

# Gasification of Silicone Fluids Under External Thermal Radiation. Part 2. Gasification Products — Characterization and Quantitation

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The gasification behavior for a wide range of polydimethylsiloxane fluids in a nitrogen atmosphere was investigated. Part 1 of this study addressed the measurement of the energy (global heat of gasification) required for the gasification of a wide range of dimethylsiloxanes. Several significant corrections were required to reconcile measured gasification energy(s) with calculated heat(s) of gasification based on fundamental thermochemical data. The identification of the dominant mode(s) of gasification via the characterization of pyrolysis products provided a firm basis and rationale for understanding and directing efforts at quantifying these correction factors. In Part 2, the gasification products were identified and quantified at various stages of the gasification process corresponding to ignition, fire growth, and steady-state burning. Pyrolysis of methylated siloxanes occurs via two modes: (1) the volatilization of short chain and intermediate chain length species native to the polymer, and (2) the volatilization of short chain and intermediate chain length species resulting from thermal degradation via siloxane rearrangement. The former process is the dominant gasification mechanism for short chain oligomers and low viscosity fluids ( $\eta < 10$  cS) and the latter process is dominant in all higher molecular weight polymers ( $\eta > 100$  cS). Both gasification mechanisms are evident in all polymers ( $\eta > 20$  cS); the dominant mechanism is dependent upon polymer size and distribution thereof, the gasification stage, and the presence of trace catalysts in the polymer. Because of their structural similarity, the combustion of all gasification products emanating from PDMS regardless of the stage of the pyrolysis process or the dominant mode of gasification will result in virtually identical combustion products, i.e.  $\text{SiO}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ . Copyright © 1998 John Wiley & Sons, Ltd. This paper was written under the auspices of the US Government and is therefore not subject to copyright in the US.

## INTRODUCTION

Silicones encompass a wide range of materials and find applications in virtually every major industry sector. The dominant polymer in the silicone industry is polydimethylsiloxane‡ (PDMS) which has a backbone structure consisting of repeating siloxane units (alternate silicon and oxygen atoms); the silicon atom has two methyl substituents. In addition to their unique physical/chemical properties, silicones exhibit advantageous fire behavior such as low heat release rates regardless of fire size or fire severity.<sup>1–4</sup> These burn characteristics are intrinsic to dimethyl substituted siloxanes. Early studies by Lipowitz<sup>5,6</sup> resulted in a proposed model for the combustion of these materials.

Low heat release rates are characteristic of dimethylsiloxane polymers; however, short chain length ( $n < 10$ ) linear oligomers and cyclic structures exhibit substantially higher heat release rates with a pronounced dependence on fire severity.<sup>4</sup> This behavior is attributed primarily to their exceptionally low heats of vaporization (Ref. 11 [Table 1]). Cyclic siloxanes assume an exceptionally prominent role within the silicone industry both as final products and as key intermediates in the manufacture of most commercial silicones. Furthermore, 'cyclics' are the major rearrangement products resulting from thermally induced degradation of silicones.<sup>7,8,9</sup> The dominant cyclic is typically  $\text{D}_3$  although a wide range of molecular weights has been observed and documented.<sup>9</sup> A review of the chemistry of these materials is given in.<sup>10</sup>

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‡ A convenient shorthand notation for PDMS polymers is:  $\text{MD}_n\text{M}$  (linear structures) and  $\text{D}_n$  (cyclic structures) where  $\text{M} = (\text{CH}_3)_2\text{SiO}_{1/2}$ ,  $\text{D} = (\text{CH}_3)_2\text{SiO}_{2/2}$ , and  $n$  is the chain length for pure oligomeric cyclics or linears and  $n$  is the average chain length for polydisperse polymers. Other structural siloxane units are represented by:  $\text{T} = (\text{CH}_3)\text{SiO}_{3/2}$ , and  $\text{Q} = \text{SiO}_{4/2}$ . Since all commercially available oligomer/homopolymer silicones from the shortest chain length (MM) to the long chain polymers are fluids (due to the exceptional flexibility of the Si–O–Si bond), these fluids/polymers are typically referred to by their viscosity in centistokes [cS], which is directly related to  $n$ . [11, see Table 1].

The identification and quantitation of the specific molecular species resulting from the pyrolysis of these polymers was addressed in this phase of the investigation to provide insight into the global heats of gasification measured in part 1<sup>11</sup> of this study on the pyrolysis of dimethylsiloxanes. Volatile pyrolysis products resulting from the volatilization of molecular species native to the polymer and/or the formation of volatile molecular species resulting from thermally induced decomposition/degradation of PDMS will determine the ignition and burning behavior of these materials. An understanding of the energy required, their rate of formation, and composition is relevant to understanding the ignition, flame spread, and general burning behavior of methylated siloxanes.

## EXPERIMENTAL METHODS/PROCEDURES

### Materials

The fluids (oligomers and polymers) used in this investigation were commercial-grade materials and supplied by Dow Corning Corporation. PDMS fluids/polymers are typically referred to by their viscosity which increases with the average chain length as shown in Table 1.<sup>11</sup> The fluids studied were octamethylcyclotetrasiloxane,  $[(\text{CH}_3)_2\text{SiO}]_4$ , and a wide range of trimethylsiloxy end-blocked polydimethylsiloxane (PDMS) fluids (0.65 to 60 000 cS). The 'monodisperse model' fluid was synthesized using a specific monomer, catalyst system and polymerization conditions to ensure a narrow distribution polymer and to minimize the presence of oligomeric cyclics and linears in the polymer. Solvents were purchased from Aldrich Chemical Company and used as received.

### Gasification apparatus

A detailed description of the gasification apparatus and its operation are given elsewhere.<sup>11,12</sup>

### Sampling/trapping of volatiles

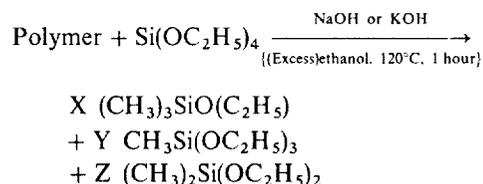
The gasification apparatus was modified to provide a means for sampling the gaseous species immediately above the surface of the fluid. A sketch of the gas sampling assembly is given in Fig. 1. The sampling system consisted of a 3 mm i.d. copper tube which could be swung into position over the center of the stainless-steel sample dish. The tube was connected to a cold trap immersed in a low temperature bath (dry ice/isopropanol) which was connected to a vacuum pump. The cold trap contained 3 mm glass beads to enhance trapping efficiency of the volatiles. The condensed volatiles were removed by adding solvent (*o*-xylene or pentane) to the cold trap and allowing the glass beads/volatiles/solvent to warm to room temperature prior to their removal from the trap system. Dodecane was used as an internal standard for quantifying molecular species identified via gas liquid chromatography.

### Analytical methods — chromatography (GLC, GPC)/mass spectroscopy

**Extraction method.** The analysis of polymers and residual polymer samples for cyclics and linears content relied on an 'acetone extraction technique'. One g of the fluid/polymer was added to a 0.02 L vial containing ~0.02 g of internal standard solution (10 g of hexane and 0.01 g of *n*-dodecane) and ~3 g of acetone (Optima Grade). The vial was vigorously shaken for 5 min and then centrifuged so as to produce a clear solvent layer for sampling and analysis. The solvent/extract was analyzed via gas liquid chromatography (GLC). Typically, 1.0  $\mu\text{L}$  was injected. The chromatograph was equipped with fused silica (30 m  $\times$  0.25 mm) columns coated with DB-1HT (0.1 mm film thickness) and a flame ionization detection (FID) system. A typical chromatogram illustrating the various species identified and quantified via this technique is given in Fig. 2. This method is limited to those cyclic and linear species which elute from the columns, i.e. less than 21 siloxane units. Note that specific identification and quantitation of cyclic and linear oligomers is readily accomplished.

