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Thermal Stabilities of Hydroxyalkyl Terminated Polydimethylsiloxane Oligomers

İskender YİLGOR and Emel YİLGOR
Koç University, Cayir Caddesi 5,
Istinye 80860, İstanbul-TURKEY

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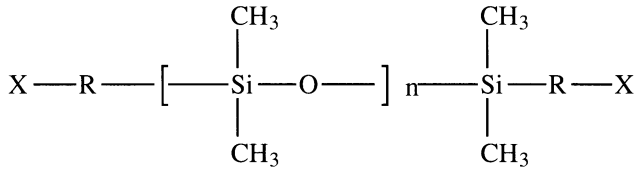
The thermal stabilities of α,ω-hydroxypropyl, α,ω-hydroxybutyl α,ω-2-hydroxypentyl and α,ω-hydroxyhexyl terminated polydimethylsiloxane oligomers were investigated. Hydroxypropyl and hydroxybutyl terminated polydimethylsiloxane oligomers showed degradation upon heating through the loss of functional end groups, as determined by FTIR spectroscopy and gel permeation chromatography. α,ω-Hydroxyhexyl and α,ω-2-hydroxypentyl terminated polydimethylsiloxane oligomers were stable under similar conditions. The instability of the end groups is due to the backbiting 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 GPC.

Introduction

α,ω-functionally terminated reactive oligomers are important starting materials and intermediates for the preparation of a wide variety of segmented copolymers and synthetic elastomers, such as polyurethanes, polyamides and polyesters [1,2]. They are also used in the toughening of brittle networks, which include epoxies and bismaleimides[3,4]. Reactive oligomers (also called macromonomers) widely used for such applications include polytetrahydrofuran (PTHF), polyethyleneoxide (PEO), polypropyleneoxide (PPO), aliphatic polyesters, hydroxyl terminated polyacrylates, polybutadiene and other vinyl based oligomers. In the last decade α,ω-organofunctionally terminated polydimethylsiloxanes (PDMS) have also gained importance because of their interesting surface and bulk properties, ease of preparation and physiological inertness[5]. The chemical structures of difunctional PDMS oligomers and possible variations in their backbone structures are shown in Figure 1.

One of the difficulties encountered in oligomer chemistry is the preparation of perfectly difunctional materials. This is an important requirement for the synthesis of linear segmented copolymers of high molecular weight with controlled structures through condensation polymerization. If the reactive oligomers are produced by ring opening polymerization, as in the case of PTHF, PEO or polycaprolactone (PCL), control of average molecular weight and end group functionality is fairly easy, as long as the reactive end groups are hydroxyl groups. If the oligomers are produced by anionic, cationic or free-radical polymerization of vinyl type monormers, the molecular weight control is still easy, but production of perfectly difunctional

oligomers is fairly difficult.



where, (X) is a reactive functional group suh as

OH, NH_2, COOH, CH = CH_2, CH$\diagdown\!\!\diagup$O$\diagdown\!\!\diagup$$CH_2$, NCO, Halogen, etc.

(R) is a short hydrocarbon segment, usually in the range of C_3- C_{10}, and

(n) is the number of repeat units in the range of 1-300 or higher

Figure 1. General structures of functionally terminated polydimethylsiloxane oligomers

There are several major advantages offered by organofunctionally terminated PDMS oligomers These include ease of preparation with a wide variety of functional end-groups, production of perfectly difunctional oligomers, flexibility in the modification of backbone structures, and ease of their molecular weight control[5]. Organofunctionally terminated siloxane oligomers can be prepared by acid or base catalyzed equilibration or redistribution reactions of octamethylcyclotetrasiloxane (D_4) and a disiloxane end-blocker, as shown in Figure 2. Since (Si—-O) bonds are partially ionic, they can be cleaved by strong acids such as sulfuric, trifluoromethanesulfonic (TFA) or trifuoroacetic acid, or by strong bases such as potassium hydroxide or tetramethylammonium hydroxide (TMAH)[6]. The average molecular weight of the oliomer 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[5], except for hydroxyl terminated systems, where some side reactions may take place, giving rise to the loss of end group functionality, depending on the structure of (R) group as defined in Figure 1. Unfortunately, this has not been observed by many researchers for some time, including our own group, where hydroxypropyl or hydroxybutyl terminated PDMS oligomers were utilized to prepare siloxane-urethane segmented copolymers[7–10]. Most of these efforts yielded only low molecular weight materials with poor mechanical properties or products with no mechanical integrity at all[7,8]. On the other hand, through 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, a large amount of acid is necessary during these reactions[12]. Formation of ester linkages protects the hydroxyl end groups from any side reactions such as back-biting or dehydration. The end groups can be regenerated at the end of the equilibration reactions by mild hyrolysis with sodium carbonate. However, this is a very tedious procedure.

