

The thermal degradation behaviour of a series of siloxane copolymers - a study by thermal volatilisation analysis

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ABSTRACT:

The thermal degradation behaviour of novel high number average molecular mass polysilalkylenesiloxanes is reported. These have been synthesised using anionic ring-opening polymerisation of 1,1,3,3,14,14,16,16-octamethyl-2,15-dioxa-1,3,14,16-tetrasilacyclohexacosane and octamethylcyclotetrasiloxane (D4) mixtures. The thermal degradation behaviour of these materials was evaluated by a combination of thermogravimetric analysis (TGA) and thermal volatilisation analysis (TVA) and compared with a commercial sample of PDMS. The results demonstrated that the thermal degradation of the polysilalkylenesiloxanes is more complex than the PDMS, with the polysilalkylenesiloxanes exhibiting a lower degradation peak maximum temperature. The major volatile degradation products evolved from the PDMS were identified as D3 to D6 cyclic siloxane oligomers, in addition to higher molecular mass cyclic siloxane oligomers. The polysilalkylenesiloxanes, on the other hand, evolved short chain aliphatic hydrocarbons, cyclic and linear siloxane oligomers and silanes. The TVA results indicate that the polysilalkylenesiloxanes degrade mostly by random chain scission of the polymer backbone, whereas the commercial PDMS degrades by the accepted depolymerisation reaction which involves “back-biting” reactions.

KEYWORDS:

Polydimethylsiloxane; Polysilalkylenesiloxane; Thermal degradation

1. INTRODUCTION

Polydimethylsiloxane (PDMS) is one of the most widely studied inorganic polymers. Due to its unique physical properties, it has found use in a very broad set of applications. For example, silicone materials are useful in the electronics industry as sealants, adhesives, wire insulation and conformal coatings on printed circuit boards. For these and possibly other applications, the relatively high thermal stability of PDMS-based formulations is advantageous. Continued improvements to this already desirable property are the focus of the polymers reported upon herein.

Approximately fifty-five years ago, a hybrid polymer structure was reported that combined paraffin-like properties of long alkyl chains with the properties of dimethylsiloxane in a polysilalkylenesiloxane (PSAS). As shown in Figure 1, these materials possess regularly alternating alkylene units and siloxane units. Many interesting examples have been prepared via one of three synthetic routes; condensation, hydrosilylation and ring-opening polymerization (ROP). This class of polymers was first reported by Sommer and Ansul [1] who synthesised a C4 alkylene.

In order to prepare PSAS having truly high molecular mass, both condensation and hydrosilylation polymerization schemes present significant challenges. Nevertheless, condensation of bis-silanol structures has been reported by Benouargha *et al.* [2] for the preparation of C6 and C10 PSAS. Their synthetic scheme yielded polymers having a number average degree of polymerisation (DP_n) of less than 200. Hydrosilylation polymerization between α,ω -dienes and 1,1,3,3-tetramethyldisiloxane result in low DP_n examples of polysilalkylenesiloxane; most recently Kühn *et al.* [3] reported on the stoichiometry-controlled preparation of α,ω functionalized C10 PSAS oligomers. Limitations to this synthetic scheme are well documented. Both Weber and Sargent [4] and Dvornic *et al.* [5,6] have demonstrated that isomerization of the terminal double bond to a more substituted internal position [7] results in limitations to the desired stoichiometric balance required for such a step-growth polymerization.

Alternative to the aforementioned, a chain growth scheme can be used to prepare PSAS structures. Others have reported the preparation of ethanylene [8], propanylene [9] and butanylene [1] cyclosilalkylenesiloxane monomers. We have previously reported the preparation of larger hexanylene, octanylene, decanylene and tetradecanylene cyclic monomers and dimers [10]. These monomers undergo ring-opening polymerization under either anionic or cationic conditions to yield high number average molecular mass polymers. Not surprisingly, the cyclosilalkylenesiloxane monomers can undergo well controlled co-polymerization with standard dimethylsiloxane monomers [11] to form well controlled structures. Interestingly, the ethylene system has been used as a model system for ROP kinetic studies [12, 13].

Many of the applications in which polysiloxanes are employed involve elevated temperatures. Their thermal degradation behaviour must, therefore, be fully understood if they are to be successful in such applications. A number of studies have been carried out concerning the thermal degradation behaviour of these materials, the most significant of which was the work by Grassie and MacFarlane [14] that aimed to determine the basic thermal degradation mechanisms of the simplest polysiloxane, PDMS. Grassie and MacFarlane reported that the major products of degradation of PDMS were a mixture of cyclic siloxane oligomers with ring sizes D3 to D11 as well as lower levels of higher oligomeric siloxane species. The most abundant product observed was the trimer (D3) with decreasing levels of the tetramer (D4), pentamer (D5) and higher oligomers. Degradation of the PDMS was proposed to occur *via* a depolymerisation reaction which involves a “back-biting” reaction in which the hydroxyl chain end attacks the polymer backbone. This forms cyclic siloxane oligomers, as the hydroxyl group reacts at different points along the polymer backbone yielding cyclic oligomers of various sizes. Grassie and MacFarlane also proposed that a second intra-molecular “back-biting” reaction, not involving the chain ends, can occur, in which the polymer chain folds back upon itself and rearrangement occurs to form *via* a new Si-O bond a cyclic siloxane oligomer. This was similar to the mechanism proposed by Patnode and Wilcock [15] and Thomas and Kendrick [16]. Presented in Figure 2 are both “back-biting” mechanisms showing the formation of a D3 siloxane compound, reactions at

points further along the polymer backbone will lead to cyclic oligomers of greater ring sizes. The intramolecular “back-biting” mechanism is proposed to be the predominant degradation mechanism in end-blocked polysiloxanes which do not possess hydroxyl chain ends [14].

More recently, Camino *et al.* [17,18] have made use of thermogravimetry in combination with kinetic analysis and computer simulation methods to study the thermal degradation of low crosslink density tri-methyl siloxy end-blocked PDMS, finding that that the rate of degradation is limited primarily by the diffusion of volatile cyclic oligomers from the system. Molecular modelling studies showed that the cyclisation is energetically favoured due to the overlap of empty silicon d-orbitals with the orbitals of oxygen and carbon on a neighbouring chain segment. This interaction stabilizes the chain folded conformation necessary for the cyclisation reaction to take place.

Although the thermal degradation behaviour of simple siloxane polymer systems has been well studied and is relatively well understood, many commercial siloxane polymer systems are significantly more complex than the simple PDMS model systems generally studied. It must be remembered that commercial siloxane polymers are often heavily filled, crosslinked and chemically modified and their degradation behaviour is more complex and less well understood than the simpler model systems. For example, Lewicki *et al.* [19] studied the effect of a well-known filler, organically modified montmorillonite clay on the thermal degradation behaviour of a crosslinked PDMS. Using the thermal volatilisation analysis (TVA) technique also used herein, they demonstrated that the PDMS-montmorillonite blend degraded under non-oxidative conditions primarily through a thermal depolymerisation processes that closely correlated with the accepted model of the thermal degradation of linear PDMS. The TVA analysis demonstrated that the clay acted to destabilise the PDMS although the major products of the thermal degradation were the D3 – D7 cyclic oligomeric siloxanes (with the D3 cyclic being the most abundant) and a series of higher oligomeric siloxane residues that were effectively identical to those of pure polymer. Although the presence of the montmorillonite within the network did not affect the distributions of these major products, it did, however, promote the formation of small

amounts of benzene (from the di-phenyl-methylsilanol end-capper) and dimethylsilanone, both via unexpected radical cleavages of the network.