**Internal standard method.** The analysis of volatile products for specific molecular species identification and quantitation also relied on GLC. Typically, 1.0  $\mu\text{L}$  of the solvent (pentane or *o*-xylene with internal standard) used to rinse/solvate the condensibles in the cold trap was injected onto the GLC column. A typical chromatogram is given in Fig. 2. Note that 'peak areas' provide a reliable measure of the concentration of each species rather than 'peak heights'. This is especially important for higher molecular weight eluents; so, although a chromatogram visually appears to indicate a reduced concentration of higher molecular weight species, this is not necessarily the case. The FID detector response was verified to be constant for all species which elute and demonstrated no structural (cyclic vs linear) dependence.

**Ethylorthosilicate derivatization (EOS).** A novel base-catalyzed digestion/derivatization technique was used to assay residual fluids/polymers for end-block units  $[M = (\text{CH}_3)_3\text{SiO}_{1/2}]$  and monomethyl substituted siloxane units  $[T = \text{CH}_3\text{SiO}_{3/2}]$  which presumably result from methyl cleavage during pyrolysis. An excess of ethylorthosilicate (tetraethoxysilane) is equilibrated with an organosilicon compound (polymer or residual fluid) in the presence of a base catalyst to yield corresponding organoethoxy derivatives. That is,



The resultant solution was analyzed by GLC for ethoxylated species providing a measure of the M, T, and D units comprising the polymer. An internal standard was used. In this investigation, assays of M and T

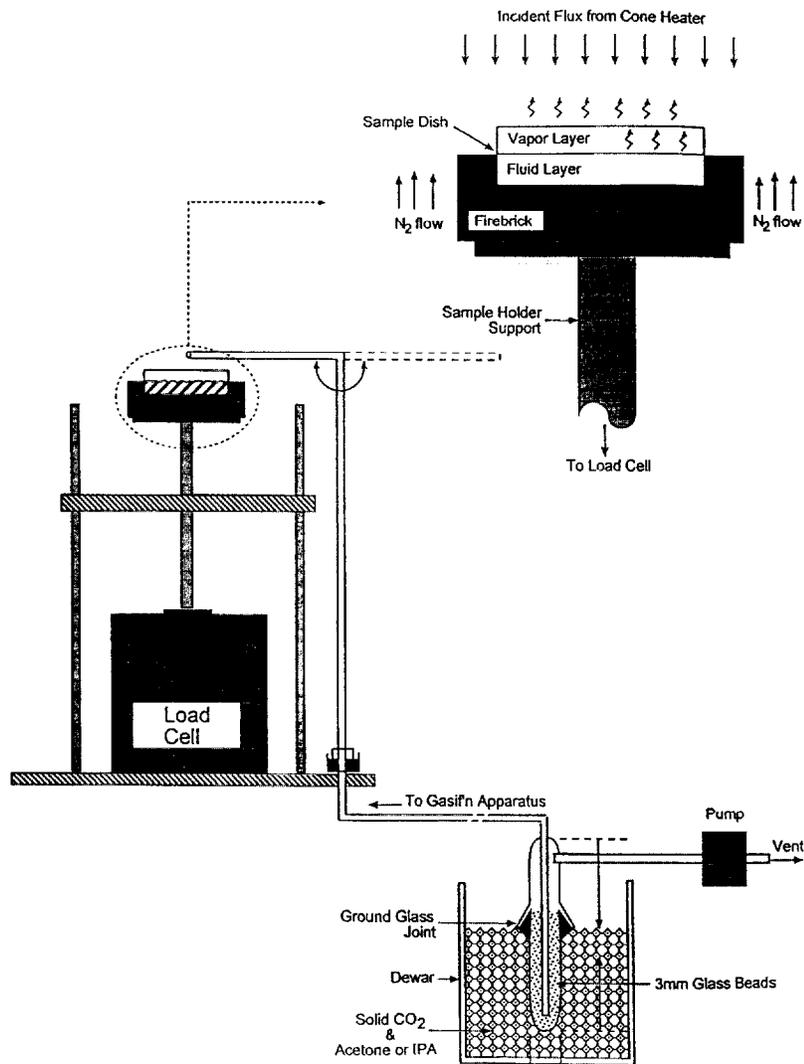


Figure 1. Sample pan assembly, load cell and volatiles sampling apparatus.

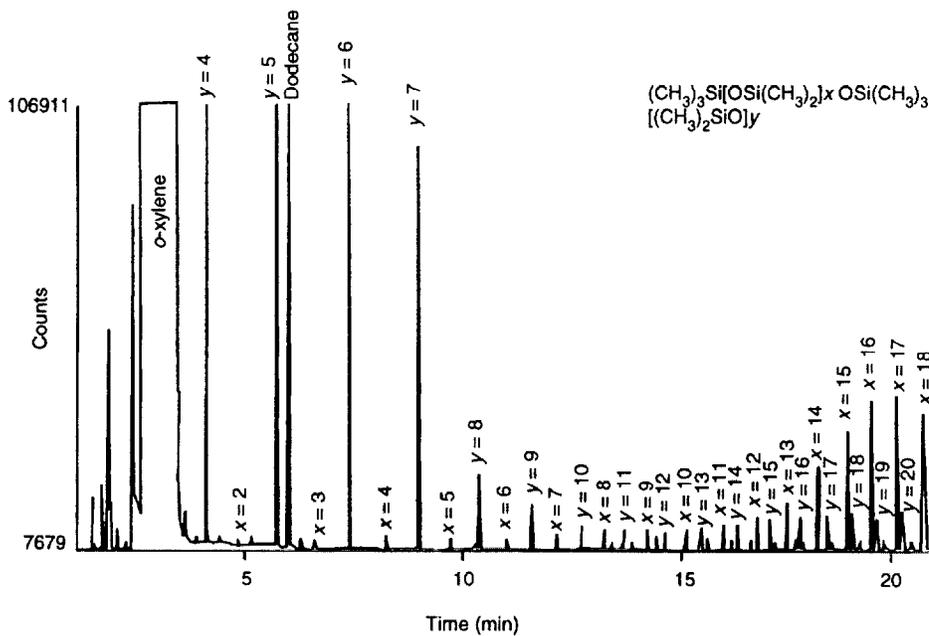
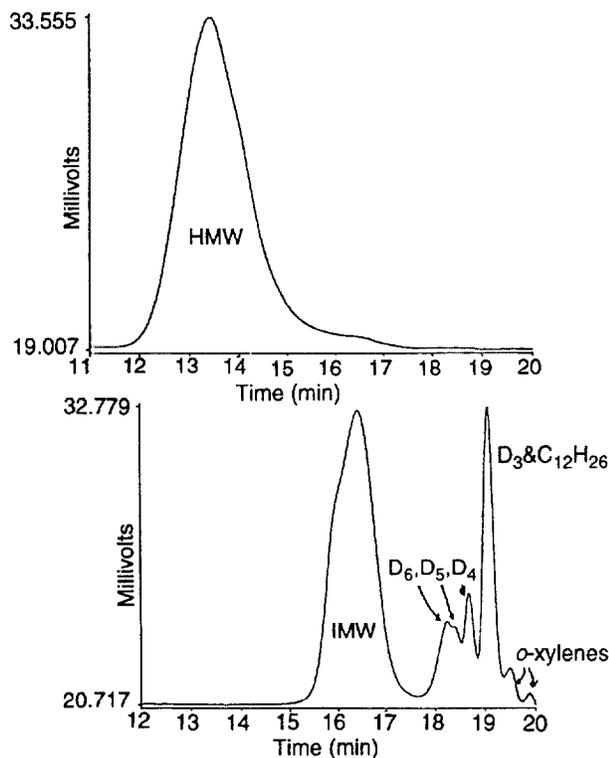


Figure 2. Gas chromatogram of cyclics ( $D_x$ ,  $x \leq 20$ ) and linear ( $MD_xM$ ,  $x \leq 18$ ).

provided insight into the gasification mechanisms (volatilization or degradation/volatilization) and the extent of methyl loss via methyl cleavage during pyrolysis.

