UCRL-15159

SYNTHESIS OF BLOCK COPOLYMERS OF METHYL SILOXANE, PHENYL SILOXANE, VINYL SILOXANE, ETC.

Summary report for the period August 1, 1978
to June 30, 1979, Sub-Contract No. 1212009
between the Regents of the University of
California and Michigan Molecular Institute

MASTER

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Synthesis of Block Copolymers of Methyl Siloxane, Phenyl Siloxane, Vinyl Siloxane, etc.

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Introduction

Synthesis of homo poly(dimethylsiloxane) PDMS, homo poly(diphenyl siloxane PDPS, and di- and tri- block copolymers of PDMS and PDPS have been carried out by anionic living polymerization, using the following reagents: hexamethylcyclotrisiloxane, HMTS and hexaphenylcyclotrisiloxane, HPTS (monomers), n-BuLi and dilithium diphenyldisilanolate, DLS (initiators), DMSO and THF (promoters) and Toluene (solvent). Lithium based catalysts are used in order to minimize siloxane rearrangement (equilibration) reactions. The use of cyclic siloxane trimers is due to their much greater reactivity with lithium catalysts over the analogous higher ring systems. The presence of aprotic polar solvents (DMSO and THF) is necessary for the formation (from catalyst molecules) of free radical anions that initiate the polymerization.

General Procedure

Equipment: Since anionic species are easily killed by moisture and O_2, all glassware equipment are thoroughly cleaned, dried and assembled under N_2. Polymerization is carried out in a multi-necked, round bottom flask to which the following are attached: a septum cap (for delivery of reagents by means of airtight syringes), a reflux condenser with inlet/outlet stopper (for continuous passage of N_2), a separatory funnel (for transfer of monomer solutions under N_2), and a mechanical stirrer. A water heated jacket is employed to enable a direct sublimation of HMTS into the reaction flask).

Purification of Reagents: Toluene is first treated with concentrated sulfuric acid (to remove thiophene) and then distilled over Na-Benzophenone (to remove H_2O and O_2). THF is also distilled over Na-benzophenone. HMTS is purified by sublimation. HPTS is dissolved in Toluene and dried over alumina under N_2.

Polymerization of Cyclic Trimers

Homo polymerization of HMTS has been successfully carried out as follows: The required amount of HMTS is sublimed into the reaction flask, and THF is added (about 30 wt. %); the mixture is equilibrated at 65°C before the required amount of catalyst (n-BuLi or DLS) is added by means of an airtight syringe. The reaction mixture is refluxed at the above temperature for 2-1/2 hours; then chlorotrimethylsilzne (CTMS) is added to terminate the reaction. The viscous fluid is usually treated with sodium bicarbonate and washed with water (to remove excess CTMS) before precipitation in methanol.

Copolymerization of HMTS (M) and HPTS (P) has been carried out to obtain MP di-block (using n-BuLi as initiator) and PMP tri-block samples (using DLS as initiator). The M block is first obtained as described above; then the required amount of HPTS solution (in Toluene) is added. Refluxing at 65°C is continued for 30 minutes; then the solvent is expelled with a stream of N_2 and the temperature raised to 200°C. Heating at this temperature is done for about 3 hours before the reaction is terminated with CMTS. The resulting product is a white solid, sometimes colored yellow due to decomposed catalyst residues. Product is extracted with Toluene and precipitated in methanol.

Product Characterization

Characterization of homo and copolymer products has been carried out using viscometry, gel permeation chromatography and thermal analysis.

Results

Homo poly(dimethylsiloxane), PDMS. Four samples of PDMS (with theoretical $\overline{M}n$ values of 100,000 to 135,000) have been made with THF as promoter. Product yields are greater than 80%, and experimental $\overline{M}n$ values are within 25-30% of the theoretical value. Samples of PDMS made with DMSO as promoter have low $\overline{M}n$ values, which seems to indicate the occurrence of chain transfer reactions. THF will therefore be used exclusively in the future.

Homo poly(diphenylsiloxane), PDPS. A sample of PDPS has been made with theoretical $\overline{M}n$ of ~40,200, using DLS as initiator. The product is a highly insoluble white crystalline solid. The sample without thermal history exhibits in DSC a Tg at 38.5°C, and a dual T_m at 235 and 223°C; however, on running the sample a second time, the Tg is unobservable and a single T_m occurs at 257°C.

Di-block Copolymer of PDMS (M) and PDPS (P). A sample of MP di-block has been made with $\overline{M}n$ of M block of ~100,000 and Mn of P block of ~11,400 (4 mole %). The sample is a sticky rubbery solid. Its gel permeation chromatogram in chloroform indicates a single peak in the UV and RI detectors; both peaks being coincident, indicating the presence of only copolymer molecules.

