Synthesis and Investigation of Oligosiloxanes Containing γ-Trimethylsiloxy-propyl or γ-Hydroxy-propyl Groups

QINGZENG ZHU, SHENGYU FENG, JIANHUA CHEN

Institute of New Materials, Shandong University, Jinan 250100, People's Republic of China

ABSTRACT: Oligosiloxanes having different distributions of Si—H groups were prepared, and the addition of Si—H bonds to C=C double bounds of trimethyl(2-propenyloxy)silane was utilized to obtain oligosiloxanes having different distributions of γ-trimethylsiloxy-propyl or γ-hydroxy-propyl groups as substituents. The oligosiloxanes were characterized by IR and ^{1}H-NMR spectroscopy. Viscosity was studied to investigate the effects of the substituents. Differential scanning calorimetry (DSC) was used to investigate the thermal behaviour of these oligosiloxanes. It was found that they are completely amorphous materials and, hence, show only a glass transition. We found that the viscosities and glass transition temperatures of these materials increased with the increasing of the number of substituents. Hydrogen bonds have a considerable influence on the increase of the viscosities and glass transition temperatures of oligosiloxanes. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2431–2435, 2002

Key words: viscosity; glass transition; polysiloxones; differential scanning calorimetry (DSC)

INTRODUCTION

Being designed to combine the properties of two or more polymers, block and graft copolymers have extended the frontier of polymeric materials. Among this group, siloxane-containing copolymers represent a unique class. This is particularly a result of the presence of siloxane sequences that are characterized by unusual behavior.

Polydimethylsiloxane (PDMS) has unique properties, such as low glass transition temperature, good thermal and oxidative stability, low surface energy, high hydrophobicity, high oxygen permeability, and good biocompatibility. However, these materials have two main shortcomings: very weak mechanical characteristics and incompatibility with almost all organic polymers. The weakness of PDMS can be effectively overcome through block and graft copolymerization.

Carbon-functional PDMS bearing functional groups, such as hydroxyl, etc., are of interest because of their potential importance as precursors in the block and graft copolymerization of siloxane-containing copolymers. Much work has been reported on the synthesis of hydroxyalkyl-terminated PDMS to synthesize (AB)n-type block copolymers.[1–12] The major objective of this article is to report on the synthesis of a series of oligosiloxanes having different distributions of γ-trimethylsiloxy-propyl or γ-hydroxy-propyl groups. The effects of these substituents on the glass transition temperatures and viscosities of oligosiloxanes have been investigated.

EXPERIMENTAL

Materials

Allyl acohol (Shanghai agent plant), hexamethyldisiloxane (MM), and hexamethyldisilazane (Shi-

Table I   The Properties of PDMS Containing Si—H Groups

Sample	H % (mol/g)	Viscosity (m pa s 20°C)	T_g (°C)	M_n	M_w	Polydispersity
1	0.66	14.5	−134.29	1625	1709	1.06
2	0.52	14.5	−133.65	1627	1731	1.06
3	0.45	14.5	−133.26	1639	1752	1.07
4	0.34	15.0	−131.91	1675	1821	1.08
5	0.20	15.5	−131.56	1706	1830	1.07

etsu Chemical Co. Japan) were distilled before being used. Polymethyl-H-siloxane (PHDS) and octamethylcyclotetrasiloxane (D_4) (Shietsu Chemical Co. Japan) were used as received without further treatment.

Synthesis of Trimethyl(2-propenyloxy)silane

To 12.0 g (0.21 mol) of allyl alcohol, in a flask equippd with a condenser and a drying tube, 19.3 g (0.12 mol) of hexamethyldisilazane were added. The reaction temperature was raised from room temperature to 95°C over a period of 1 h. The reaction mixture was held at 95°C for 5.0 h, with accompanying refluxing and evolution of ammonia; then the mixture was distilled to give 15.0 g H_2C=$CHCH_2OSiMe_3$; b.p. 100.2–100.8°C, n_D^{20} 1.3838, 65% yield. IR (cm^{-1}) ν(C=C), 1645; ν(Si—Me), 1251, 840; ν(Si—O—C), 1088. No OH peak at 3330 cm^{-1}. ^{1}H-NMR (ppm) δ 0.18(s, Me_3Si); 4.15(m, CH_2); 5.16(m, CH_2); 5.85(m, CH).

Synthesis of Oligosiloxanes Containing Si—H Bonds (H-PDMS)

The oligosiloxanes containing Si—H bonds were made by equilibrium polymerization of octamethylcyclotetrasiloxane (D_4), PHDS, and MM at room temperature in a reaction flask equipped with a stirrer and thermometer. The catalyst was H_2SO_4. The amount of MM used in the reaction determined the molar mass of H-PDMS. The properties of H-PDMS are shown in Table I. IR (cm^{-1}) ν(Si—H), 2154.