Herein, we report on the thermal degradation of high number average molecular mass poly(1,1,12,12-tetramethyl-13-oxa-1,12-disilatridecanylene) and poly(1,1,12,12-tetramethyl-13-oxa-1,12-disilatridecanylene-*co*-dimethylsiloxane). These materials possess a backbone structure comprising decanylene units randomly distributed with dimethylsiloxane units. The thermal degradation of an unfilled high number average molecular mass polydimethylsiloxane (Gelest DMS-S51) was also studied for comparison purposes.

2. EXPERIMENTAL

2.1 Materials

The synthesis and chemical characterization of the polymers used within this study have been published elsewhere [20]. The polysilalkylenesiloxanes employed in this work are poly(1,1,12,12-tetramethyl-13-oxa-1,12-disilatridecanylene) (M_n 111,000 g mol⁻¹) which will be referred to throughout as the homopolymer, and two poly(1,1,12,12-tetramethyl-13-oxa-1,12-disilatridecanylene-*co*-dimethylsiloxane) copolymers which have been synthesised by anionic ring opening polymerisation of 1,1,3,3,14,14,16,16-octamethyl-2,15-dioxa-1,3,14,16-tetrasilacyclohexacosane and octamethylcyclotetrasiloxane (D4) mixtures. The ratio of alkylene (A) to dimethylsiloxane (D) units was controlled by altering the quantity of D4 which was present in the mixture. The two copolymers employed in this work had an A:D ratio of 1:3.3 and 1:6.6 and will be referred to as copolymer I and II, respectively. The polydimethylsiloxane used for comparative purposes was the silanol terminated Gelest DMS-S51, M_n 139,000 g mol⁻¹.

2.2 Thermogravimetric analysis (TGA)

All TGA experiments were carried out using a Perkin Elmer TGA7 thermogravimetric analyzer with 8 - 10 mg samples being analysed. The system was initially heated to 50°C and held isothermally for five minutes. Following this, the sample was heated at a rate of 10°C min⁻¹ from 50°C to 800°C

under a flow of 30 ml min⁻¹ of helium. The mass loss as a function of temperature was monitored and from this the first derivative of the mass loss curve was calculated as a function of temperature. The temperature at which the onset of degradation occurs has been determined from the TGA curves and will be reported herein as the temperature at which the material has lost 5% of its original mass.

2.3 Thermal Volatilisation Analysis (TVA)

All TVA analyses were carried out using a TVA line which was built in-house, based upon the apparatus and techniques described by McNeill *et al.* [21]. The apparatus consists of a sample chamber (heated by a programmable tube furnace) connected in series to a primary liquid nitrogen cooled sub-ambient trap and a set of four secondary liquid nitrogen cooled cold traps. The whole system is continuously pumped to a vacuum of 1×10^{-4} Torr by means of a two-stage rotary pump and oil diffusion pumping system. Volatile condensable products can be initially trapped at two stages: the water jacket cooled 'cold-ring' immediately above the heated area of sample tube which condenses high boiling point materials that are not volatile under vacuum at ambient temperature, and the primary liquid-nitrogen-cooled sub-ambient trap which collects all the lower boiling point species which are volatile under vacuum at ambient temperature but which condense under vacuum at liquid nitrogen temperatures (-196°C). A linear response Pirani gauge positioned at the entrance of the primary sub-ambient trap monitors the evolution of the total volatiles (condensable and non-condensable species) from the sample as a function of pressure vs. temperature/time. A second Pirani gauge at the exit of the primary sub-ambient trap monitors the evolution of the non-condensable volatiles (typically carbon monoxide, methane, hydrogen or ethene) as a function of pressure vs. temperature/time. Trapped, low-boiling species can be distilled into separate secondary cold traps by slowly heating the primary sub-ambient trap to ambient temperatures. These separated fractions can then subsequently be distilled into gas-phase cells for FTIR and GC-MS analysis. A series of non-linear Pirani gauges are placed at the entrance and exits of all secondary traps to monitor the pressure changes as volatile species were distilled into separate traps and gas-phase IR cells.

All TVA runs were conducted under vacuum using 25 mg samples, with the samples heated from ambient temperature to 650°C at a rate of 10°C min⁻¹. A 1 - 300 amu Hiden single quadrupole RGA mass spectrometer sampled a continuous product stream during both the degradation and differential distillation runs. Sub-ambient differential distillation of the collected volatiles was carried out by heating the primary sub-ambient trap from -196°C to ambient temperature. Volatiles were separated into four major fractions for subsequent IR and GC-MS analysis.

All FTIR analysis of the collected TVA products was carried out using a Perkin Elmer Spectrum 100 FTIR Spectrometer used in transmission mode. High boiling 'cold ring' fractions were cast from chloroform solution onto NaCl disks for analysis. Low-boiling volatiles were analyzed in the gas phase using gas phase cells with NaCl windows.

All GC-MS analysis of the collected TVA products was carried out using a Finnigan ThermoQuest capillary column trace GC and Finnigan Polaris Quadrupole Mass Spectrometer. Suitable fractions were dissolved in spectroscopy grade chloroform and subsequently analyzed.

3. RESULTS AND DISCUSSION

3.1. *TGA of polysilalkylenesiloxanes and PDMS*

TGA was employed in this study to examine the overall non-oxidative thermal degradation behaviour of the siloxane systems under study. Presented in Figure 3 are the TGA mass loss curves and the corresponding derivative thermogravimetry (DTG) curves obtained for the homopolymer, the copolymers and the commercial PDMS. Presented in Table 1 are the onset degradation and peak maxima temperatures taken from the DTG curve. It can be observed from Figure 3 and Table 1 that all of the samples exhibit a single mass loss stage. However, the polysilalkylenesiloxanes all exhibit a higher onset degradation temperature than the commercial PDMS material. More relevantly, the onset temperatures for copolymers I and II are higher than that of the homopolymer which suggests that the incorporation of dimethylsiloxane into the polymer backbone increases the thermal stability of the material as would be expected on the basis of the bond strengths (Si-C 301 kJ mol⁻¹, C-C 348 kJ mol⁻¹,

Si-O 368 kJ mol⁻¹). The DTG peak maxima, which represent the temperature at which the maximum rate of mass loss occurs, appears to confirm this as these occur for all three polysilalkylenesiloxane samples at lower temperatures than the commercial PDMS.