Tri-block Copolymers of PDMS (M) and PDPS (P). Seven PMP tri-block samples of PDMS and PDPS have been prepared. The major block M has an $\overline{M}n$ of ~135,000, while the total $\overline{M}n$ of the P blocks is varied as follows: ~15,800 (4 moles in PMPTS-2), ~23,700 (6 mole % in PMPTS-3), ~30,800 (8 mole % in PMPTB-5) ~40,200 (10 mole % in PMPTB-6) ~49,300 (12 mole % in PMPTB-7), ~58,800 (14 mole % in PMPTB-8) and ~79,200 (18 mole % in PMPTB-9). Products yields are greater than 80%

Physical Appearance of PMPTB Samples. Samples with <8 mole % of P block exhibit increasing degree of whiteness and toughness with increase in phenylsiloxane content. Above the ~8 mole % level, all samples exhibit equal degree of whiteness. Samples PMPTB-2,3,5-7 are rubbery in nature; while PMPTB-8 and 9 are less rubbery, particularly the latter.

Solubility of PMPTB samples. Samples PMPTB-2,3,5 and 6 are soluble in

Toluene, chloroform, THF and cyclohexane at room temperature. Product PMPTB-7 is fairly soluble in toluene at elevated temperatures ~80°C, while PMPTB-8 and 9 are insoluble in toluene at ~90°C, although they do swell on prolonged heating.

Gel Permeation (GP) Chromatograms of PMPTB Samples. GP chromatograms of PMPTB-2,3,5 and 6 have been obtained in chloroform at room temperature; results indicate the presence of only copolymer molecules, with no homopolymer impurities. Intrinsic viscosities determined in chloroform at 25°C are: 1.69 (PMPTB-2), 1.71 (PMPTB-3), 1.76 (PMPTB-5) and 1.43 (PMPTB-6).

Thermal Analysis of PMP Tri-block Samples. Thermal analysis of PMPTB-2,3, 5-9 have been performed mostly with the DSC. The dimethylsiloxane block in all the samples exhibits transitions at -122°C (Tg), -42°C (T_m). Transitions of the diphenylsiloxane (P) blocks are not detectable (by DSC) in samples PMPTB-2,3,5 and 6. In PMPTB-8, the P blocks show two T_m peaks at 167 and 182.5°C the first time the sample is run; subsequent runs indicate a single T_m at 171°C. Also, the P blocks in PMPTB-9 exhibit two melting point peaks: ~210°C (T_m') and ~228°C (T_m"). Both peaks remain during subsequent runs; however, their relative intensity depends on the rate at which the sample is cooled to below T_g prior to measurement; slow cooling enhances T_m" and decreases T_m', the reverse is the case for fast cooling. It does appear that there are two types of crystal formation - an imperfect unstable crystalline form (T_m') and a better more stable crystalline form (T_m").

Tensile Moduli of Uncured PMPTB Samples. The tensile moduli of uncured PMPTB-4,8 and 9 have been measured at different temperatures. Results reveal low tensile moduli (kg/cm^2); ~3.6 (PMPTB-4), ~8.01 (PMPTB-8) and ~8.3 (PMPTB-9). PMPTB-4 contains 10 mole % of diphenylsiloxane unit.

Future Plan

The next stage of the work will involve the synthesis of PMP tri-blocks containing small amounts ($< 1/2$ mole %) of vinylmethylsiloxane units in the poly(dimethylsiloxane) block. The presence of vinyl groups will lead to greater degree of crosslinking, and would probably impart low compression set property on these materials.

The new tri-block samples will be crosslinked either by radiation or by benzoyl peroxide. A detailed study of their mechanical properties will be undertaken.

Abstract

As part of the investigation of structure-property relationships in silicone polymers, a number of homo-, di- and triblock polymers of dimethylsiloxane and diphenylsiloxane have been synthesized by anionic techniques. Polymerization of the "cyclic trimers", hexamethylcyclotrisiloxane and hexaphenylcryclotrisiloxane, has been effected with lithium-based catalysts so as to avoid equilibration reactions.

Yields of the various polymers has typically been above about 80% and molecular weights are believed to be within about 25% of the designed value (typically about 150,000). Gel permeation chromatography, using both refractive index and ultraviolet detectors, shows no detectible homopolymer impurities in the block copolymers.

The physical properties of the various polymers varies dramatically in the series homopolymer PDMS to diblock polymer PDMS-PDPS to triblock polymer PDPS-PDMS-PDPS. At approximately equal molecular weight, the homopolymer is a viscous liquid, the diblock polymer is a sticky grease, while the triblock polymers are firm rubbery materials, with moduli which increase with increasing diphenylsiloxane content.

Microphase separation of the dimethylsiloxane and diphenylsiloxane blocks occurs in these block copolymers, as shown by DSC measurements. As a result, the triblock polymers behave as thermoplastic elastomers, which can be molded at temperatures above the melting point of the diphenylsiloxane blocks (∿250°C).