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Photoinitiated cationic ring-opening polymerization of a cyclosiloxane

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Summary

Hexamethylcyclotrisiloxane was found to undergo photoinitiated cationic ring-opening polymerization in solution and bulk, upon exposure to UV radiation, in the presence of either sulfonium or iodonium salts or an iminosulfonate derivative. Glass transition temperatures were below -100 °C. Molecular weights, determined by size exclusion chromatography relative to polystyrene standards, increased with photolysis lamp intensity. Use of an iodonium photoinitiator afforded poly(dimethylsiloxane) with Mn = 172,000. Polymerization of hexamethylcyclotrisiloxane was accompanied by a small increase in volume (3-4%).

Introduction

Photoinitiated polymerization serves as the basis of many important technologies, ranging from restorative dental materials to a host of coatings and imaging applications. The photoinitiated polymerization of a variety of monomers continues to receive considerable attention. The kinetics and volume changes of polymerization are important parameters for a number of important photopolymerization applications (1). The ring-opening polymerization of several cyclic monomers has been reported to occur with little shrinkage in volume, or in a limited number of instances, volume expansion (2-4).

The polyorganosiloxanes represent a class of materials having one of the widest ranges of applications of any polymeric systems and are the most important of the inoganic backbone polymers (5, 6). Their applications extend from highly mobile fluids, which may be used at very low temperatures, to elastomers and crosslinked resins, which have considerable thermal stabilities. Linear polysiloxanes of high molecular weight are readily prepared by acid or base catalyzed ring-opening of the corresponding cyclic trimer or tetramer (7, 8). The ring-opening polymerization of cyclic siloxanes is known to proceed exclusively through an ionic mechanism which can be either anionic or cationic. A wide variety of chemical initiators have been reported in the literature (9-11); most of these systems involve bases or strong protic acid catalysts.

Polydimethylsiloxane (PDMS) is probably the most important polysiloxane from a technological point of view and it is with this system that most fundamental investigations have been carried out. Though thermal cationic and anionic ring-opening polymerizations of cyclic siloxane trimers and tetramers are well known (7, 8), photoinitiated ring-opening polymerization of such monomers has not been detailed. In the present paper, we describe results of the photoinitiated cationic polymerization of hexamethylcyclotrisiloxane, **D3**, using a sulfonium salt, an iodonium salt, or an iminosulfonate as photoinitiator.

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Experimental

Materials: CH_2Cl_2 was refluxed over P_2O_5 then distilled and stored over 4 Å molecular sieves. Ether and benzene were refluxed over Na then distilled prior to use. Methanol was treated with magnesium then distilled and stored over 4 Å molecular sieves. *p*-Toluenesulfonic acid was recrystallized from 95% ethanol. Hexamethylcyclotrisiloxane was used as received from United Chemical Technologies. Tris(4-methylphenyl)sulfonium hexafluoroantimonate (12), (4-decyloxyphenyl)phenyliodonium hexafluoroantimonate (13), and 1,2,3,4-tetrahydro-1-naphthylideneimino *p*-toluenesulfonate (14), were prepared according to established methods. All other reagents were used as received from commercial suppliers. All reactions were conducted under a dry nitrogen atmosphere. Photopolymerizations were conducted in sealed quartz tubes by irradiation with an UV lamp (either a 450-Watt Hanovia medium pressure Hg arc lamp or a 12-Watt Hanovia low Pressure Hg arc lamp).

Measurements: Densities of the monomer and polymers were determined by pycnometry with distilled water at 26 °C. ^1H NMR spectra were recorded on a Bruker AC-200 spectrometer ($CDCl_3$ solution, referenced to the residual $CHCl_3$ resonance at 7.27 ppm). FT-IR spectra were recorded on a Nicolet Impact 400 spectrometer. DSC analyses were secured using a DuPont Model 2100 DSC instrument using a scan rate of 20 °C/min (under N_2). Molecular weight distributions were determined by size exclusion chromatography (SEC,Waters 510 RI, 40 °C, 1 mL/min) in THF solutions using a series of Waters Styragel columns (HR 1, HR 3, and HR 4) calibrated with polystyrene standards. Number-average (Mn) and weight-average (Mw) molecular weights were calculated.

