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Thermal stabilities of end groups in hydroxyalkyl terminated polydimethylsiloxane oligomers

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Summary

Thermal stabilities of α,ω-hydroxypropyl, α,ω-hydroxybutyl, α,ω-2-hydroxypentyl and α,ω-hydroxyhexyl terminated polydimethylsiloxane (PDMS) oligomers were studied. Hydroxypropyl and hydroxybutyl terminated polydimethylsiloxane oligomers showed degradation upon heating, through the loss of functional end groups as determined by FT-IR spectroscopy and gel permeation chromatography. α,ω-Hydroxyhexyl and α,ω-2-hydroxypentyl terminated polydimethylsiloxane oligomers were stable under similar conditions. Instability of the end groups is due to the back biting of the terminal silicon in the PDMS by the primary hydroxyl oxygen, leading to the formation of 5 and 6 membered, stable, heterocylic compounds. Loss of end groups also resulted in a dramatic increase in the molecular weights of the oligomers produced, as determined by gel permeation chromatography.

Introduction

α,ω-Organofunctionally terminated polydimethylsiloxane (PDMS) oligomers are versatile starting materials for the preparation of a wide variety of segmented copolymers, such as polyurethanes, polyamides, polyimides and polyesters(1,2). They are also used as reactive intermediates in the toughening of brittle networks such as epoxies, bismaleimides and others(3,4). Interest in PDMS as a reactive oligomer or a modifier is due to its unique combination of properties, which includes extremely low glass transition temperature (-123°C), excellent thermal, oxidative and UV stability, very low surface energy (surface activity), high gas permeability and physiological inertness (biocompatibility)(5,6).

There are several other advantages offered by α,ω-organofunctionally terminated PDMS oligomers. These are, (i) their ease of preparation with a wide variety of functional end-groups, (ii) production of perfectly difunctional oligomers with controlled molecular weights, and, (iii) flexibility in the modification of their backbone structures(1,5). Organofunctionally terminated siloxane oligomers can be prepared by the acid or base catalyzed equilibration reactions of octamethylcyclotetrasiloxane (D_4) and a disiloxane end-blocker(1). Since (Si—O) bonds are partially ionic, they can be

cleaved by strong acids such as sulfuric, trifluoromethanesulfonic or trifluoroacetic acid or with strong bases such as potassium hydroxide or tetramethylammonium hydroxide. Average molecular weight of the oligomer is controlled by the initial ratio of D_4 to the end-blocker. Detailed procedures are given in the literature for the preparation of well defined organofunctionally terminated PDMS oligomers(1), except for hydroxyl terminated systems, where control of end group functionality was somewhat difficult(7). Unfortunately, this has not been noticed by many researchers for some time, where hydroxypropyl or hydroxybutyl terminated PDMS oligomers were utilized to prepare siloxane-urethane segmented copolymers(8–10). Most of these efforts yielded only low molecular weight materials with poor mechanical properties or products with no mechanical integrity at all(8,9). On the other hand, by differential scanning calorimetry studies it was possible to observe two distinct glass transition temperatures, one for the siloxane and the other for the hard segment, because of the extreme incompatibility of very non-polar siloxane soft segments and very polar urethane hard segments.

It has been shown that when sulfuric acid is used as the equilibration catalyst hydroxyl end groups may undergo dehydration reactions yielding vinyl end groups(11). Trifluoroacetic acid is a useful catalyst for laboratory scale synthesis, however, since it first forms an ester with the hydroxyl end groups, large amounts of acid is necessary during these reaction(7). Formation of ester linkages protect the hydroxyl end groups from side reactions such as back-biting or dehydration. End groups can be regenerated at the end of the reactions by mild hydrolysis with sodium carbonate(7).

In this study thermal stabilities of various hydroxyalkyl terminated PDMS oligomers were investigated using FT-IR spectroscopy and gel permeation chromatography (GPC). Molecular weight distribution and end group structures of these oligomers were determined. Mechanisms for the loss of end group functionality were provided. It was demonstrated that, thermal stability of the end group (Si—R—X) was directly related to the structure of the hydrocarbon bridge (R).