**Gel permeation chromatography.** Gel permeation chromatography (GPC) utilized a Waters system (510 reciprocating pump, 410 differential refractometer, WISP 712 autosampler). Toluene was the mobile phase. Three PL-gel columns manufactured by Polymer Laboratories were used to affect separation. Calibration was based on narrow distribution polydimethylsiloxane standards ranging in molecular weight from 1330 to 852 000 [g/mole]. Polymers/residual fluids were diluted in HPLC-grade toluene prior to injection; solvated samples from the cold traps (pentane or *o*-xylene) were injected directly. The latter samples provided an analysis of those samples which did not elute quantitatively from the GLC columns. GPC chromatograms showing the various ranges of molecular weight species of interest are given in Fig. 3: high molecular weight polymer (HMW) (ET (elution time) < 15), intermediate molecular weight polymer (IMW) (15 < ET < 17.5), and cyclic oligomers (17.5 < ET < 19.5). GPC analysis complemented the GLC procedure by providing identification and approximate quantitation of short chain oligomers (ET = 17.5 to 19.5) as well as intermediate (ET = 15.0 to 17.5) and high (ET < 15) molecular weight materials. The GLC internal standard (dodecane) co-elutes with D<sub>3</sub> (ET = 19.1). Utilizing GLC analysis, the GPC data were



**Figure 3.** GPC chromatograms of high polymer (HMW); intermediate molecular weight polymer (IMW), oligomeric cyclics (D<sub>3</sub>, ..., D<sub>6</sub>), dodecane (GLC internal standard), and *o*-xylenes (solvent).

corrected for the 'dodecane/D<sub>3</sub> overlap'. Peaks associated with xylenes(s) are observed but do not interfere since their elution times are displaced from the siloxanes of interest.

**Mass spectroscopy.** The mass spectral analysis utilized in this study involved direct analysis of pentane solutions containing unknown PDMS species by electrospray mass spectrometry.<sup>13</sup> A 90/10 solution of pentane and isopropanol containing 5 mM ammonium acetate (NH<sub>4</sub>OAc) was prepared and delivered to the electrospray ion source at a constant flow rate of 15 μL/min using a Harvard Apparatus Model 22 syringe pump. Cationized PDMS species were admitted to a Perkin-Elmer API 300 triple quadrupole mass spectrometer and mass analyzed. Abundant ammoniated pseudomolecular ions, {M + NH<sub>4</sub>}<sup>+</sup> with no fragmentation were observed in the mass spectrum, thereby providing a direct measure of the molecular weights of the unknown silicone species. To discern the chemical structure of these unknown PDMS species, MS-MS collisional activation at a collision energy of 25 eV using nitrogen collision gas was performed on selected {M + NH<sub>4</sub>}<sup>+</sup> ions to confirm the polymer end-groups and repeat units.

## RESULTS AND DISCUSSION

The gasification/pyrolysis products for PDMS fluids ranging in viscosity from 1.5 to 60 000 cS were identified and quantified at various stages of gasification. An applied heat flux of 40 kW/m<sup>2</sup> was used to 'gasify' the samples. These results complement gasification energy measurements on these materials reported elsewhere.<sup>11,12</sup> Data on the excellent repeatability of the complete experimental protocol (gasification, sampling and trapping of volatiles, and the analysis-characterization methods) are given elsewhere.<sup>12</sup>

### Pyrolysis — oligomers

1.5 cS fluid consists almost entirely of a single molecular species (MD<sub>2</sub>M). Volatiles were sampled/collected during the mass loss interval of 30 to 15 g, i.e. sampling commenced after 70% of the sample was gasified and continued until 85% of the sample was volatilized. GLC analysis of volatiles showed them to consist exclusively of MD<sub>2</sub>M. No evidence for thermal degradation or thermal induced rearrangement of the fluid was observed. Thus, gasification occurs only via volatilization of the original fluid species. This is consistent with the measured and calculated gasification energy measured in Part 1 of this study.<sup>11,12</sup>

5 cS fluid consists of a distribution of linear molecular (MD<sub>n</sub>M) species. Nearly all of the species in this fluid eluted from the GLC column. Volatiles were sampled and collected during several pyrolysis (mass loss) intervals: 100 to 97 g, 55 to 50 g, and 15 to 10 g. GPC and GLC data for the 5 cS fluid, volatiles samples, and the residual fluid are given in Figs 4 and 5, respectively. The absence of cyclic structures (e.g. D<sub>3</sub>, D<sub>4</sub>) in the volatiles is indicative of no thermal rearrangement/degradation

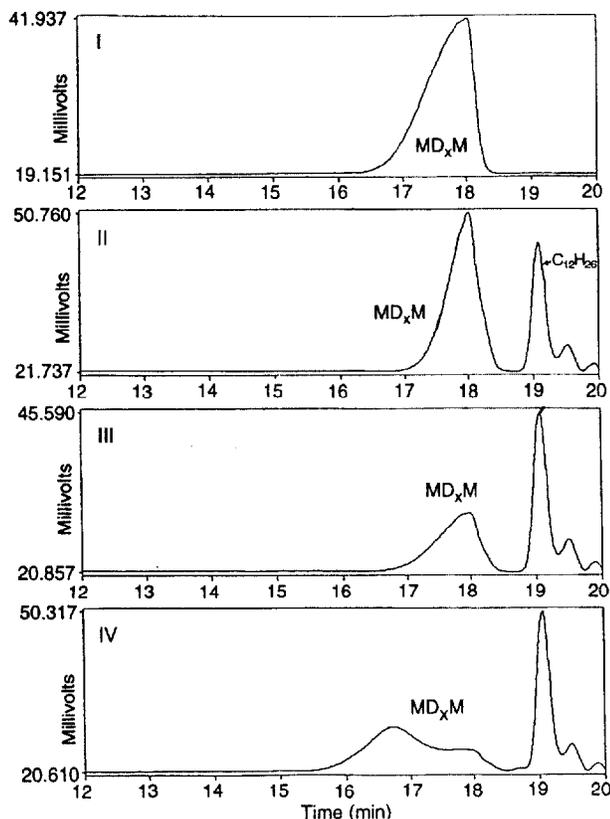


Figure 4. GPC chromatograms of volatiles from 5 cS fluid: I, 5 cS fluid; II, 100–97 g volatiles; III, 55–50 g volatiles; IV 50–10 g volatiles.

occurring at these stages of the pyrolysis. The gasification of this fluid is dictated by the vapor pressure of the respective species comprising the fluid, i.e. not unlike a distillation process. It is particularly noteworthy that siloxane species with twenty or more siloxane molecular units volatilize readily and gasify intact.

### Pyrolysis — fluids/polymers

A range of higher viscosity (higher molecular weight) fluids was investigated to provide insight into the dominant mechanisms occurring in fluids/polymers used in commercial products such as sealants, rubber, foams and gels. The fluids ranged in viscosity from 50 to  $6 \times 10^4$  cS. A 'model' fluid containing no intermediate molecular weight species (neither cyclic or linear) was synthesized. This polymer was used to obtain unequivocal evidence for the formation of specific intermediate molecular weight species (macrocylics) during the pyrolysis of silicone fluids.

50 cS fluid was pyrolyzed and volatiles were collected at various mass loss intervals. GPC data on these materials and the original and residual fluid are given in Fig. 6. The initial volatiles (100–99 g mass loss) consist almost entirely of intermediate molecular weight linears which are native to the fluid suggesting that native fluid components dictate the ignition behavior of this material. The

intermediate molecular weight peak shifts to progressively higher molecular weight (lower ET) throughout the gasification of the fluid. As gasification proceeds, thermal degradation commences and results in the formation of the expected cyclic oligomers ( $D_3$ ,  $D_4$ , ...), but throughout the gasification process, the volatilization of native linear species is the dominant gasification mechanism.