3.2 TVA of Polysilalkylenesiloxanes and PDMS

3.2.1 Degradation Profile

TVA was employed in this study to examine the thermal degradation behaviour of the materials under vacuum and to allow characterisation of the volatile degradation products being evolved. During the TVA of the polysilalkylenesiloxane materials a small quantity of non-condensable gases was evolved. These were identified by online mass spectrometry as primarily ethene and methane. Non-condensable volatiles were, however, not observed during the TVA of the commercial PDMS sample. This indicates that these non-condensable degradation products originate from the long alkyl chain component of the polysilalkylenesiloxane materials and not from the dimethylsiloxane component. In addition to the non-condensable material, a significant quantity of condensable volatile material was evolved from all of the polymer samples. The TVA plots showing the rate of total volatiles evolution as a function of pressure vs. furnace temperature are presented in Figure 4 and the corresponding onset degradation and evolution rate peak maxima temperatures are summarised in Table 2.

It can be observed from Figure 4 that degradation of the siloxane samples occurs *via* a one stage process, which is consistent with the TGA results; however, the temperatures at which the onset of degradation and the peak maxima occur are lower than those obtained from the TGA curves. This is a common phenomenon as the volatilisation is facilitated under vacuum, although the effect here is more marked than anticipated. An alternative explanation comes from the observation from Table 2 that the *order* of onset temperatures at which degradation to yield volatile material commences also differs from the TGA results. The commercial PDMS exhibits the lowest onset degradation temperature which is in agreement with the TGA results; however, overall the onset degradation temperatures of the polysilalkylenesiloxane samples decreases in the order homopolymer > copolymer I > copolymer II >

PDMS, in contrast to the TGA results. It is interesting to speculate that this may be due to catalytic effects on the surface of the borosilicate glass TVA pyrolysis vessel, as has been reported by Nielsen [22] and Zeldin *et al.* [23]. As this would affect the siloxane component, the effect would trend with siloxane content as observed. The TVA peak maxima temperatures follow a similar trend to those obtained from the DTG curves, with the peak temperature for the polysilalkylenesiloxane samples clustering lower than that of the commercial PDMS.

Another important observation from the TVA data is the difference in the level of the volatiles evolved from the siloxane samples. It can be observed in Figure 4 that the PDMS sample evolves a significantly larger quantity of total volatile degradation products than the polysilalkylenesiloxane materials; however, this is in contrast to the TGA results which indicated that the samples all exhibit a similar total mass loss. This again may be partly due to glass-induced catalysis, but an explanation also comes from the nature of the TVA technique which is not able to monitor the evolution of the high molecular mass material which is not volatile at ambient temperatures under vacuum and which condenses in the water jacket cooled cold-ring at the top of the sample tube. The presence of a significant mass loss event during TGA with no significant equivalent volatile evolution during TVA indicates that a material has evolved a significant quantity of high molecular mass material which will condense in the cold-ring fraction during the TVA experiment. These results, therefore, suggest that the polysilalkylenesiloxane materials yield a large quantity of high molecular mass species, whereas the PDMS sample yields a greater quantity of lower molecular mass volatiles. This, therefore, indicates that the nature of the degradation products is significantly different between the PDMS and the polysilalkylenesiloxanes, and in turn suggests that the mechanisms of degradation are different.

3.2.2 Product Characterisation

A colourless liquid cold-ring fraction was collected from all of the siloxane samples and was analysed by FTIR spectroscopy, with the spectra presented in Figure 5. It can be observed from the FTIR spectra that the cold-ring fraction from the PDMS sample consist of high molecular mass siloxane oligomers, with characteristic peaks near 2960, 1260, 1090 and 800 cm^{-1} . The GC-MS chromatogram

for the PDMS cold-ring fraction, presented in Figure 6, confirms the presence of a series of high molecular mass siloxane oligomers and indicates that these are cyclic in nature with ring sizes of D7 and greater. These products are consistent with the depolymerisation mechanism reported in the literature [14-18]. The FTIR spectra from the polysilalkylenesiloxanes also show characteristic siloxane peaks and the GC-MS analysis of these cold-ring fractions reveals that they too contain siloxane oligomers. Presented in Figure 7 is the GC-MS chromatogram of the cold-ring fraction obtained from copolymer I, which is representative of all the polysilalkylenesiloxanes samples. It can be observed from Figure 7 that whilst the cold-ring fractions do contain the D7 - D9 cyclic oligomers, the peaks observed after a retention time of 12.17 minutes are not of the same retention times or pattern as those observed for the commercial PDMS sample. For the polysilalkylenesiloxane samples a number of additional silicon-containing peaks are observed which have not been positively identified but are proposed to be linear, aliphatic siloxane and silane oligomers which originate from random chain scission of the polymer backbone. ^{13}C NMR analysis of the cold-ring fractions obtained from the polysilalkylenesiloxane samples, an example of which presented in Figure 8, confirms the presence of five aliphatic carbons having chemical shifts between 17 and 33 ppm. This is identical to those reported for the alkylene units within the virgin polymers [20] suggesting that some Si-alkylene-Si units can volatilise intact from the degrading copolymers despite the relatively low Si-C bond strength. Analysis of the cold-ring fractions, therefore, reveals that the polysilalkylenesiloxanes degrade to yield high molecular mass materials which are structurally different to those obtained from the commercial PDMS sample.

The condensable volatiles collected from each sample in the first stage of the analysis were separated by means of sub-ambient differential distillation and characterised by online MS and gas-phase FTIR analysis. Presented in Figure 9 are the differential distillation plots showing all of the volatile degradation products evolved from the siloxane samples. Supplementary Figure 1 shows only the volatiles evolved from -200 to -25°C which allows the peaks corresponding to the low molecular mass volatiles to be viewed in more detail. The identities of each of the products evolved during the sub-ambient differential distillation are presented in Table 3. It can be observed from Figure 9 that the

commercial PDMS sample evolves a significantly greater quantity of volatiles during sub-ambient distillation compared to the polysilalkylenesiloxanes, which is in agreement with the results presented in Figure 3 and explanation thereof. The PDMS sample yields only a low level of water and a significant quantity of higher molecular mass volatiles which are evolved between -30°C and ambient temperature. Identification of these higher molecular mass volatiles has been achieved by a combination of FTIR, online MS and GC-MS. Presented in Supplementary Figure 2 is the FTIR spectrum which shows characteristic siloxane peaks at ~ 2970 , 1260, 1040 and 820 cm^{-1} . The GC-MS chromatogram for this fraction of volatiles, presented in Figure 10, confirms that peaks 5 and 6 consist primarily of the cyclic siloxane oligomers with ring sizes D3 to D6. Again, this is consistent with the literature.

Degradation of the polysilalkylenesiloxane materials, however, yields very much smaller quantities of these D3 – D6 oligomers alongside a number of lower molecular mass products identified as short chain aliphatic hydrocarbons that were not observed during the thermal degradation of the commercial PDMS sample. These are likely to arise from thermal degradation by random chain scission of the long chain alkyl units within the polysilalkylenesiloxanes. Furthermore, the GC-MS analysis of the higher molecular mass volatiles (peaks 5 and 6) reveal further differences between the commercial PDMS and the polysilalkylenesiloxanes. In addition to the cyclic siloxane oligomers, linear siloxanes and silanes also appear to be present and again are likely to have originated from the chain scission of the long alkyl chain units within these polymers. The absence of significant quantities of D3 – D6 oligomers will reflect the blocking effect of the alkylene segments on the back-biting cyclisation.