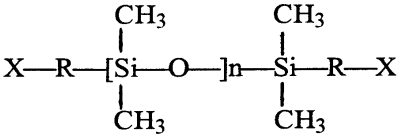
Experimental

Materials

α,ω-Hydroxypropyl (HPPDMS), α,ω-hydroxyhexyl (HHPDMS) and α,ω-2-hydroxy-pentyl (2HPPDMS) terminated oligomers with nominal number average molecular weights of 1000 and 2000 g/mole were products of Goldschmidt, Essen, Germany. 1,4-bis(γ-hydroxybutyl)tetramethyldisiloxane (HBDSX) and α,ω-hydroxybutyl terminated PDMS oligomers (HBPDMS) with number average molecular weights of 1000 and 2000 g/mole were obtained from Huels, Bristol, PA. Chemical structures of these oligomers are given in Fig. 1. All materials were used as received.

Experimental procedure

100 g samples each of HPPDMS, HBPDMS, HHPDMS, and 2HPPDMS oligomers were separately introduced into 250 ml pyrex round bottom flasks and vacuum distilled at 0.1 mmHg between 130 and 150°C. Amounts of distillate and the residue were determined gravimetrically. They were then analyzed by FT-IR spectroscopy and GPC.



R—X = $(CH_2)_3$—OH HPPDMS

R—X = $(CH_2)_4$—OH HBPDMS

R—X = $(CH_2)_6$—OH HHPDMS

R—X = $(CH_2)_3$—CH—CH_3 2HPPDMS
OH

Fig. 1. Chemical structures of PDMS oligomers

Characterization methods

FT-IR spectra were recorded on a Nicolet Impact 400D spectrophotometer using neat fluids on KBr discs. GPC curves were obtained on a Polymer Laboratories PL110 GPC, equipped with microstyrogel columns of 100, 500 and 1000°A and a refractive index detector. Measurements were done at 23°C, with a flow rate of 1.0 ml/min. Tetrahydrofuran was used as the solvent. A GPC calibration curve (Fig.2) was also constructed by using HBDSX, D_4 and narrow molecular weight carboxypropyl terminated siloxane oligomers, fractionated by using supercritical carbondioxide(12).

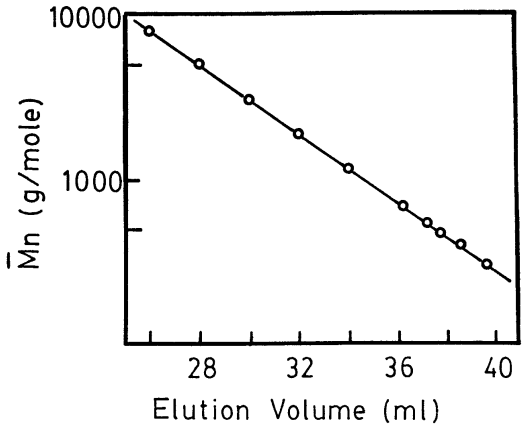


Fig. 2. GPC calibration curve for organofunctionally terminated PDMS oligomers

Results and discussion

Hydroxyalkyl terminated siloxane oligomers are important intermediates for the preparation of siloxane-urethane, siloxane-carbonate and siloxane-ester type block copolymers which find applications as biomaterials(13), membranes(14) and surface modifying additives(15) for various plastics. They are also used in the preparation of specialty coatings with low surface energies and good environmental resistance(5,16).

A major problem related to the preparation of well-defined, difunctional, hydroxyalkyl terminated siloxane oligomers with controlled molecular weights have been the stability of their end groups. It has been shown that under strong acid catalysis, hydroxyalkyl groups undergo dehydration yielding vinyl type end groups(11). This is a major drawback since these oligomers are usually obtained by the acid catalyzed equilibration reactions of D_4 and hydroxyalkyl terminated disiloxane end-blockers(1). In our previous studies we have shown that when hydroxybutyl terminated siloxane dimer is heated in the presence of catalytic amounts of triflic acid, it degrades according to the reaction mechanism shown in Fig. 3. It was also shown by 1H-NMR and GPC studies that in these reactions an equilibrium is established where the ratios of compounds 3-I, 3-II and 3-III are about 38, 25 and 37% by weight respectively(17).