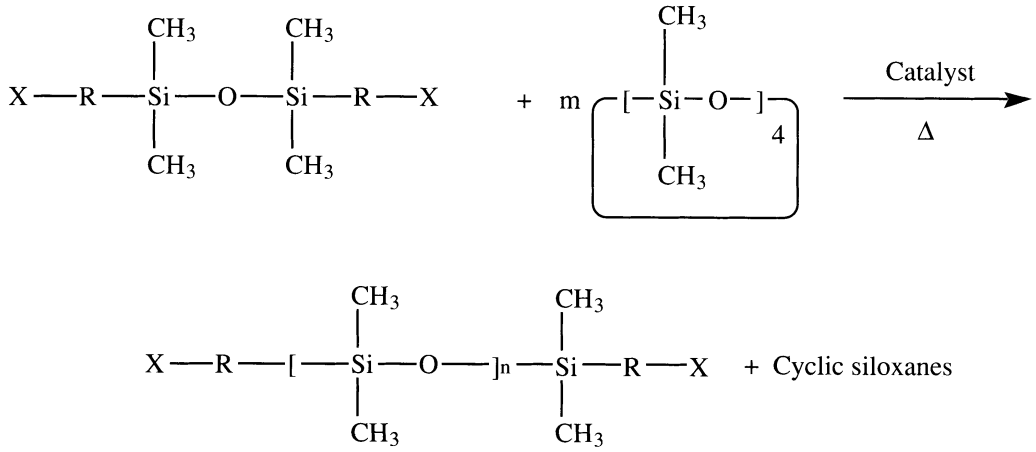


Figure 2. Equilibration reaction scheme for the preparation of organofunctionally terminated PDMS oligomers

In this study, the thermal stabilities of various hydoxy terminated PDMS oligomers were investigated by FT-IR spectroscopy and gel permeation chromatography (GPC). Base catalyzed equilibration reactions of respective dimers with D_4 were also investigated for the preparation of high molecular weight oligomers. The molecular weight distribution and end group structures of these oligomers were determined. Mechanisms for possible side reactions were provided. The results were compared with those of disiloxanes and polydimethylsiloxanes terminated with long hydroxyalkyl or secondary hydroxyl groups.

Experimental

Materials: 1,3-bis(γ-hydroxypropyl)tetramethyldisiloxane (HPDSX) was obtained from Silar Laboratories Inc., Scotia, NY. 1,4-bis(γ-hydroxybutyl)tetramethyldisiloxane (HBDSX), α,ω-hydroxybutyl terminated PDMS (HBPDMS) and 1,1-dimethyl-1-sila-2-oxacyclohexane (DSOCH) were products of Huels, Bristol, PA. α,ω-Hydroxypropyl-(HPPDMS), α,ω-hydroxyhexyl-(HHPDMS) and α,ω-2-hydroxypentyl-(2HPPDMS) terminated siloxane oligomers were obtained from Th. Goldschmidt AG, Essen, Germany. They had average molecular weights of 1000 and 2000 g/mole. Octamethylcyclotetrasiloxane, (D_4), was a product of Dow Corning Corporation. All materials were used as received.

Procedures:

Stability under neutral conditions: HPDSX, HBDSX, HPPDMS, HBPDMS, HHPDMS and 2HPPDMS were separately introduced into pyrex round-bottom flasks and vacuum distilled at 0.1 mm Hg between 130 and 150° C. The distillate and the residue were analyzed at the end of this process by FT-IR and/or GPC.