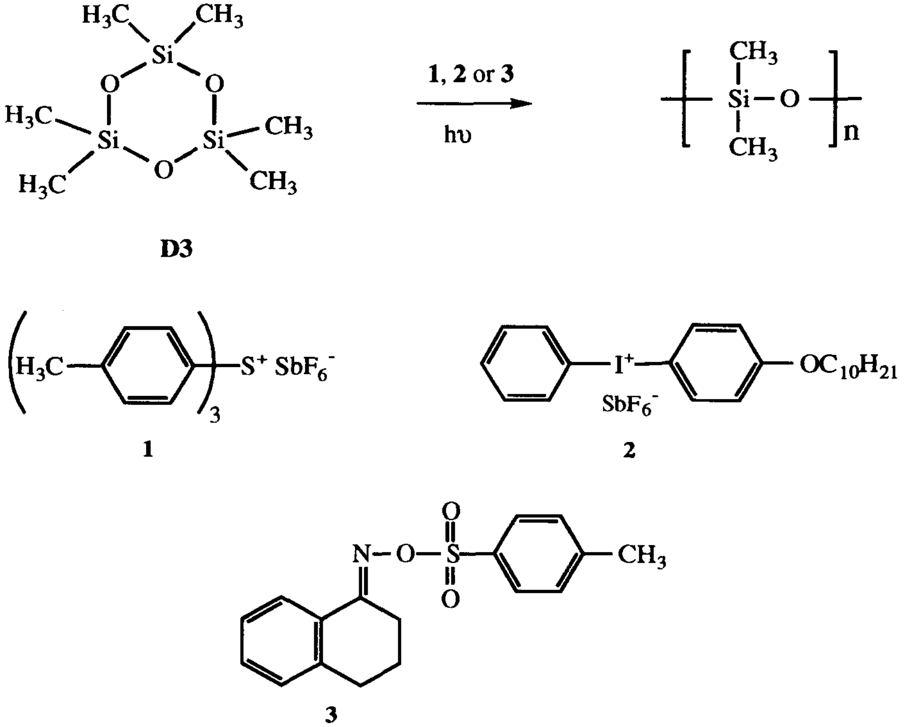
Solution photopolymerization, typical procedure: In a sealed quartz tube, 350 mg of hexamethylcyclotrisiloxane (1.57 mmol), 1mL of CH_2Cl_2, and 4.6 mg of (4-decyloxyphenyl)phenyliodonium hexafluoroantimonate (0.007 mmol, 0.5 mol%) were irradiated with an UV lamp at room temperature for 20 min. The polymer product was isolated from the resulting viscous solution by precipitation with methanol. A colorless viscous liquid was obtained, washed with methanol repeatedly, and dried in vacuo at room temperature, affording 234 mg (67% yield).

Bulk photopolymerization, typical procedure: In a sealed quartz tube, 538 mg of hexamethylcyclotrisiloxane (2.42 mmol) and 7 mg of (4-decyloxyphenyl)phenyliodonium hexafluoroantimonate (0.01 mmol, 0.5 mol%) were irradiated with an UV lamp at 70 °C for 20 min. The mixture was then maintained at 70 °C for another 2 h after irradiation. The polymer product was isolated from the resulting viscous material by precipitation with methanol. A colorless viscous liquid was obtained, washed with methanol repeatedly, and dried in vacuo at room temperature, affording 143 mg (32% yield).

Results and discussion

The photoinitiated polymerization of hexamethylcyclotrisiloxane, **D3**, was performed either in CH_2Cl_2 solution or in bulk by irradiation with an UV lamp (Scheme 1). Solution polymerization was carried out at room temperature, while that in bulk was at 70 °C (molten state). Results are shown in Table 1. When polymerizations were carried out in CH_2Cl_2, a viscous liquid polymer resulted with each initiator. However, no polymer

Scheme 1. Photoinitiated cationic polymerization of hexamethylcyclotrisiloxane



was obtained during attempted bulk polymerization of **D3**, at 70 °C, with sulfonium salt **1**, due to poor solubility of **1** in the siloxane monomer. On the other hand, iodonium salt **2** was soluble in **D3** at 70 °C, and resulted in successful photochemical polymerization to produce a viscous liquid polymer. The yield for bulk polymerization was, however, lower than for solution polymerzation (32 versus 63 °C) and the molecular weight was also lower (Mn 25,000 versus 172,000). Use of iminosulfonate **3** afforded low conversion of monomer to polymer, though the Mn was relatively high (69,000). The viscous liquid polymers obtained in these experiments had NMR and IR characteristics of a typical poly(dimethylsiloxane).

Higher molecular weight averages were obtained when a higher intensity UV light source was employed. Comparison of results from polymerization of **D3** with the sulfonium salt **1** photoinitiator revealed a Mn of 81,000 for irradiation with the medium pressure lamp while a Mn of only 15,000 resulted when the low pressure lamp was utilized. A higher yield also resulted with the medium pressure lamp. Similar results were secured upon photopolymerization of **D3** with the iodonium salt photoinitiator **2**. In these experiments, Mn averages of 172,000 and 76,000 were obtained using the medium pressure and low pressure lamps, respectively. Polymer yields were independent of lamp intensity in polymerizations in which the iodonium salt was used as initiator. Glass transition temperatures (Tg), obtained by DSC, were in the range of -126 to -100 °C, characteristic of poly(dimethylsiloxane)s.

Table 1. Photoinitiated polymerization of cyclic siloxane **D3**

Initiator	Lamp	Conditions	Yield (%)	T_g (°C)	Mn (g/mol)	Mw (g/mol)	Volume Change
1	medium	solution	66	-100	81,000	135,000	+2.8%
1	low	solution	39		15,000	19,000	
2	medium	solution	63	-113	172,000	304,000	+4.1%
2	low	solution	67	-110	76,000	103,000	
2	medium	bulk	32	-126	25,000	34,000	
3	low	solution	17		69,000	98,000	

Densities and of the monomer and polymers, obtained via solution polymerization using the medium pressure lamp and the two onium salt photoinitiators, were measured by pycnometry. The density of **D3** was 1.061 ± 0.003 g/mL and densities of polysiloxanes obtained with **1** and **2** were 0.970 ± 0.003 and 0.956 ± 0.018 g/mL, respectively. This afforded volume increases (expansion) of 2.8% and 4.1% for the polymerization of **D3** using sulfonium **1** and iodonium **2** initiators, respectively. For comparison, the volume change for the free radical polymerization of methyl methacrylate was determined using this technique and found to occur with a 19.7% volume decrease (shrinkage).

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