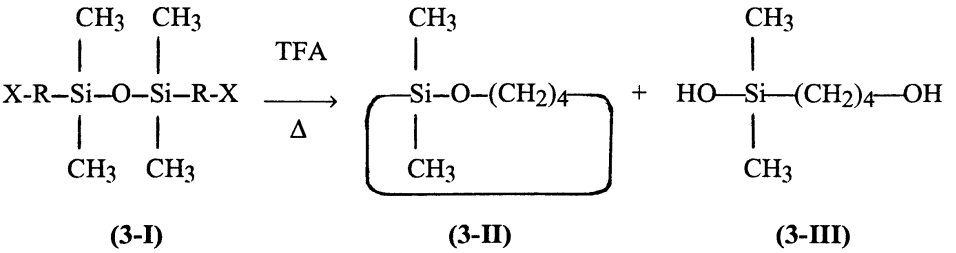


Fig. 3. Suggested degradation mechanism of HBDSX under triflic acid catalysis

When HPPDMS and HBPDMS oligomers were vacuum distilled under neutral conditions, substantial amounts of distillate were obtained, which were thought to be cyclic side products,typical of such equilibration reactions(1). However, there was negligible amount of distillate for HHPDMS and 2HPPDMS oligomers. Table 1 gives the compositional data on the distillation products.

Surprisingly, when FT-IR spectra of the residues were examined, there was only an extremely small peak for hydroxyl absorption in the distilled HPPDMS and HBPDMS oligomers. On the other hand there were very strong hydroxyl absorption peaks in the distillates. GPC curves also showed a dramatic increase in the molecular weights of these oligomers. Fig. 4-a shows the FT-IR spectrum of the HPPDMS-2000 oligomer. A very strong hydroxy peak at 3300 cm^{-1}, asymmetric CH_3 stretching just below 3000 cm^{-1}, symmetric CH_3 deformation at 1260 cm^{-1}, asymmetric Si-O-Si stretching doublet between 1000-1100 cm^{-1} and a strong Si-C stretching and asymmetric CH_3 rocking peak at 800 cm^{-1} are all expected(18) and are all present in the spectrum.

After distillation, FT-IR spectrum of the residue (Fig. 4-b), which is the spectrum of the oligomer produced, shows all of the peaks in Fig. 4-a, except the strong hydroxy peak. On the other hand, FT-IR spectrum of the distillate, which is reproduced in Fig. 4-c, shows a very strong hydroxy peak together with other peaks, typical of low molecular weight siloxanes(18). These FT-IR spectra clearly show that even in the absence of any acid or base catalyst, HPPDMS-2000 follows a degradation mechanism described in Fig. 3 while being vacuum distilled between 130–150°C.

Table 1. Gravimetric analysis of distillation of distillation products

Sample code	Original sample (g)	Residue (g)	Distillate (g)
HPPDMS-1000	100	78.3	21.7
HPPDMS-2000	100	82.4	17.6
HBPDMS-1000	100	78.7	21.3
HBPDMS-2000	100	82.1	17.9
HHPDMS-1000	100	98.8	1.2
HHPDMS-2000	100	99.1	0.9
2HPPDMS-1000	100	98.3	1.7