Further evidence of this was obtained by pyrolyzing 50 cS fluid to various stages and analyzing the residual fluids via GPC and assaying for end-group content ( $M = (\text{CH}_3)_3\text{SiO}_{1/2}$ ) via the EOS/GLC derivatization analysis method. GPC chromatograms for the residual fluids and the original fluid are given in Fig. 7. The EOS/GLC derivatization analysis and GPC results ( $M_n$ , PDI) are summarized in Table 1 (Series I). The gasification process results in the preferential removal of the lightest species as evidenced by the loss of materials with the higher elution times (lower molecular weight members). It is evident from these data that gasification proceeds largely via volatilization of the most volatile molecular species in the fluid. In Table 1, further evidence for this is the reduction in polydispersity of the polymer as evidenced by the polydispersity index ( $M_w/M_n$ ) for the residual fluid. Polymer chain endblock (M-content) measured via the EOS/GLC derivatization procedure is also listed along with M-content as calculated based on the number-average molecular weight ( $M_n$ ) obtained from GPC analysis. An excellent correlation is noted between M-content measured via the EOS/GLC assay method and that the calculated from GPC molecular weights.

A similar investigation of the pyrolysis behavior of 100 cS fluid and 60 000 cS fluid resulted in evidence for contrasting pyrolysis behavior between intermediate viscosity and high viscosity fluids. Residual fluids from the gasification of 100 and 60 000 cS fluids were analyzed. The GPC chromatograms (Fig. 8) and the M-content results from both EOS/GLC derivatization and GPC- $M_n$  (Table 1—Series II) suggest significantly different dominant mechanisms for the gasification of these two materials, i.e. for the 100 cS fluid, narrowing of the molecular weight distribution and a shift to higher molecular weights is observed whereas for the 60 000 cS fluid, a broadening of the molecular weight distribution and a shift to lower molecular weights is observed. Narrowing of the distribution results from the preferential removal of lower molecular weight species based on their slightly higher volatility (vapor pressure). Broadening of the distribution results from thermal induced rearrangement and results in a shift to lower molecular weights due to the presence of excess end-block (M-content) since fluid is lost via volatilization and perhaps large cyclic structures are formed which require no end-blocker. Good agreement is noted for the M-content values for both the original and residual 100 cS fluid. For the 60 000 cS fluid, a wide disparity is noted between the assayed M-content and the calculated M-content based on number-average molecular weight (GPC). The assayed content (2900 ppm) is far lower than the anticipated content (5400 ppm) which suggests that a significant number of molecular species may be large cyclic species requiring no terminal end-groups.

To further characterize the intermediate stages of pyrolysis, gasification products were collected and analyzed for various stages of pyrolysis of a 10 000 cS fluid. The

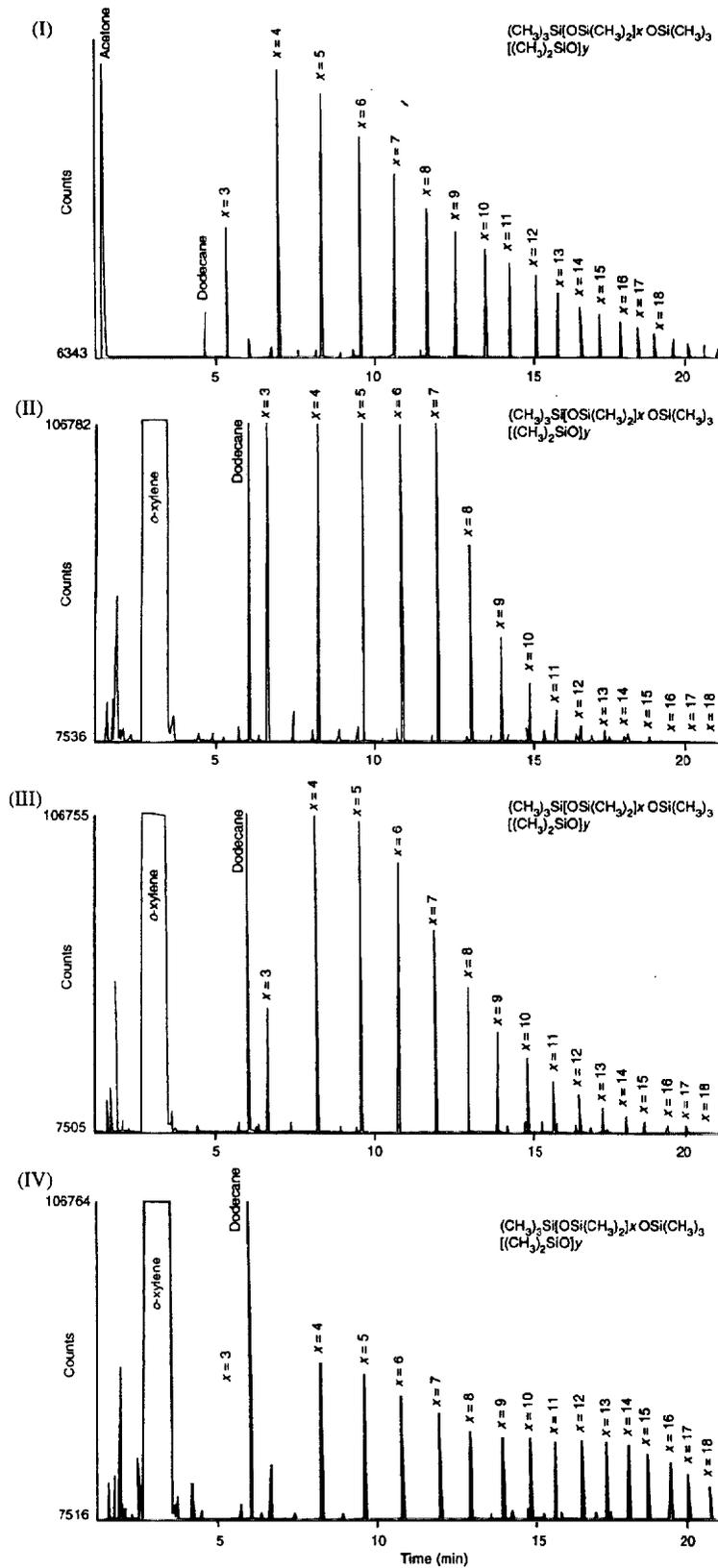


Figure 5. GPC chromatographic analysis volatiles from 5 cS fluid; I, 5 cS fluid; II, 100–97 g volatiles; III, 55–50 g volatiles; IV 50–10 g volatiles.

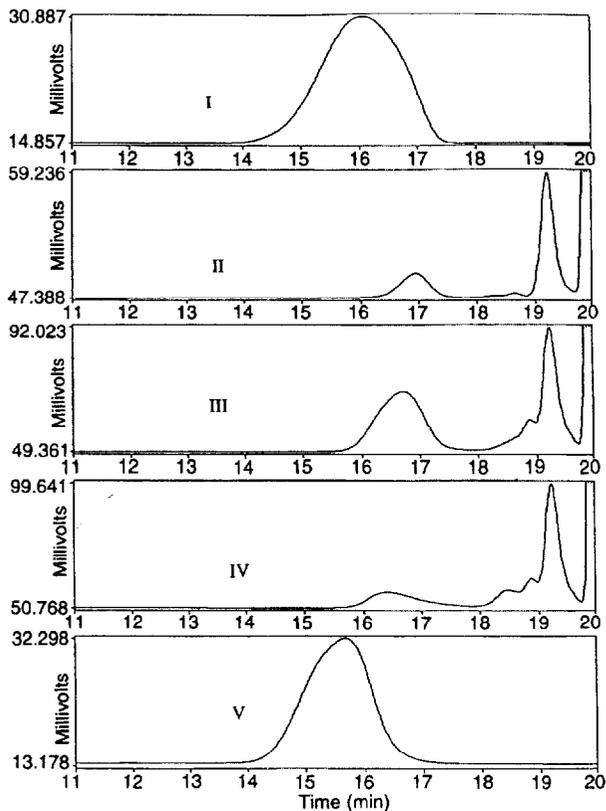


Figure 6. GPC chromatograms of I, 50 cS fluid original fluid; samples of volatiles at: II, 100-99 g; III, 75-70 g, IV, 35-30 g, V, the residual 30 g fluid.