3.2.3 *TVA Summary*

The TVA results, therefore, reveal significant differences in the thermal degradation behaviour of the polysilalkylenesiloxanes compared with the commercial PDMS. The results indicate that the commercial PDMS degrades to yield a high quantity of condensable volatiles which have been identified primarily as D3 to D6 cyclic siloxane oligomers, in addition to a cold-ring fraction consisting of higher molecular mass cyclic siloxane oligomers with a ring size of D7 or greater. Degradation of the polysilalkylenesiloxanes, on the other hand, yields a significantly lower quantity of condensable

volatiles which consist of short chain aliphatic hydrocarbons, D3 to D6 cyclic siloxane oligomers and linear siloxanes and silanes, in addition to a significant cold-ring fraction consisting of D7 to D9 cyclic oligomers and linear siloxanes and silane species.

3.2. Discussion and Conclusions

This work has demonstrated that the thermal degradation of polysilalkylenesiloxanes is more complex than their simpler PDMS counterpart. The PDMS degrades by a depolymerisation reaction to yield a high quantity of condensable volatiles, identified primarily as D3 to D6 cyclic siloxane oligomers, in addition to a cold-ring fraction consisting of higher molecular mass cyclic siloxane oligomers with a ring size of D7 or greater. Degradation of the polysilalkylenesiloxanes, on the other hand, yields a significantly lower quantity of condensable volatiles which consist of short chain aliphatic hydrocarbons, D3 to D6 cyclic siloxane oligomers and linear siloxanes and silanes. Instead, degradation to yield a large quantity of high molecular mass cold-ring material comprised of cyclic and linear siloxanes and silanes appears to be favoured in these materials. The difference in the nature of the degradation products of these materials compared to PDMS is proposed to be due to the presence of the long alkyl chain segments which block the backbiting route to larger oligomers.

5. REFERENCES

- [1] Sommer NLH, Ansul GR. J Am. Chem. Soc. 1955; 77:2482-2485
- [2] Benouargha A, Boutevin B, Caporiccio G, Essassi E, Guida-Pietrasanta F, Ratsimihety A. Eur. Polym. J. 1997; 33:1117-1124
- [3] Louis E, Jussofie I, Kuhn FE, Herrmann WA. J. Organomet. Chem. 2006; 691:2031-2036
- [4] Sargent JR, Weber WP. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 1999; 40:60-61
- [5] Dvornic PR, Gerov VV. Macromolecules 1994; 27: 1068-1070
- [6] Dvornic PR, Gerov VV, Govedarica MN. Macromolecules 1994; 27: 7575-7580
- [7] Speier J. Adv. Organomet. Chem. 1979; 17: 407-447

- [8] Piccoli WA, Haberland GG, Merker RL. *J. Am. Chem. Soc.* 1960; 82: 1883-1885
- [9] Andrianov KA. *Dokl. Akad. Nauk SSSR* 1935; 160:1307
- [10] Tapsak MA, Grailer T, Miller D, Benz ME, DiDomenico E. *J. Inorganic Organomet. Polym.* 1999; 9: 35-53
- [11] Tapsak MA, DiDomenico E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 2000; 41: 572-573
- [12] Suryanarayanan B, Peace BW, Mayhan KG. *J Polym Sci: Polym Chem Ed.* 1974; 12: 1089-1107
- [13] Chojnowski J, Mazurek M. *Die Makrom Chemie.* 1975; 176: 2999-3023
- [14] Grassie N, MacFarlane IG. *Eur. Polym. J.* 1978; 14: 875-884
- [15] Patnode W, Wilcock DF. *J Am. Chem. Soc.* 1946; 68:358.
- [16] Thomas TH, Kendrick J, *J. Polym. Sci: Polym. Chem. Ed.* 1969; 7: 537-549
- [17] Camino G, Lomakin SM, Lazzari M. *Polymer* 2001; 42:2395-2402
- [18] Camino G, Lomakin SM, Lazzari M. *Polymer* 2002; 43:2011-2015
- [19] Lewicki JP, Liggat JJ, Patel M. *Polym. Degrad. Stabil.* 2009; 94: 1548-1557
- [20] Radzinski SC, Tapsak MA. *Silicon* 2011; 3: 57-62
- [21] McNeill IC, Ackerman L, Gupta SN, Zulfiqar M, Zulfiqar S. *J. Polym. Sci: Polym. Chem. Ed.* 1977; 15: 2381-2392
- [22] Nielsen JM. *J. Appl. Polym. Sci., Appl. Polym. Symp.* 1979; 35: 223
- [23] Zeldin M, Qian B, Choi SJ, *J. Polym. Sci. Polym. Chem. Ed.* 1982; 21: 1361-1369

Figure 1: General structure of polysilalkylenesiloxanes.

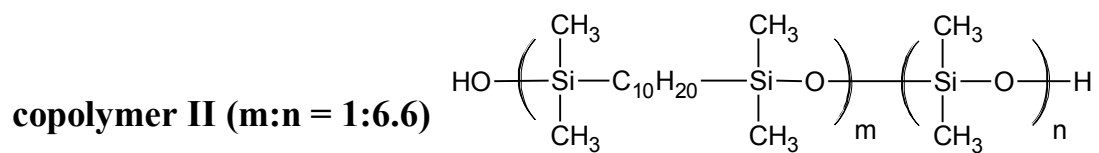
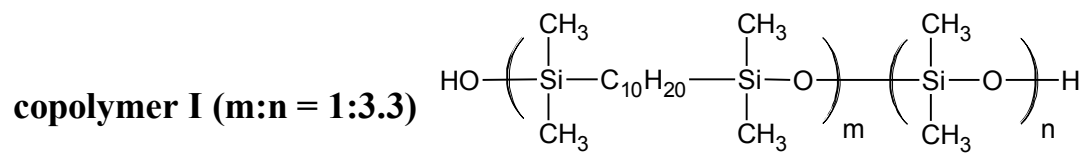
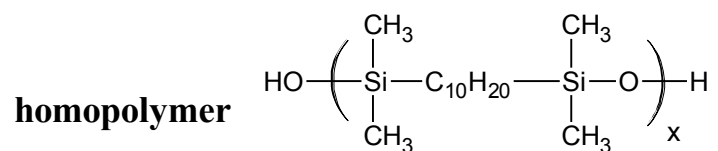


Figure 2: Mechanisms for the thermal degradation of the commercial PDMS *via* depolymerisation reactions showing the formation of the most abundant product (D3). Reaction at points further along the polymer backbone leads to cyclic oligomers of increasing size.