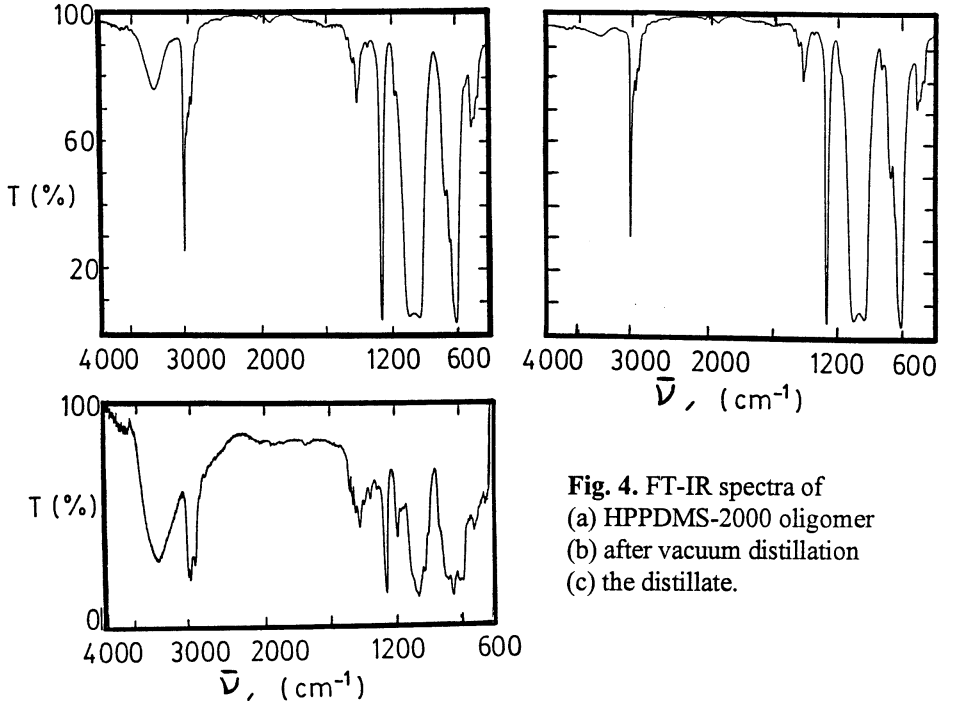


Fig. 4. FT-IR spectra of
(a) HPPDMS-2000 oligomer
(b) after vacuum distillation
(c) the distillate.

GPC chromatograms, also provided valuable supporting information regarding the change in the average molecular weight of the oligomers before and after vacuum distillation. GPC chromatogram of the commercial HPPDMS-2000 oligomer is given in Fig. 5-a. It contains substantial amount of low molecular weight cyclic products which are usually a mixture of D_4, D_5 and D_6, eluting between 36.5 and 38.5 ml in our system. Mn calculated for HPPDMS-2000 oligomer from GPC calibration curve is 1900 g/mole. Chromatogram for the distilled product is given in Fig. 5-b. As expected, all of the cyclic side products are completely removed from the system. However, as it can also clearly be seen, there is a dramatic shift in the oligomer peak to higher molecular weights. Mn calculated from the calibration curve for the stripped oligomer is 3700 g/mole, which is almost double of the original molecular weight. This is due to the condensation of silanol (Si—OH) end groups formed in the oligomer as a result of end group loss as described in Fig. 3 (3-III) at distillation temperatures.

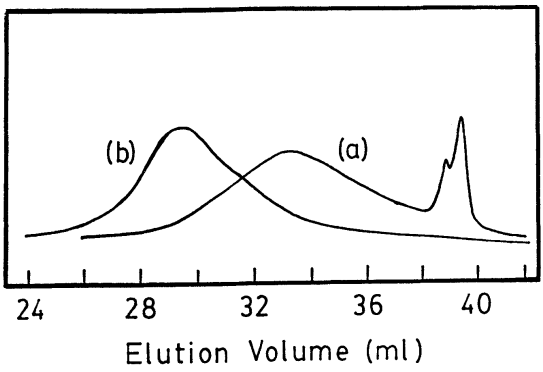


Fig. 5. GPC curves for HPPDMS-2000 oligomer (a) before and (b) after distillation

When HBPDMS-1000 oligomer was subjected to a similar vacuum distillation process, the result was almost the same. Original oligomer had an average molecular weight of 1300 g/mole, determined by GPC. After vacuum distillation the average molecular weight increased to 2550 g/mole (Fig. 6). FT-IR spectrum of the original material and the vacuum distilled product showed exactly the same behavior as that of HPPDMS, indicating complete loss of end group functionality.