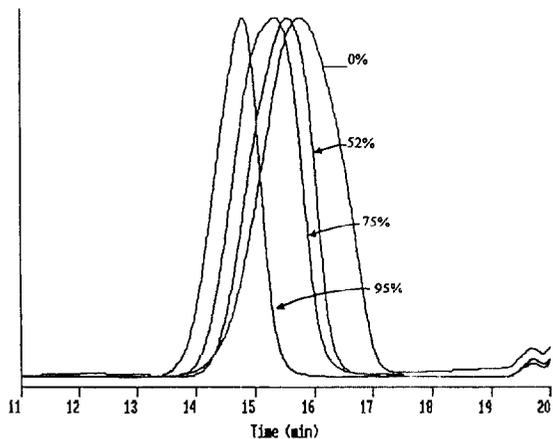


Figure 7. GPC chromatograms of 50 cS residual fluids at various stage of gasification (0%, 52%, 75%, 95%).

GPC and GLC chromatograms are given in Figs 9 and 10. The initial gasification sample ( $\Delta m = 100$  to 98 g) consists of  $\sim 70\%$  intermediate molecular weight species and  $\sim 30\%$  cyclic oligomers and larger (macro) cyclics. It is uncertain whether all of these macrocyclics result from thermal rearrangement/degradation of the fluid or are

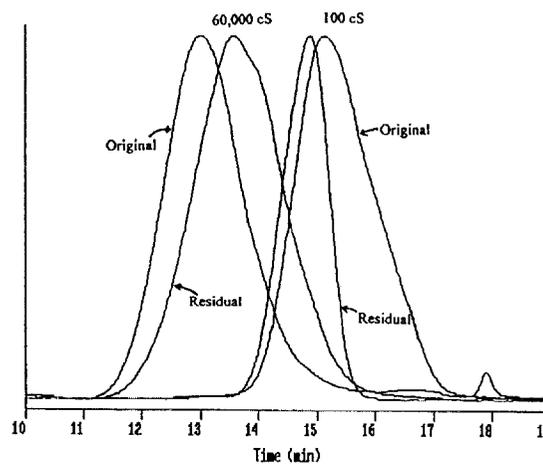


Figure 8. GPC chromatograms of original and residual fluids for 100 cS and 60 000 cS fluids.

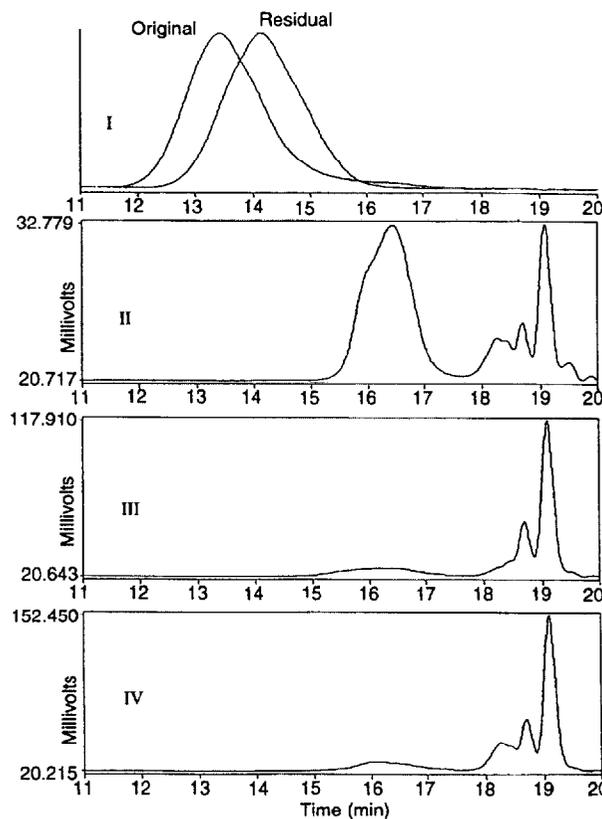


Figure 9. GPC chromatograms of  $10^4$  cS fluid: I, original and residual (7 g) fluid; II, 100-99 g volatiles; III, 75-70 g volatiles; IV, 12-7 g volatiles.

native to the fluid since the original fluid contains small amounts of macrocyclics. The GLC analysis indicates that a distribution of intermediate molecular weight linears similar to that observed for the 50 cS fluid is present in these volatiles. These are native to the fluid and are not a product of rearrangement since they are observed only

**Table 1. Characterization data — original and residual fluids. GPC( $M_w$ , PDI) and fluid structural analysis**

Fluid	Residual [q]	$M_n$ (GPC)	PDI <sup>a</sup>	$M^b$ [Calc'd]	$M^c$ [Meas'd]	$T^d$ [Meas'd]
<b>Series I</b>						
50 cS	100	3540	1.44	45 800	43 500	230
50 cS	51	6130	1.2	26 400	25 200	—
50 cS	49	5400	1.3	30 000	28 700	311
50 cS	37	5590	1.26	29 000	29 300	319
50 cS	37	5550	1.26	29 200	30 000	466
50 cS	25	6800	1.3	23 800	23 500	366
50 cS	22	4650	1.4	34 900	33 500	416
50 cS	5	12 500	1.2	13 000	12 900	—
50 cS	4	17 350	1.4	9300	8700	430
50 cS	3	14 500	1.3	11 200	10 800	—
<b>Series II</b>						
100 cS	100	5060	1.6	32 000	26 300	125
100 cS	23	11 700	1.2	13 800	13 900	1063
60 000 cS	100	55 600	1.9	2900	2400	183
60 000 cS	5	30 000	2.1	5400	2960	4400
<b>Series III</b>						
50 cS	100	3460	1.5	45 800	43 500	230
50 cS	30	5800	1.3	27 900	27 100	400
50 cS	15	6800	1.3	23 800	23 100	570
1000 cS	100	13 200	2.4	12 300	8700	5200
1000 cS	98	14 200	2.3	11 450	8750	5200
1000 cS	90	14 900	2.2	10 900	8500	5100
1000 cS	45	12 900	1.9	12 500	8700	6100
1000 cS	20	10 900	2.0	14 900	9200	6900
10 000 cS	100	23 500	2.5	4600	4300	180
10 000 cS	7	17 900	1.7	9050	5660	4100
60 000 cS	100	55 600	1.9	2900	2550	200
60 000 cS	15	22 700	1.8	7100	4030	3550
Model fluid	100	30 200	1.2	5370	3150	n.d. (< 50 ppm)
Model fluid	15	12 200	2.1	13 300	6960	1100

<sup>a</sup>PDI = Polydispersity Index ( $M_w/M_n$ ) (GPC analysis)

<sup>b</sup> $M$  [ppm] =  $[2 \times 81/M_n(\text{GPC})] \times 10^6$

<sup>c</sup> $M$  [ppm] = M-content as measured via the EOS/GLC derivatization method

<sup>d</sup> $T$  [ppm] = T-content as measured via the EOS/GLC derivatization method

in the earliest stage of gasification. Thus, in this earliest stage of pyrolysis, volatilization of native species is a dominant mechanism although some depolymerization of the fluid is occurring as evidenced by the presence of cyclics  $D_3, \dots, D_7$ . Thereafter, thermal induced depolymerization is the dominant gasification mechanism resulting in major concentrations of small cyclic structures ( $D_3 \gg D_4 > D_5, \dots, D_n$ ) and a significant concentration of intermediate molecular weight cyclic structures. Note in the second and all later samplings of gasification products, the trend toward increased small cyclic species; the linear content ( $MD_xM$ ) is substantially reduced whereas the prominence of macrocyclics remains pretty much constant throughout the gasification of the material suggesting that these are a product of the thermal rearrangement/degradation process.