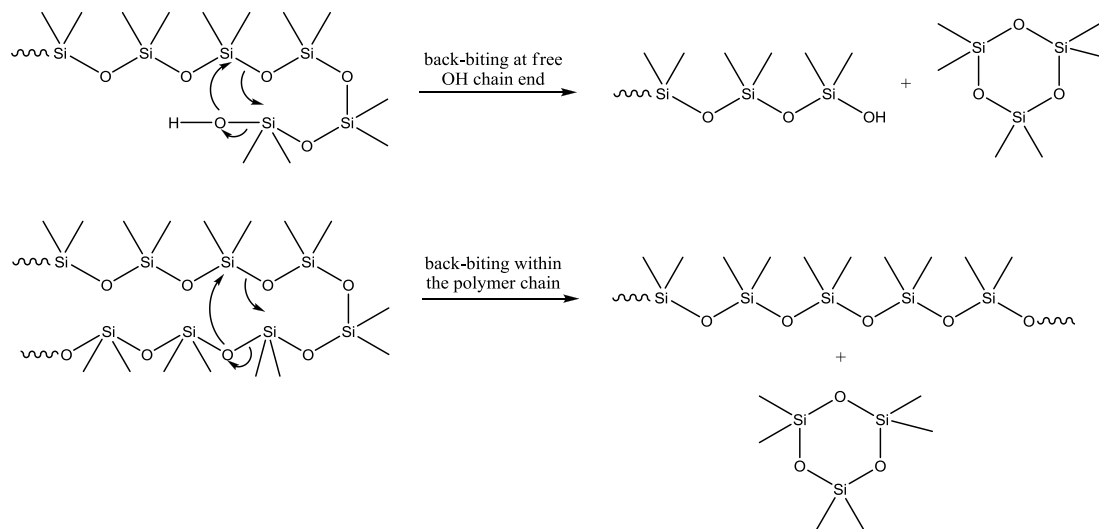


Figure 3: TGA mass loss curves for the siloxane systems. The solid line represents the homopolymer, the dashed line copolymer I, the line + \circ copolymer II and the line + \square the commercial PDMS sample.

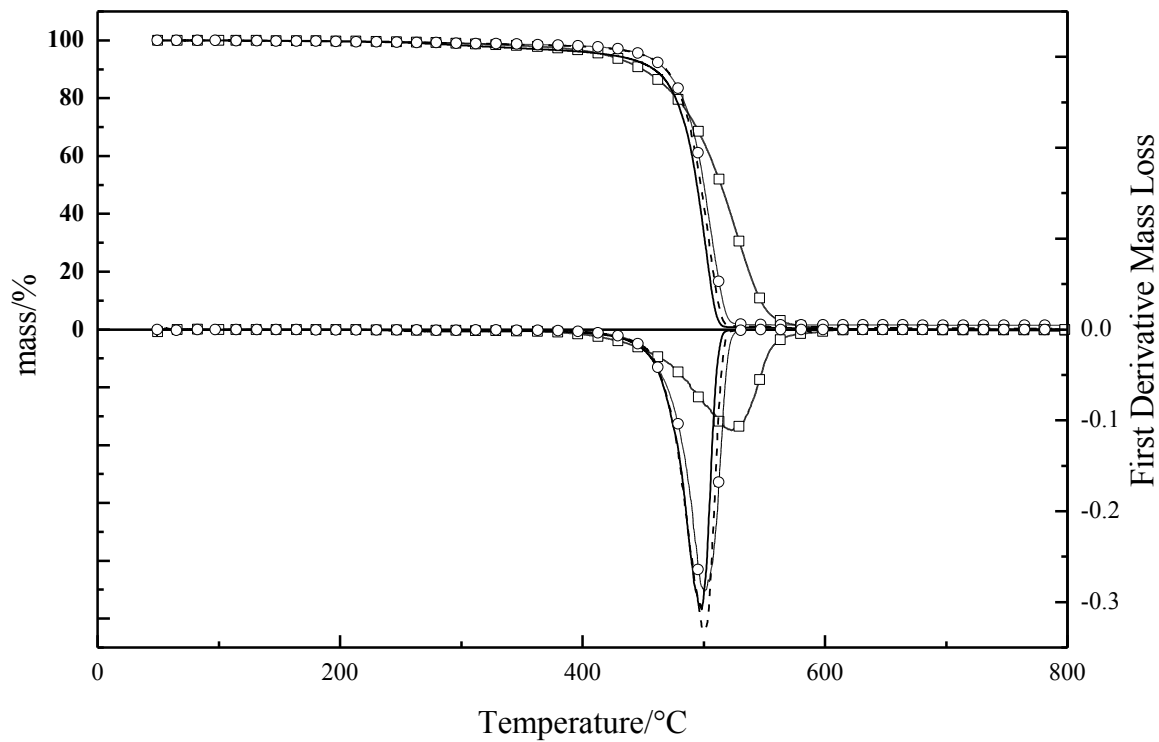


Figure 4: TVA plots of the degradation of the siloxane systems showing the rate of total volatiles evolution as a function of pressure vs. furnace temperature. The solid line represents the homopolymer, the dashed line represents copolymer I, the line + \circ represents copolymer II and the line + \square represents the commercial PDMS sample. The heavy black line represents the furnace temperature as a function of time.

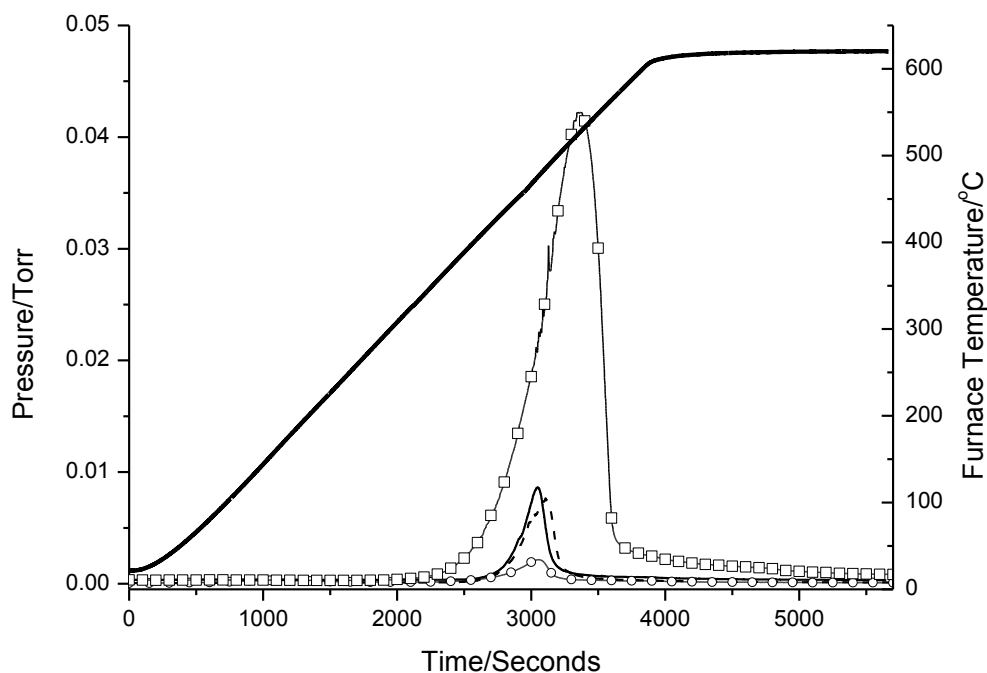


Figure 5: FTIR spectra of the cold-ring fractions collected from the siloxane systems. Lines numbered 1 to 4 correspond to the cold-rings collected from the homopolymer, copolymer I, copolymer II and the commercial PDMS sample, respectively.