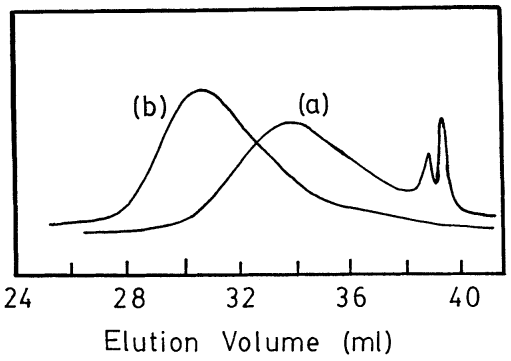


Fig. 6. GPC curves for HBPDMS-1000 oligomer (a) before and (b) after distillation

For HPPDMS-2000, (Mn of 1900 g/mole from GPC), hydroxypropyl end groups make up 6.2% of the oligomer by weight. GPC (Fig. 5-a) also shows substantial amounts of residual cyclics. After distillation, weight loss is 17.6% by weight (Table 1). This suggests that there was about 11.4% cyclics left after the equilibration reactions, which were completely removed by distillation, as can clearly be seen in Fig. 5-b. For HBPDMS-1000 (Mn of 1300 from GPC), the backbone is made up 11.2% by weight of hydroxybutyl end groups. There is also large amount of cyclic siloxanes, (Fig. 6-a). After distillation weight loss is 21.3% by weight as given in Table 1. This indicates that initially there were about 10.1% by weight of cyclic siloxanes in the system, which were completely removed after distillation.

Although PDMS oligomers with α,ω-hydroxypropyl and α,ω-hydroxybutyl termination showed loss of end groups under vacuum distillation, α,ω-2-hydroxypentyl and α,ω-hydroxyhexyl terminated PDMS oligomers were completely stable under similar conditions. In fact GPC scans of the oligomers (as received) showed no cyclic siloxane residues in the system. FT-IR spectra of original HHPDMS-1000 and the residual product after vacuum distillation were identical as given in Fig. 7. It is clear that there is no degradation or change in the end group structure. There was no change in the GPC chromatograms of HHPDMS-1000 oligomers before and after distillation, either.

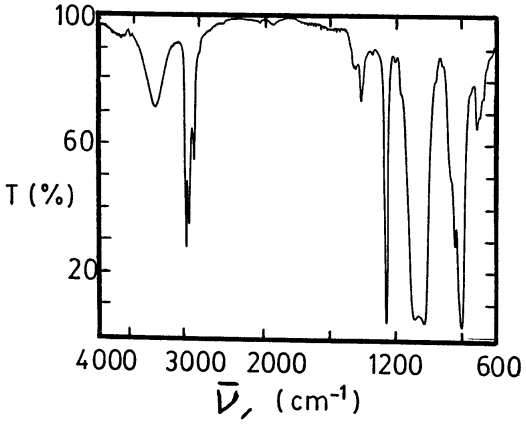
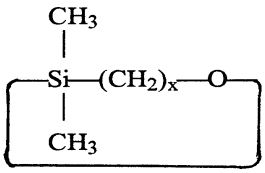


Fig. 7. FT-IR spectrum of HHPDMS-1000 before and after vacuum distillation

Conclusions

All these studies clearly show that α,ω-hydroxpropyl and α,ω-hydroxybutyl terminated PDMS oligomers are not stable under neutral conditions when subjected to high temperatures. This is because of the back biting of the oxygen of the primary hydroxyl end group, the terminal silicon of the PDMS. This produces a 5 or 6 membered, stable heterocyclic ring, from hydroxypropyl and hydroxybutyl terminated oligomers respectively with the structure shown below:



where x=3 for hydroxypropyl and x=4 for hydroxybutyl PDMS. This is basicly the reverse of the reaction used for the preparation of HBDSX by the hydrolysis of 1,1-dimethyl-1-sila-2-oxacyclohexane(19). For hydroxyhexyl terminated PDMS oligomers if the back biting were effective, the ring structure formed would be an 8 membered ring, which is not favorable. For 2-hydroxypentyl terminated systems, the

end-group stability may be due to the steric effects and also due to the reduced nucleophilicity of the secondary hydroxyl. In order to have well defined, clean hydroxybutyl or hydroxypropyl terminated PDMS oligomers, the best approach seems to be the chemical protection of the hydroxyl end groups (e. g. by esterification) before equilibration, followed by vacuum stripping and finally deprotection under mild reaction conditions(7).

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