To establish unequivocally that macrocyclics are formed in the pyrolysis of these materials, a 'model' polymer (trimethylsilyl end-blocked) was synthesized. The bimodal distribution (see Fig. 11 Part I) is believed to result from the presence of both trimethylsilyloxy end-blocked linear species (the dominant component) and

a significant concentration of very large macrocyclic species. Most importantly, this polymer contained no intermediate molecular weight (IMW) species as measured by GPC, Fig. 11 (part I) (ET = 15.7 to 18). Therefore, any gasification products which elute in this region of the GPC chromatogram are in fact formed during the pyrolysis/gasification process. The GPC/GLC data on the original and residual fluids and pyrolysis volatiles at various stages of pyrolysis are summarized in Figs 11 and 12. Note the absence of low molecular weight trimethylsilyloxy end-blocked linears in all of the polymers and volatiles. The volatiles consist entirely of cyclic species. Only very minor amounts of cyclics ( $D_x$ , where  $x = 3, 6, 9 \dots$ ) are present in the original fluid. Since there are virtually no linears present in the volatiles, the IMW species (ET = 15.7 to 18) formed in the thermal rearrangement of the fluid are large cyclic structures (see Fig. 12 Part III and IV). Confirmation of their cyclic structures was provided by mass spectral analysis, Fig. 13. Molecular species containing fewer than nine siloxane units are not observed in the mass spectra since they are too volatile to be captured in the volatilization/

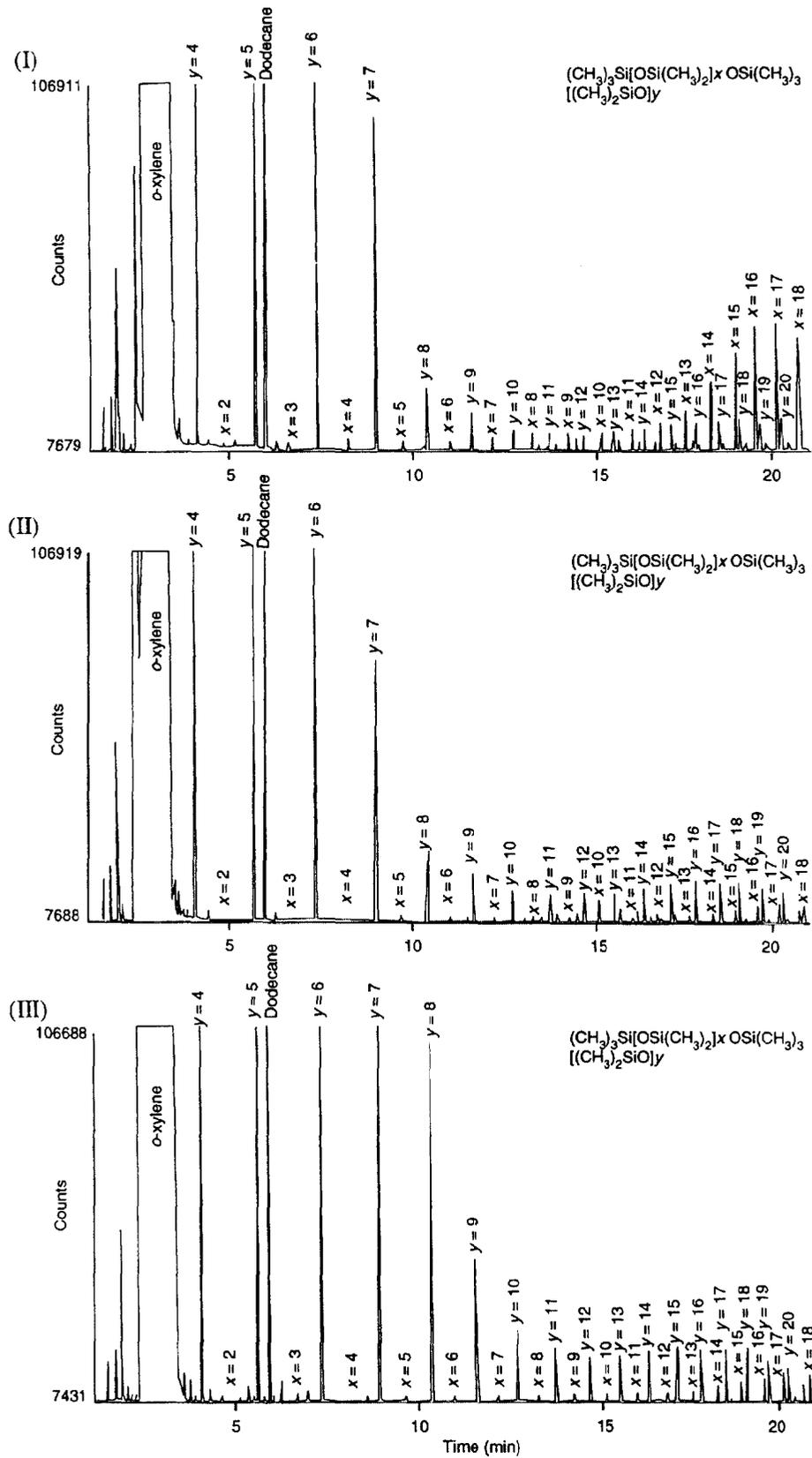


Figure 10. Gas chromatographic analysis of  $10^4$  cS fluid volatiles samples: I, 100–99 g; II, 75–70 g; III, 12–7 g.

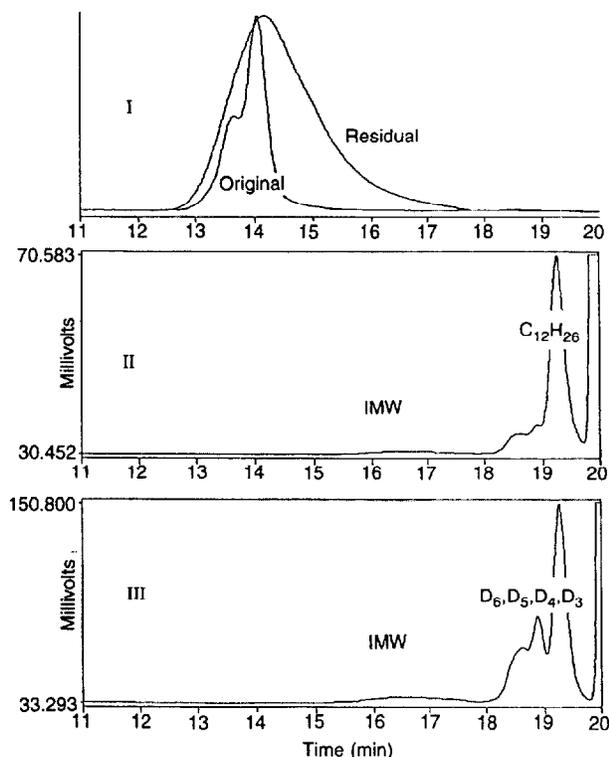


Figure 11. GPC chromatograms of model fluid: I, original and residual (15 g) fluids; II, 100–99 g volatiles; III, 20–15 g volatiles.

ionization/detectionscheme. In the 'original' fluid, only trace amounts of cyclics are observed and these are always multiples of  $D_3$ , Fig. 13 (Part I). These species are a direct result of the polymerization of the starting material,  $D_3$ . The immediate formation of all intervening cyclic species during pyrolysis is evident in all gasification samples (Fig. 13 Parts II and III, Fig. 12 Part II and III). Also, note the enhanced concentration of these species in the residual fluid at the cessation of the gasification process. Cyclic species ( $D_x$ , where  $x > 37$ ) are observed in the residual fluid suggesting that the formation of substantial quantities of very large cyclic structures is a significant mode of degradation and a consequence of the thermally induced random chain scission.

The pyrolysis of PDMS silicone fluids involves gasification via vaporization or thermal degradation (siloxane rearrangement) to volatile oligomers or a combination of these regimes. The dominant mode of gasification is dependent upon the viscosity (chain length) of the polymer and the stage of the pyrolysis. The presence of catalytic species in the silicone material will promote the onset of thermal rearrangement at lower temperatures. The role of potentially catalytic agents was not included in the scope of this investigation.

A wide range of polymers was 'gasified' and the volatiles were characterized at various stages of their gasification. The dependence of volatiles composition on polymer viscosity and stage of gasification are evident

from the data in Table 2. The areas under respective regions of the GPC curves provided a relative measure of the intermediate molecular weight species (IMW) and the short chain cyclics (SCC) ( $D_x$ , where  $3 \leq x < 10$ ) in the volatiles samples. The SCC area was corrected for the presence of the internal standard (dodecane); GLC analysis separates and quantifies dodecane and  $D_3$  allowing this correction to be made. In Table 2, results of the gasification products analyses are summarized for these polymers at various stage of gasification.