Equilibration reactions with KOH: Calculated amounts of disiloxane end-blocker (HPDSX or HBDSX), D_4 and 0.1 mole % of KOH (based on the end-blocker concentration) were introduced into two-neck, round-bottom pyrex reaction vessels equipped with overhead stirrer and dry nitrogen inlet. The system was then immersed into a constant temperature oil bath at 80° C. Reactions were monitored by GPC. At the end of the reaction, the catalyst was neutralized by treating it with dilute aqueous acetic acid and the siloxane oligomer was then extracted with THF. Cyclics were removed by vacuum distillation.

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 refractive index and UV detectors. Measurements

were made at 23° C, with a flow rate of 1.0 ml/min. Solvents used for GPC experiments were reagent grade toluene or tetrahydrofuran. A GPC calibration line was also contructed by using HBDSX, DSOHC, D_4 and narrow molecular weight carboxypropyl terminated siloxane oligomers, fractionated with supercritical carbondioxide[13]. The GPC calibration curve is given in Figure 3.

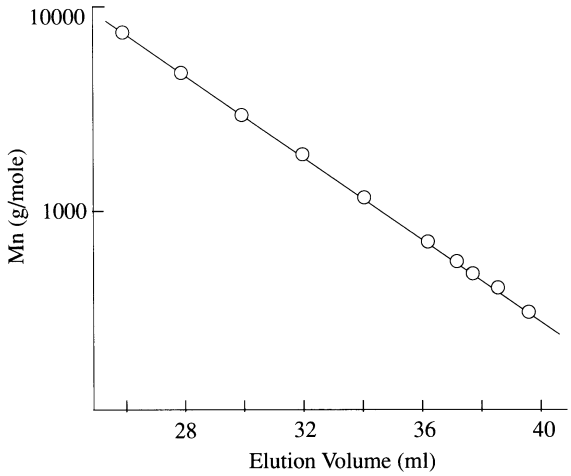


Figure 3. GPC Calibration curve for organofunctionally terminated PDMS oligomers

Results and Discussion

Hydroxyalkyl terminated siloxane oligomers are important intermediates for the preparation of siloxane-urethane, siloxane-carbonate and siloxane-ester type segmented or block copolymers with applications as biomaterials[14], membranes[15] and surface modifying additives[16] for various plastics. They also play important roles in the preparation of siloxane containing specialty coatings with low surface energies and environmental resistance[5,17]. A major problem related to the preparation of well-defined, difunctional, hydroxyalkyl terminated siloxane oligomers with controlled molecular weights is 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 as shown in Figure 2. In our previous studies we have also 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 Figure 4. We have further shown through 1H-NMR and GPC studies that in these reactions, conducted between 65 and 85° C, an equilibrium is established where the ratios of compounds 4-I, 4-II and 4-III are approximately 38, 25 and 37% by weight, respectively[18].

Since hydroxybutyl terminated siloxane dimer was not stable under acidic conditions, a base, KOH, was used as the catalyst during equilibration reactions in this study. The reactions were followed by GPC. We attempted to prepare oligomers with molecular weights of 1000, 2000 and 5000 g/mole. Figure 5 gives the GPC curves of the equilibration reaction of HBDSX and D_4 at various stages of the reaction. The final desired molecular weight of the oligomer in this reaction was 1000 g/mole. As seen in Figure 5, the molecular weight of the oligomer increased steadily during the reaction and went well beyond the aimed molecular weight of 1000 g/mole. This we believe was due to the formation of alkoxides from hydroxyl end groups, which are very strong bases and therefore can also act as catalysts, as shown in Figure 6. The result is the loss of end groups and the molecular weight control, where much higher molecular weights than expected are observed. Another important result of these side reactions was the formation of oligomers

containing hydrolytically unstable Si—O—C linkages. After neutralization and removal of the catalyst, when the cyclic side products, which are usually between 4- 12% by weight in such equilibrium reactions, were removed under vacuum, a dramatic increase in the molecular weight of the oligomers was observed. For further investigation of this anomaly, a comparative study was conducted between oligomers produced in our laboratories and commerically available oligomers.

