opening polymerization of neat **1** with tetrabutylammonium hydroxide as initiator afforded poly(1,2-ethylene-bis(dimethyl-siloxane)) within a few hours. Polymer molecular weights obtained with neat monomer (Table 1) were somewhat higher than those obtained by Suryanarayanan² in tetrahydrofuran. As expected, the molecular weights were inversely proportional to the concentration of catalyst.

Table 1. Molecular Weights and Polydispersities of Polymers prepared under varying Initiator Concentrations

Mole % Bu ₄ NOH	Mw (g/mole) (x 10 ⁴)	Mn (g/mole) (x 10 ⁴)	Pd
0.5	8.53	5.73	1.49
0.1	9.81	6.67	1.47
0.05	13.10	8.30	1.57

NMR Characterization of Polymer. The conversion of **1** to polymer led to slight changes in the chemical shifts of the bridging ethylene and methyl hydrogens in the ¹H NMR spectrum from δ_H = 0.71 and 0.10 in the monomer to δ_H = 0.65 and 0.21 in the polymer. This phenomenon is attributed to the release of ring strain which has the effect of returning shielding electron density from the methyl groups to the previously strained methylenes.² Chemical shift perturbations of a similar order were observed for the ethylene and methyl carbons between the ¹³C NMR spectra of **1** with δ_C = 9.45 and 0.48 and the polymer with δ_C = 10.29 and -0.03. A much more pronounced difference in chemical shifts was observed between the ²⁹Si NMR spectra of the monomer, δ_{Si} = 22.83, and polymer, δ_{Si} = 7.59.

Measurement of Shrinkage. Shrinkage was measured based on changes in volume observed with polymerization of the neat monomer. In all cases, volume losses between 3.3-4.7% were observed (Table 2). Polymerizations performed in sealed containers resulted in similar shrinkage values suggesting monomer evaporation is not a significant contributor to shrinkage in this system. This amount of shrinkage is similar to that exhibited by the ring opening polymerization of cyclic lactams (3.4-9.6%), but is less than observed with the ring opening polymerization of octamethylcyclotetrasiloxane (-1.77%).¹

Table 2. Negative Volume Changes in Neat Monomer **1** Polymerizations under varying Initiator Concentrations

Mole % Bu ₄ NOH	Initial Volume (ml)	Volume Loss (ml)	% Loss	SD(ml)
0.5	4.74	-0.16	-3.38 %	0.09
0.1	4.90	-0.23	-4.69 %	0.06
0.05	4.66	-0.18	-3.86 %	0.07
0.5 (sealed)	5.03	-0.23	-4.57 %	0.07
0.1 (sealed)	5.06	-0.25	-4.94 %	0.04
0.05 (sealed)	5.03	-0.24	-4.77 %	0.03

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The ease with which the low molecular weight oligo(1,2-ethylene-bis(dimethyl-siloxane)) was depolymerized to synthesize 1 (*vide supra*) led us to investigate the depolymerization of the high molecular weight polymer for the purpose of recycling. Pyrolysis of the polymer at 280 °C in the presence of solid sodium or potassium hydroxide afforded pure monomer 1 (97% by GC) in good yields (64-82%). Yields did not appear to vary with polymer molecular weight, although pyrolysis of materials with significantly higher molecular weight did take slightly longer to complete.

Conclusions

Ring-opening polymerization of 1 in the absence of solvent permits the preparation of poly(1,2-ethylene-bis(dimethyl-siloxane)) with relatively low degrees of shrinkage. This, coupled with the polymer's colorless transparency, make the 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane ring system a potentially attractive reactive functionality for constructing new encapsulants. Furthermore, the ability to recycle the polymer back to monomer in high yields, makes it more economically attractive. Future work will involve analysis of residual initiator's effect on the polymer's thermal stability as well as characterization of the oligomer obtained directly from the acyclic precursors of monomer 1.

Acknowledgments

We would like to acknowledge Duane Schneider and Kamyar Rhaminian for their assistance with NMR measurements and Martin Peterson for his assistance with GPC. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000.

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