Synthesis of Oligosiloxanes Containing γ-Trimethylsiloxy-propyl Groups (PDMS-APOSiMe₃) or γ-Hydroxy-propyl Groups (PDMS-APOH)

Oligosiloxanes having different distributions of γ-trimethylsiloxy-propyl or γ-hydroxy-propyl groups were prepared. A typical procedure is as follows: 50 g oligosiloxane containing 0.52% (mol/g) Si—H groups, 40.6 g trimethyl(2-propenyloxy)silane and 0.2 mL chloroplatinic acid (0.1 M Pt in isopropanol) was heated under reflux for 8 h. IR showed that the Si—H peak at 2154 cm^{-1} disappeared. The residue was evaporated and gave PDMS–APOSiMe₃. Methanol and acetic acid was added to PDMS–APOSiMe₃ and the mixture was refluxed for another hour to effect hydrolysis of the —SiMe₃. The residue was evaporated and gave PDMS–APOH. IR (cm^{-1}) ν(OH), 3600; ν(Si—Me), 1259, 842; ν(Si—O—Si), 1024–1091; ν(Si—CH₂), 1412, 800. No peak at 2100–2250 (Si—H) and 1070 (Si—O—C).

Measurements

General analysis

^{1}H-Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL FX-90Q (Japan) spectrometer: the results are given as values in ppm. IR spectra were recorded on a Nicolet FTIR 20SX spectrometer, by using films for liquids.

GPC Analysis of PDMS Containing Si—H Groups

The GPC (gel permeation chromatography) analysis of PDMS containing Si—H groups were done in toluene, using GPC system consisting of a Waters 515 pump, two Waters styragel columns (HT4, HT5), and a Waters 2410 refractive index detector. The system was calibrated using narrow molecular weight polystyrene standards.

Differential Scanning Calorimetry

A Rheometric Scientific DSC-SP differential scanning calorimetry interfaced to a RSI ORCHESTRATOR microprocessor was used for this investigation. The temperature scale of the instrument was checked and effects due to thermal lag in the

Table II Glass Transition Temperatures and Viscosities of PDMS–APOSiMe₃

PDMS-APOSiMe$_3$	T_g (°C)	Viscosity (m pa s 20°C)
1-a	−105.03	83
2-b	−108.39	55
3-c	−110.16	53
4-d	−117.27	40
5-e	−120.26	29

PDMS–APOSiMe$_3$ 1-a, 2-b, 3-c, 4-d, and 5-e were prepared from sample 1, 2, 3, 4, and 5, respectively.

Table III Glass Transition Temperatures and Viscosities of PDMS–APOH

PDMS–APOH	T_g (°C)	Viscosity (m pa s 20°C)
1-A	−83.002	3900
2-B	−89.456	1700
3-C	−94.529	1450
4-D	−108.86	500
5-E	−114.64	300

PDMS–APOH1-A, 2-B, 3-C, 4-D and 5-E were prepared from PDMS–APOSiMe$_3$ 1-a, 2-b, 3-c, 4-d, and 5-e, respectively.

system were corrected by regular calibration using indium and zinc standards. To assure a consistent thermal history in each case, the following conditions were employed throughout the experiments. The DSC cell containing the sample and reference was rapidly cooled to 103 K at a rate of 49 K/min, and held at this temperature for 3 min to allow the system to attain thermal equilibrium. The cell was then heated to 473 K at a rate of 20 K/min. The thermal events over the temperature range scanned were recorded by the microprocessor. An atmosphere of high-grade nitrogen was used for the experiments.

Viscosity

The bulk viscosities of the samples were measured using a NDJ-79 rotation viscometer (Tongji University China). The measurements were carried out at 20°C.

RESULTS AND DISCUSSION

Bulk Viscosity

The viscosity of polymer is an involved function of many interaction variables, such as molar mass, structure, and conformation of polymer molecules. We investigated the effects of γ-trimethylsiloxy-propyl or γ-hydroxy-propyl groups in the molecular chain on the bulk viscosity (η). The bulk viscosities of PDMS–APOSiMe$_3$ and PDMS–APOH at 293 K are listed in Tables II and III. The viscosities of oligosiloxanes containing γ-trimethylsiloxy-propyl groups increase with the increasing of molar percentage of substituents in the chain. This is because, with the increasing number of the bulkier substituents, the interference

with free rotation along the chain backbone increases, and thus impedes the chain motion. Certainly, increasing molecular weight of the PDMS–APOSiMe$_3$ also affects its viscosity, but here it is not the primary factor. The viscosities of PDMS–APOH were much higher than those of the corresponding PDMS–APOSiMe$_3$, from which the respective PDMS–APOH were prepared. The increased interchain hydrogen bonding and intramolecular hydrogen bonding interactions decrease rotational freedom and lead to higher viscosity. Clearly, as the number of the substituents increases, the segmental flexibility decreases, and hence the value of viscosity increases.