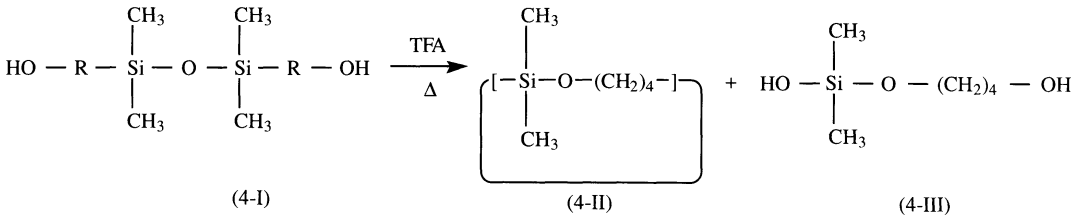


Figure 4. Degredation mechanism of HBDSX under triflic acid catalysis

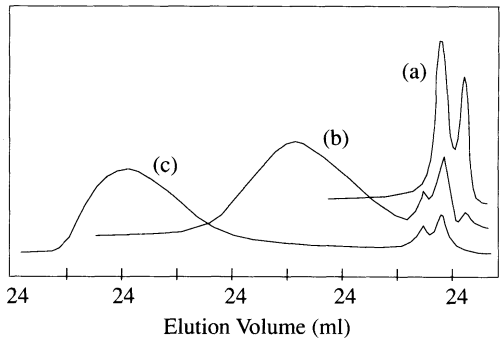


Figure 5. GPC curves for the equilibration of HBDSX and D_4 under KOH catalysis at 80° C. (a) Initial reaction mixture (b) After 12 hours of reaction (c) After 24 hours of reaction

Interestingly, when commercially available oligomers were vacuum distilled under neutral conditions, depending on the structure of their end groups, loss of the end group functionality and a dramatic increase in the molecular weight were observed, similar to oligomers synthesized in our laboratories. Figure 7 shows the FT-IR spectrum of the commerical HBPDMS oligomer with an average molecular weight of 2000 g/mole. 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[19] and are clearly visible in the spectrum. After distillation, FT-IR spectrum of the residue (Figure 8), which is the spectrum of the oligomer prdouced, shows all of the peaks in Figure 7, except the strong hydroxy peak. On the other hand, the FT-IR spectrum of the distillate , which is reproduced in Figure 9, shows a very strong hydroxy peak along with other peaks, typical of low molecular weight siloxanes[19]. These FT-IR spectra clearly show that for HBPDMS, even in the absence of any acid or base catalyst, the degradation mechanism depicted in Figure 4 is effectively taking place at high temperatures.