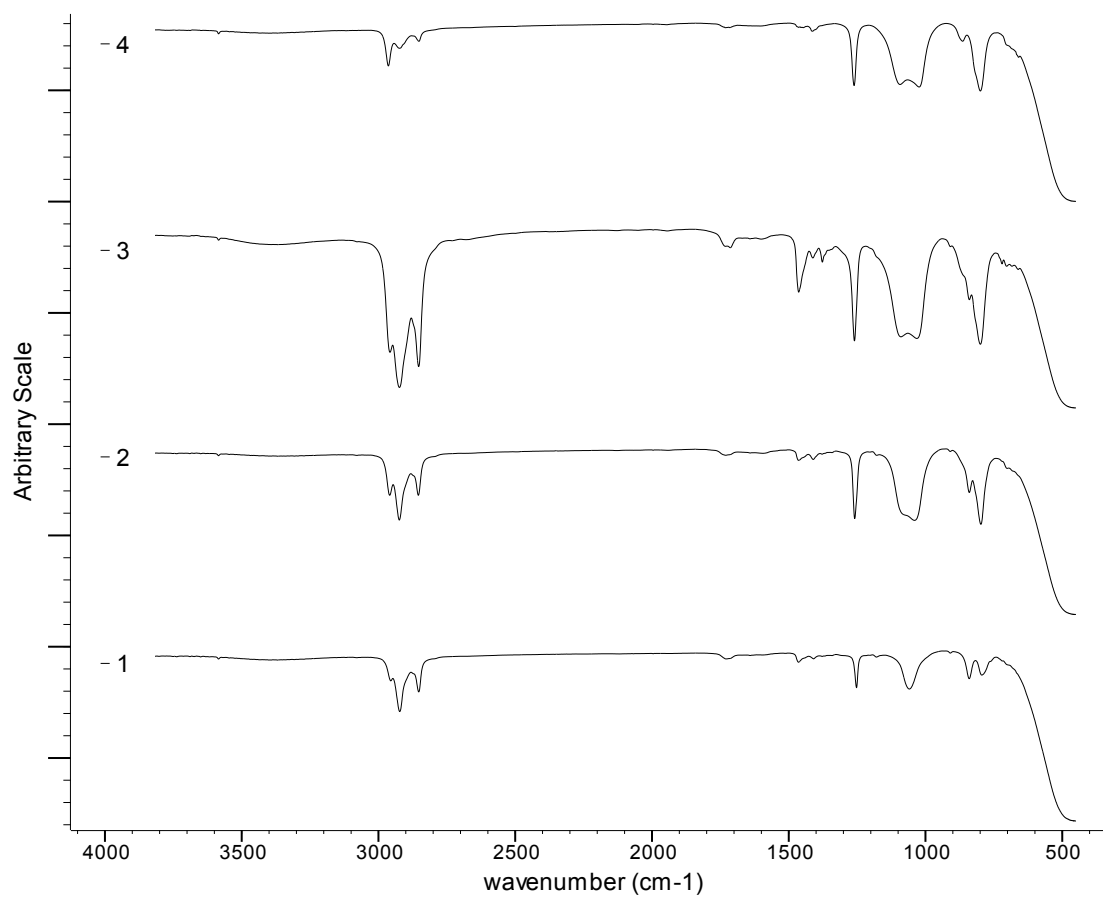


Figure 6: GC-MS chromatogram of the cold-ring fraction collected from the PDMS control sample showing a series of cyclic siloxane oligomers with ring sizes D7 or greater.

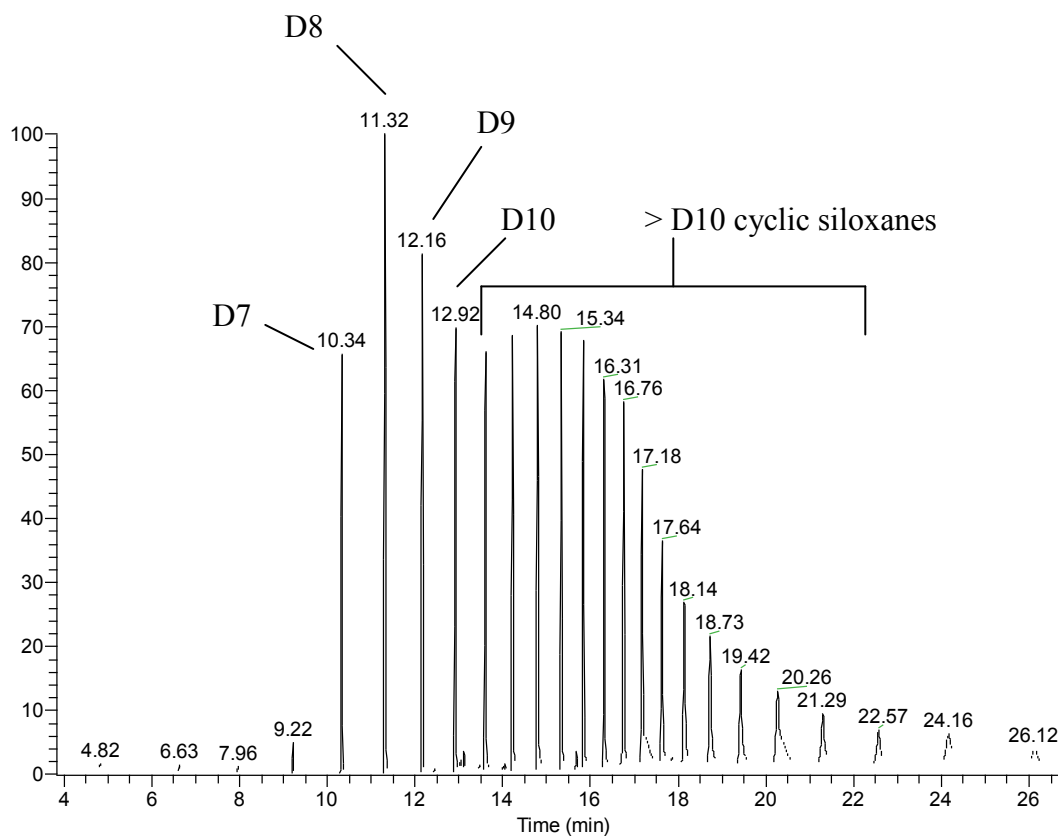


Figure 7: GC-MS chromatogram of the cold-ring fraction collected from copolymer I.