Glass Transition Temperature (T_g)

The glass transition temperatures of oligosiloxanes with Si—H, γ-trimethylsiloxy-propyl or γ-hydroxy-propyl groups, as determined by DSC,
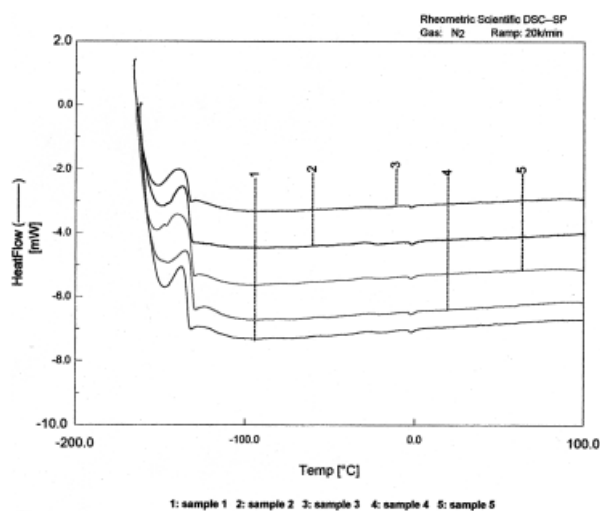
Figure 1 DSC curves of H-PDMS.

are illustrated in Figures 1, 2, and 3, respectively. Their glass transition temperature values are shown in Tables I, II, and III, respectively. The T_g values were determined using the midpoint of the glass transition step.

—Si—O— chains are more flexible backbones, so oligosiloxanes have a very low value of T_g. From Table I, we can see that the T_g values decrease with increasing number of Si—H groups in the chains of the oligosiloxanes. Compared with hydrogen, methyl is a stiffening substituent that increases T_g.

PDMS–APOSiMe$_3$ and PDMS–APOH show only a glass transition on reheating from 103 to 473 K. The absence of cold crystallization or polymer crystalline melting peaks shows that the oligomers are amorphous materials. These samples show remarkable behavior in that their T_g values have been found to increase with increasing number of substituents. The T_g values of PDMS–APOH are much higher than those of the corresponding PDMS–APOSiMe$_3$ that the PDMS–APOH were prepared from.

T_g is a function of rotational freedom: whatever restricts rotation should increase T_g. Compared with methyl, the large substituents, such as γ-trimethylsiloxy-propyl and γ-hydroxy-propyl in PDMS, will cause considerable steric hindrance, and have a considerable influence on the glass transition. It follows that, the more the substituents on the polymer backbone, the less will be the rotational freedom and the higher the T_g.

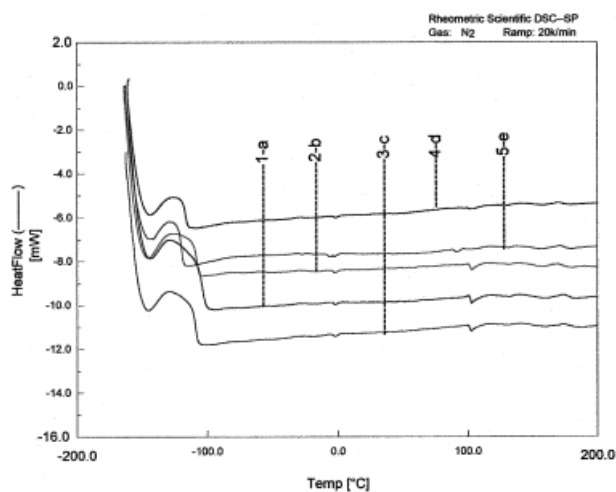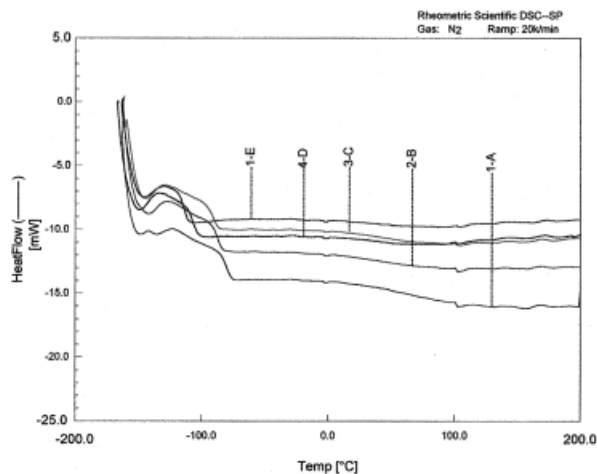In addition to size, polarity influences T_g. Intramolecular hydrogen bonds and intermolecular

Figure 3   DSC curves of PDMS-APOH.

hydrogen bonds would be expected to reduce chain mobility and, hence, raise T_g. A comparison of PDMS–APOSiMe$_3$ with PDMS–APOH illustrates the importance of hydrogen bonding in the increasing of T_g (see Tables II and III).

CONCLUSION

A series of oligosiloxanes having different distributions of substituents, γ-trimethylsiloxy-propyl groups or γ-hydroxy-propyl groups, were prepared. They have been found to be completely amorphous materials. The viscosities and glass transition temperatures of these materials increased with increasing the number of substituents. The bulkier substituents lead to higher viscosities and glass transition temperatures of oligosiloxanes. Hydrogen bonds have a considerable influence on the glass transition temperature and viscosity.

Figure 2   DSC curves of PDMS-APOSiMe$_3$.

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