Further elucidation of the significant role of 'vaporization' of materials native to the polymer in the very early stages of pyrolysis is evident from results given in Fig. 14. These species are expected to play a dominant role in the ignition behavior of silicone fluids. 1000 cS fluid (100 g) was pyrolyzed until mass losses of 2, 10, 45, and 80 g were achieved in successive experiments. The residual fluid was analyzed via GPC to assess changes in the pyrolyzing polymer. It is evident that during the initial loss of about 10% of the fluid, the lowest molecular weight species are preferentially removed via volatilization. The GPC curves for the fluid pyrolyzed for longer intervals (45 g, 80 g) clearly indicate that extensive rearrangement occurs resulting in an overall shift of the distribution to lower molecular weights. The tendency of these intermediate molecular weight species to gasify suggests a prominent role for them in influencing the ignition behavior of PDMS fluids/polymers.

In Table 1 (Series III), a summary of M and T structural data from EOS/GLC derivatization analysis on the original and residual fluids is given. There is good agreement between  $M_{EOS}$  and  $M_{GPC}$  for those materials which pyrolyze primarily via volatilization of native species, e.g. 50 and 100 cS fluids. For higher molecular weight fluids in which rearrangement to cyclics is a dominant gasification regime, a wide disparity occurs between  $M_{EOS}$  and  $M_{GPC}$  for the residual fluid; this disparity tends to increase with increasing viscosity of the original fluid. A plausible explanation is that very large cyclic structures are formed during pyrolysis and because of their molecular size do not volatilize. The  $T_{EOS}$  results in Table 1 also demonstrate an interesting trend. Methyl cleavage increases at higher temperatures and consequently the increased formation of monosubstituted T-species is expected for the higher molecular weight materials wherein gasification results primarily from thermally induced rearrangement. These data also indicate that methane formation resulting from cleavage of methyl substituents on silicon is not a significant factor in the gasification of these materials or for that matter in their fire behavior.

#### Pyrolysis products-gasification energy-catalysts

The heat(s) of gasification for a range of oligomers reported in Part 1 (Ref. 11 [Fig. 13]) of this study agreed very well with calculated values based on the heat capacity and heat of vaporization values for these oligomers. Recall that a major correction for vapor absorption (attenuation) of the incident radiant energy was necessary in those measurements. The volatiles identified and quantified in this investigation confirm that these oligomers are gasified intact with no molecular degradation/rearrangement evident. Consequently, good agreement between

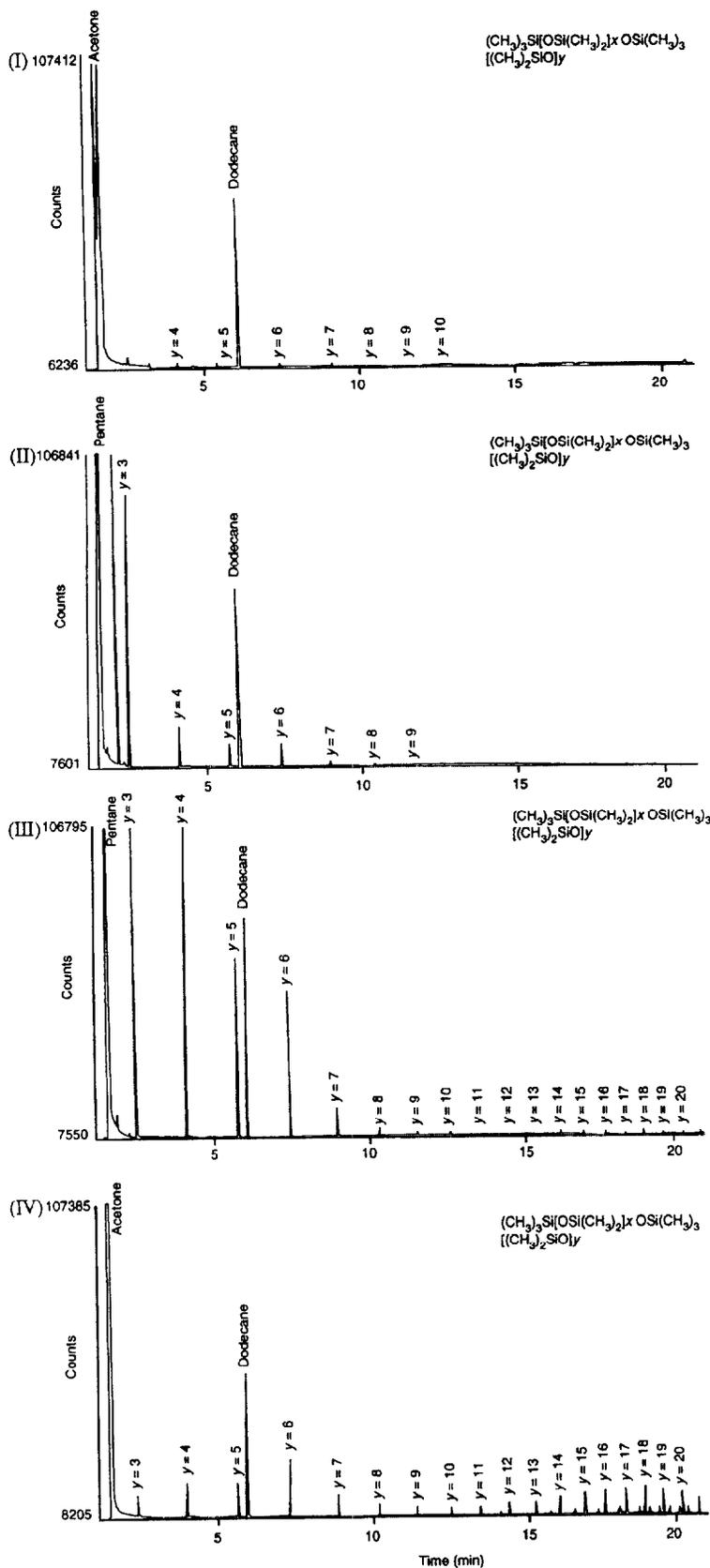


Figure 12. Gas chromatographic analysis of the model fluid: I, original; IV, residual fluid 15 g; II, 100-99 g volatiles; III, 95-90 g volatiles.