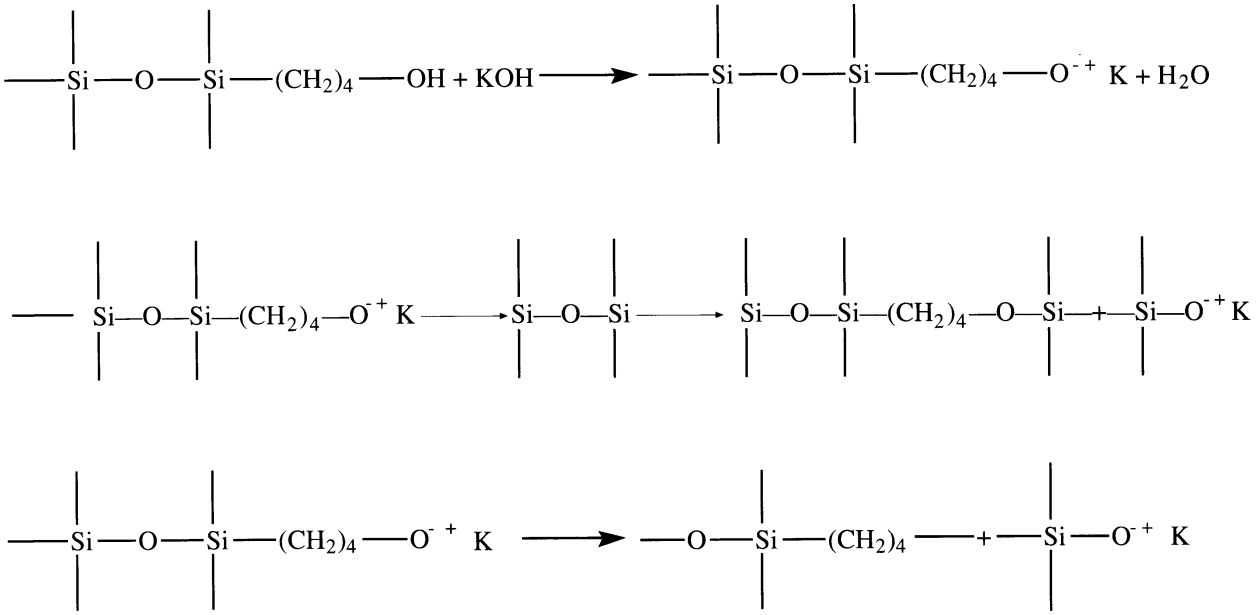


Figure 6. Formation of Alkoxides and resulting Side Reactions in the Preparation of Hydroxybutyl Terminated PDMS Oligomers

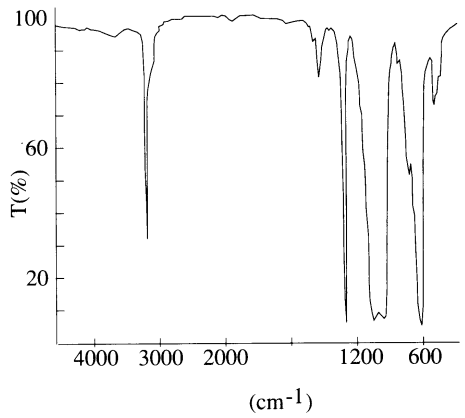


Figure 7. FT-IR spectrum of a commerical HBPDMS sample (Mn= 2000 g/mole)

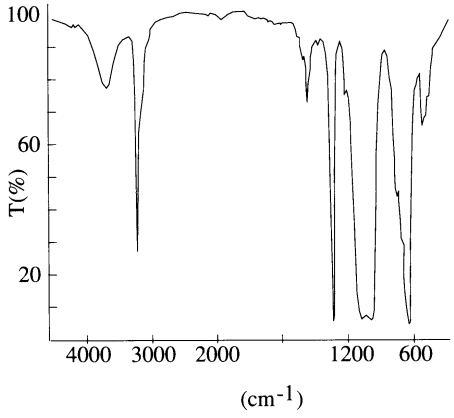


Figure 8. FT-IR spectrum of the remaining oligomer after vacuum distillation of HBDDMS sample of Figure 7

GPC chromatograms provided valuable supporting information regarding the change in the average molecular weight of the oligomers before and after stripping. The GPC chromatogram of the commericial HBPDMS oligomer (Mn$\sim$ 2000 g/mole) is given in Figure 10a. It is interesting to note that it also contains many low molecular weight cyclic products. Mn calculated using the GPC calibration curve in 1850 g/mole. The chromatogram for the same product after stripping is given in Figure 10b. As expected, all of the cyclic side products, which are usually a mixture of D_4, D_5 and D_6 and which elute between 36.5 and 38.5 ml in our system, are completely removed from the equilibration mixture. However, as can be clearly seen there is a dramatic shift in the oligomer peak to higher molecular weights. The Mn calculated from the calibration curve for the stripped oligomer is 3600 g/mole, which is almost double the original molecular weight.