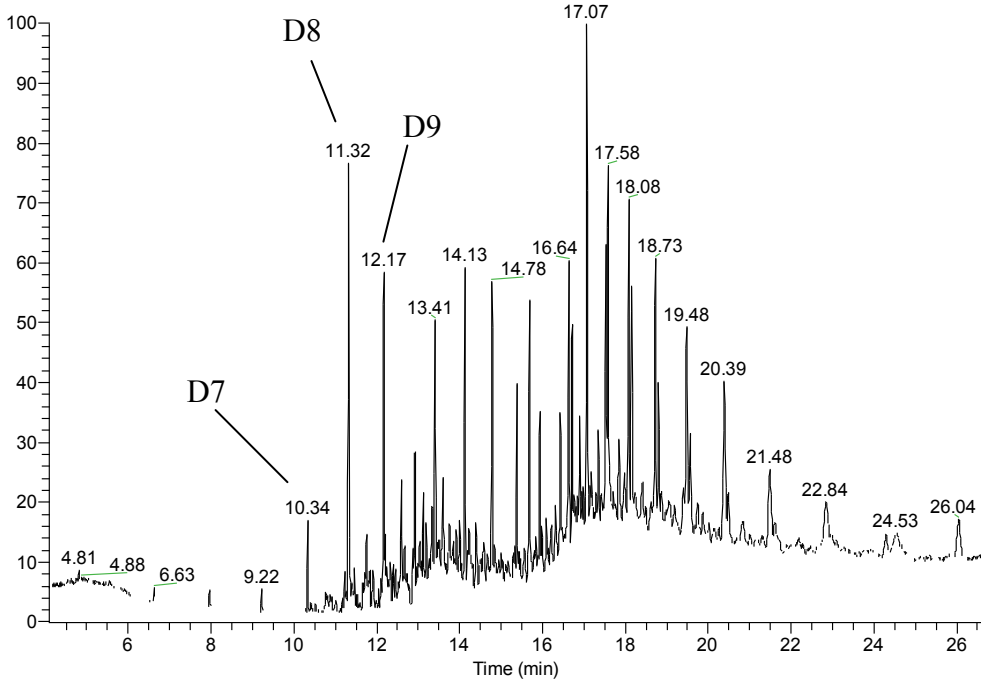


Figure 8: ^{13}C NMR spectrum of the cold-ring fraction obtained from homopolymer.

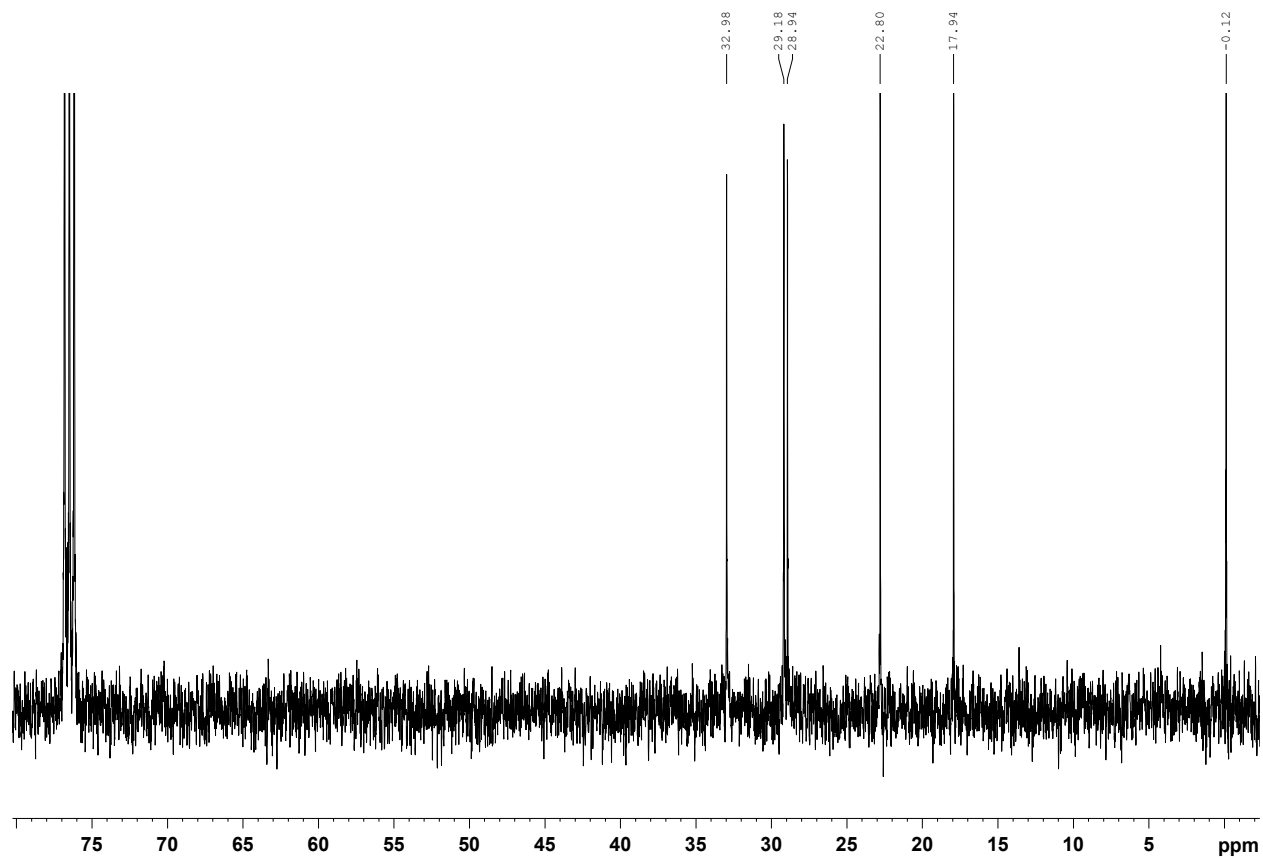


Figure 9: Sub-ambient differential distillation plots showing all of the different volatile degradation products evolved from the siloxane samples. The solid line represents the homopolymer sample, the dashed line represents copolymer I, the line + \circ represents copolymer II and the line + \square represents the commercial PDMS sample.

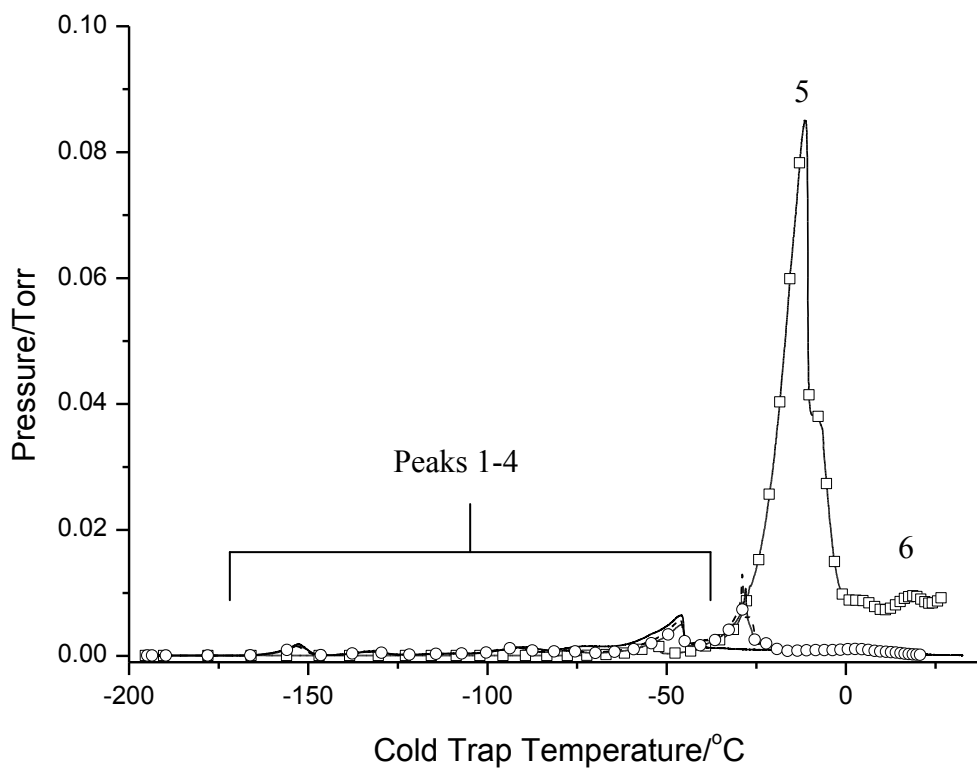


Figure 10: GC-MS chromatogram of the higher molar mass volatiles (peaks 5 and 6) evolved during the sub-ambient differential distillation of the PDMS sample.