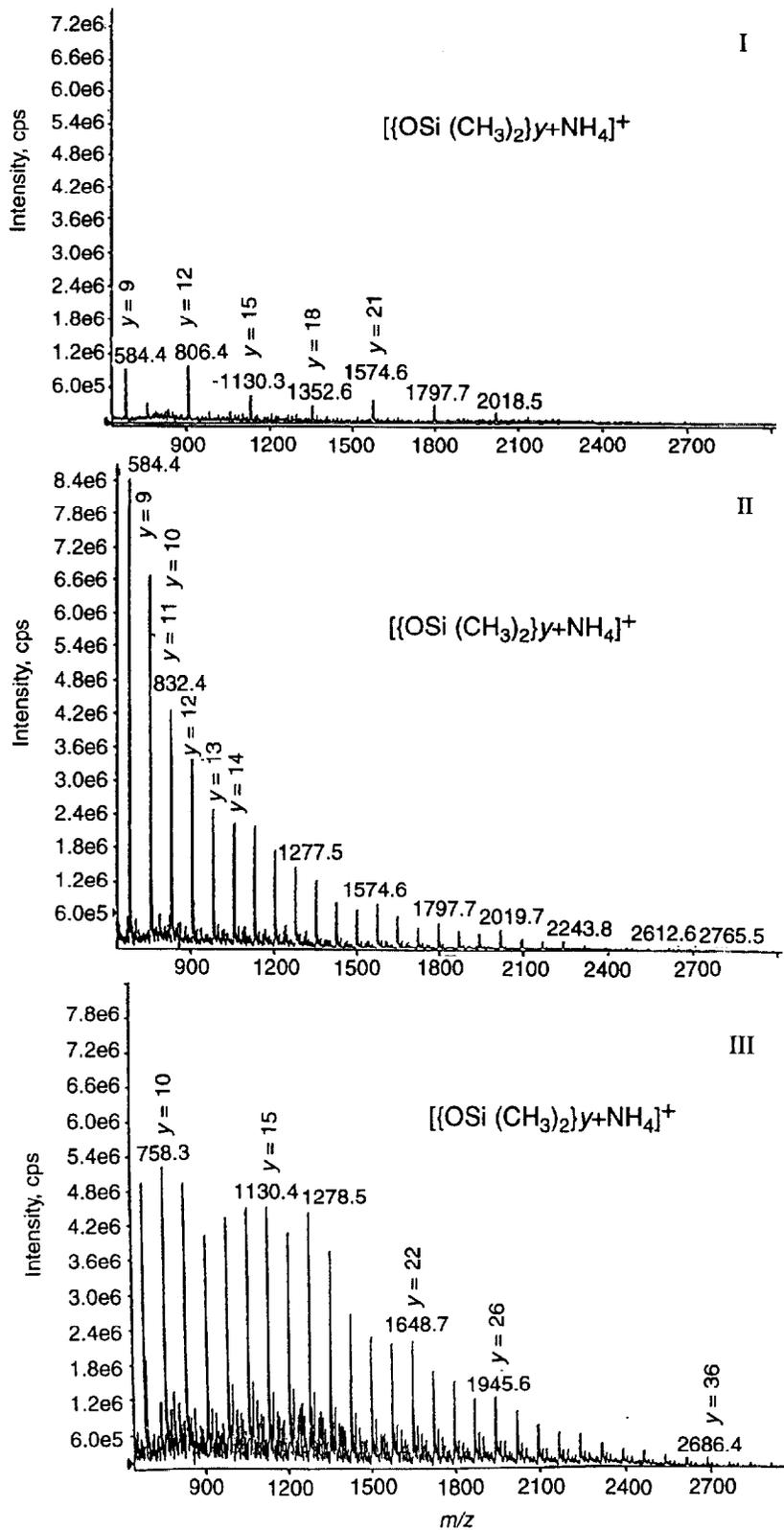
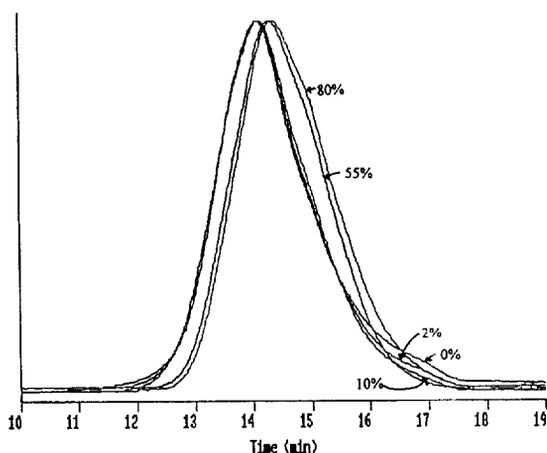


Figure 13. Mass spectral analysis of model fluid: I, original fluid; II, 95–90 g volatiles; III, residual fluid (15 g).

**Table 2. Volatiles analysis/characterization-GPC**

Polymer Volatiles	50 cS		10 <sup>3</sup> cS		10 <sup>4</sup> cS		6 × 10 <sup>4</sup> cS		Model	
	IMW	SCC	IMW	SCC	IMW	SCC	IMW	SCC	Poly	CVC
Mass loss range										
100 → 98	90	10	62	38	70	30	20	80	7	93
95 → 90	—	—	49	51	—	—	14	86	7	93
75 → 70	56	44	35	65	21	79	12	88	—	—
55 → 50	—	—	32	68	9	91	—	—	9	91
35 → 30	26	74	12	88	—	—	—	—	—	—
20 → 15	18	82	9	91	18	82	25	75	9	91



**Figure 14.** GPC chromatograms of the original and residual fluids from various stages of 1000 cS fluid gasification: 0%, 2%, 10%, 55% and 80% gasification.

the measured global heat of gasification and the calculated value based on heat capacity and heat of vaporization is expected and was observed.

The pyrolysis data for commercial-grade silicone polymers (PDMS) as reported in Part 1<sup>11</sup> are well represented by the solid curve in Fig. 14.<sup>11</sup> The heat(s) of gasification for these fluids (50 to 60 000 cS) were virtually constant and ranged from 1200 to 1300 KJ/kg. Except for the 50 cS fluid, the dominant gasification route for these polymers after the initial ~10% of mass loss (see Table 2) is that of thermal induced degradation/rearrangement to short chain cyclic oligomers (primarily D<sub>3</sub>) along with a wide range of intermediate chain length cyclic siloxanes. This composition of volatiles is expected to be representative for all PDMS polymers with viscosities of 1000 cS and higher. The gasification of the 50 cS fluid occurs via a combination of two routes volatilization and thermal induced degradation (see Table 2). Volatilization of native species is dominant during most of the pyrolysis of this fluid. Nevertheless, the overall pyrolysis rate of this fluid parallels that of the higher polymers and this is perhaps fortuitous. Polymers between 50 and 1000 cS are expected to gasify via both mechanisms; rearrangement is expected to play

a significant gasification role earlier in the pyrolysis for higher viscosity materials.

Trace catalyst residues which may remain from the polymer manufacturing process or from inadvertent addition via some other route may significantly alter the pyrolysis rate of PDMS (Ref. 11[Fig.14]) and presumably the mode of gasification of the fluid. The influence of catalytic behavior on pyrolysis product composition was beyond the scope of our current study.

## SUMMARY

Recent modification of the NIST-BFRL gasification apparatus provides the capability for sampling, identifying and quantifying the pyrolysis products at any stage in the gasification of a material. Based on the identification of the pyrolysis products, insight into the dominant gasification mechanism(s) may be inferred.

Methylated siloxane oligomers undergo gasification via volatilization. In fact, relatively high molecular weight species gasify intact via volatilization, e.g. 50 cS ( $M_n \sim 4400$ ) and 100 cS ( $M_n \sim 7000$ ) gasify largely via volatilization of linear molecules native to these fluids. The characterization of both the residual fluids and the volatile products revealed they consisted almost entirely of molecular species native to the original fluids.

The gasification of intermediate ( $\eta \geq 1000$  cS) and higher viscosity silicone fluids occurs via two modes: (1) the volatilization of molecular species native to the polymer, and (2) the volatilization of molecules resulting from thermally induced degradation of the polymer via siloxane rearrangement. The dominant mode of gasification is dependent upon the composition of molecular sizes of species in the original polymer and the stage of the gasification, i.e. each dimethylsiloxane fluid exhibits its own unique gasification pattern. That is, the initial gasification via volatilization is subsequently superseded by a regime consisting perhaps exclusively of thermal induced degradation via siloxane rearrangement of the polymer to cyclic species. The evolved cyclics consist of a bimodal distribution consisting largely of very short chain species ( $[D_3] \gg [D_4] > [D_5], \dots [D_n]$ ) and a significant concentration of intermediate and higher molecular

weight cyclic structures. Their rate of formation and volatilization dictate the burning rate of silicones. Because of their structural similarity, the combustion of all gasification products from PDMS will result in virtually identical final combustion products, i.e.  $\text{SiO}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ .

As noted earlier, unusually high molecular weight PDMS molecular species gasify intact. This suggests that the volatilization of polymer components native to these fluids will in all likelihood dictate the ignition behavior of most silicones. Hence improvements in ignition resistance may require: (1) the elimination and/or minimization of low molecular weight species ( $M < 5000$ ) in the polymer, and/or (2) improved thermal stability to forestall thermally induced degradation and formation of volatile cycles.

Finally, the identification of the pyrolysis products for all of the silicone fluids used in this study provides a good rationale for the measured global heats of gasification in Part 1 of this study.

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