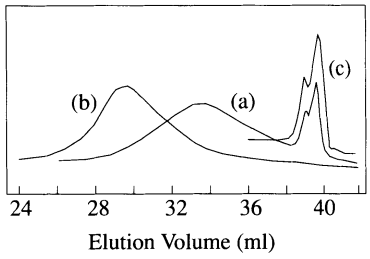


Figure 9. FT-IR spectrum of the distillate, after vacuum distillation of HBPDMS sample of Figure 7

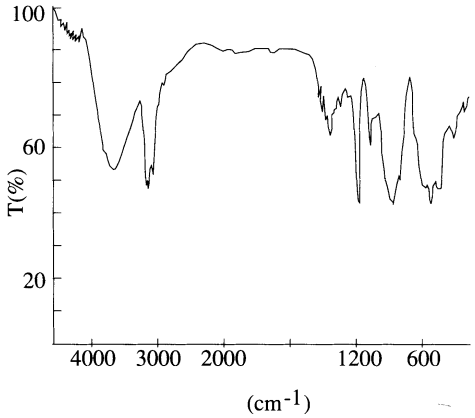


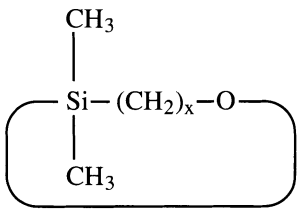
Figure 10. GPC chromatograms of HBPDMS before and after distilllation (a) Original sample (b) Oligomer after distillation (c) The distillate

When a commercially available HPPDMS oligomer with an average molecular weight of 1000 g/mole was subjected to a similar vacuum distillation process, the result was almost the same. The original oligomer had an a average molecular weight of 1250 g/mole, determined by GPC. After removal of the cyclics by vacuum distillation the molecular weight increased to 2600 g/mole (Figure 11). The FT-IR spectrum of the original material and the vacuum distilled product again showed a similar behavior to that of HBPDMS, indicating an almost complete loss of end group functionality. As expected, similar behavior was observed with hydroxybutyl and hydroxypropyl terminated PDMS oligomers with varying molecular weights.

Although commerically available or laboratory equilibrated PDMS oligomers having α,ω-hydroxpropyl and α,ω-hydroxybutyl termination showed loss of end group functionalities under vacuum distillation, commercially available α,ω-2-hydroxypentyl and α,ω-hydroxyhexyl terminated PDMS oligomers were completely stable under similar vacuum distillation conditions. The FT-IR spectra of original α,ω-hydroxyhexyl terminated PDMS (Mn $\sim$ 1000 g/mole) and the residual product after vacuum distillation were identical, as shown in Figure 12. It is clear that there is no degradation or change in the end group structure. There was also no change in the GPC chromatogram of the two products.

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 backbiting of the oxygen of the primary hydroxyl end group of 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 strucure shown below:



where x=3 for hydroxypropyl and x=4 for hydroxybutyl PDMS. For hydroxyhexyl, if the backbiting were effective, the ring structure formed would be an 8-membered ring, which is not very stable. For 2-hydroxypentyl terminated systems, the end-group stability may be due to the steric effects and also 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[12].

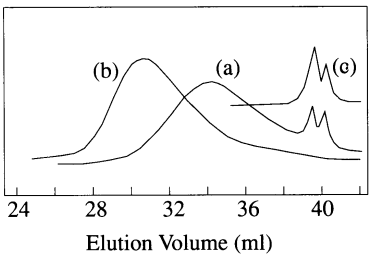


Figure 11. GPC chromatograms of HPPDMS before and after distillation (a) Original sample (b) Oligomer after distillation (c) The distillate

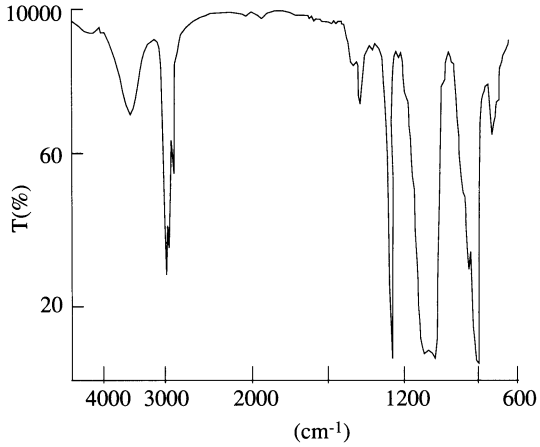


Figure 12. FT-IR spectrum of a commercial HHPDMS sample (Mn=1000 g/mole) before and after vacuum distillation

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