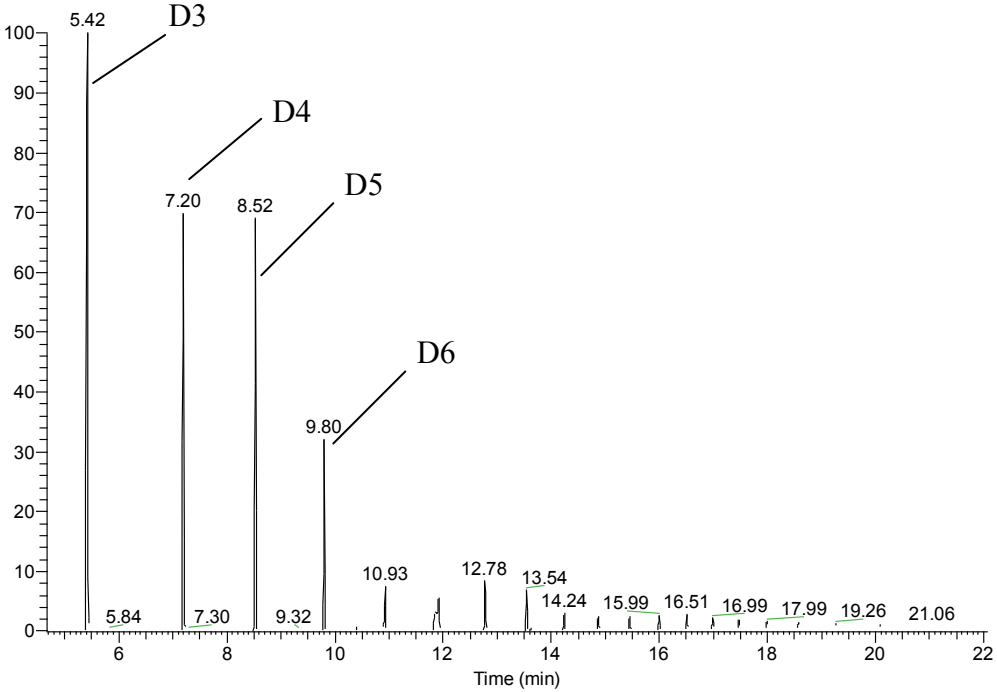


Table 1: TGA onset degradation and DTG peak maxima temperatures for the siloxane samples.

Material	Onset Degradation Temperature/°C	DTG Peak Maximum Temperature/°C
Homopolymer	423	500
Copolymer I	450	504
Copolymer II	450	503
PDMS	418	524

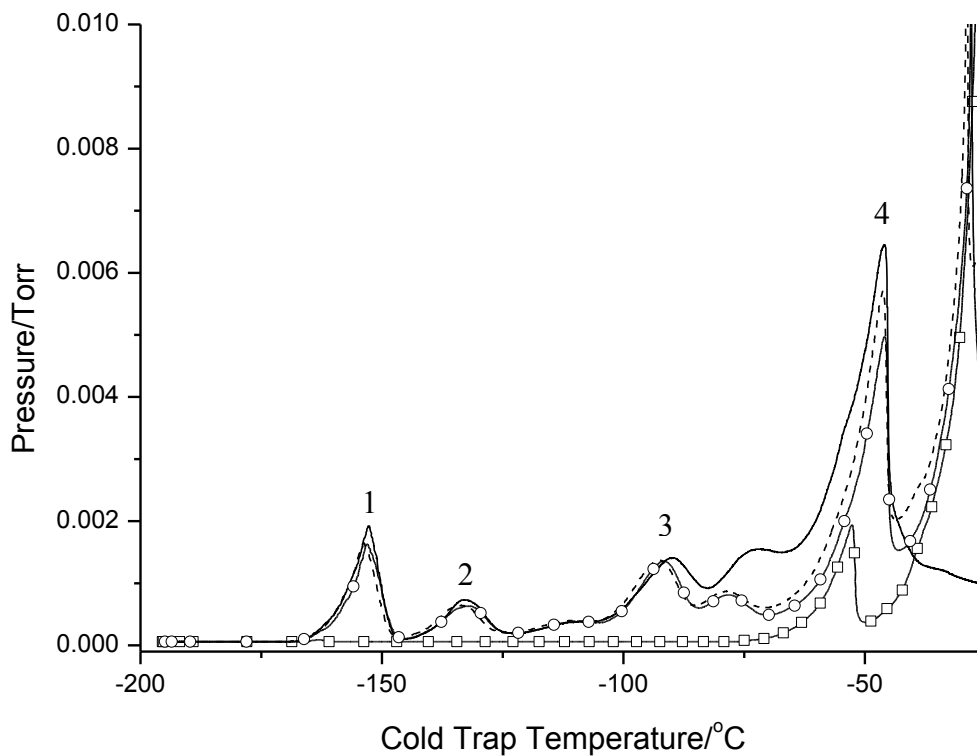
Table 2: TVA onset degradation and maximum volatile evolution rate peak temperatures for the siloxane samples.

Material	Onset Degradation Temperature/°C	Maximum evolution rate peak temperature/°C
Homopolymer	~370	457
Copolymer I	~365	461
Copolymer II	~340	465
PDMS	~310	487

Table 3: Sub-ambient differential distillation product distributions for the PDMS controls and the polysilalkylenesiloxane samples.

Peak	PDMS	Polysilalkylenesiloxanes
1-3	Not present	C3-C6 hydrocarbons
4	Water	Water
5, 6	D3 to D6 cyclic siloxane oligomers	D3 to D6 cyclic siloxane oligomers (although in much smaller yield than PDMS) and other high molar mass silicon-containing products

Supplementary Figure 1: Sub-ambient differential distillation plots showing the volatile degradation products evolved over the temperature range -200 to -25°C. This is an enlarged section of Manuscript Figure 9. The solid line represents the homopolymer sample, the dashed line represents copolymer I, the line + ○ represents copolymer II and the line + □ represents the commercial PDMS sample.



Supplementary Figure 2: FTIR spectrum of the higher molar mass volatiles evolved during the sub-ambient differential distillation of the PDMS sample (peaks 5 and 6)

