mp 95.0–96.0 °C; $[\alpha]^{25}_D$ −47.5° (*c* 1, $CHCl_3$).

Anal. Calcd for $C_{27}H_{28}O_5$: C, 74.98; H, 6.52. Found: C, 74.92; H, 6.50.

Other Materials for Polymerization. 1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (LGTBE) was prepared as described previously[3] and finally recrystallized from *n*-butyl chloride: mp 90.0–91.0 °C (lit.[12] mp 89.5–90.5 °C); $[\alpha]^{25}_D$ −31.6° (*c* 2.7, $CHCl_3$) (lit.[12] $[\alpha]^{25}_D$ −30.5°).

Polymerization catalysts and methylene chloride were purified as described previously.[3,13]

Polymerization. Polymerization was carried out in methylene chloride using the high-vacuum technique.[3,11] The polymerization was terminated by the addition of methanol. The polymer was purified by dissolution–reprecipitation using chloroform–petroleum ether system and was finally freeze-dried from benzene.

Debenzylation of the Polymer. 2,3,4-Tri-*O*-benzyl-(1→6)-α-D-allopyranan was dissolved in 1,2-dimethoxyethane, and the solution was added to liquid ammonia containing sodium at −78 °C. The reaction was allowed to continue for 1–1.5 h, followed by successive additions of ammonium chloride and water. The solution of debenzylated polymer in water was dialyzed with running water for several days. The polymer was freeze-dried from water.

Periodate Oxidation. The periodate oxidation of the free polysaccharide was carried out according to the procedure of Frechet and Schuerch.[4]

Measurements. The 40-MHz ^{31}P NMR spectrum of the polymerization system was measured by means of a JEOL PS-100 spectrometer with external phosphoric acid as reference. The 400-MHz ^1H and 100-MHz ^{13}C NMR spectra were recorded on a JEOL GX-400 spectrometer in chloroform-*d* and methylene-d_2 chloride, respectively, with tetramethylsilane as internal standard. The 25-MHz ^{13}C NMR spectrum of (1→6)-α-D-allopyranan was measured on the DMF–N_2O_4 solution by means of a JEOL PS-100 spectrometer. Gel permeation chromatography was run on 1% solutions of polymers in chloroform by means of a Toyo Soda high-speed chromatograph (Model HLC 802UR). The number-average molecular weight determined by gel permeation chromatography was based on the standard polystyrene samples and was almost the same as the value determined by membrane osmometry. The optical rotation was measured in chloroform or water at 25 °C using a Perkin-Elmer Model 241 polarimeter.

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Mass Spectral Characterization and Thermal Decomposition Mechanism of Poly(dimethylsiloxane)

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ABSTRACT: The thermal decomposition of poly(dimethylsiloxane) (PDMSi) was studied by direct pyrolysis–mass spectrometry (DP–MS). The mass spectral data show that the pyrolytic breakdown of PDMSi, pure or containing NaOH, leads to the formation of cyclic oligomers through an intramolecular exchange process. An estimate of the pyrolysis product distribution has been performed. It has been ascertained that the addition of a catalyst in the PDMSi lowers its maximum polymer decomposition temperature (PDT) without sensibly altering the relative amounts of pyrolysis products. PDMSi contains a mixture of cyclic oligomers, formed together with the high polymer in the synthesis. The MS analysis allowed the simultaneous detection and identification of these cyclic oligomers.

Introduction

The characterization of polymers by direct pyrolysis in the mass spectrometer yields important structural information and is becoming increasingly appreciated.[1–6] Typical applications of this method include structural identification of polymers, differentiation of isomeric structures, copolymer composition and sequence analysis, identification of oligomers formed in the polymerization reaction, and identification of volatile additives contained in polymer samples.[1] Furthermore, direct pyrolysis in the MS provides unique information on the primary processes of thermal decomposition of polymers.[7–9]

In the DP–MS technique, polymers are introduced via the direct-insertion probe and the temperature is increased gradually to a point at which thermal degradation reactions occur; the volatile compounds formed are then ionized and detected.

The mass spectrum of a polymer obtained under these conditions is therefore that of a mixture of oligomers formed by pyrolysis. An advantage of this technique is that pyrolysis is accomplished under high vacuum and, if polymers contain oligomers formed in the polymerization reaction, the latter become volatile at relatively low temperatures and can be detected by MS, while polymers remain undecomposed.[9]

This report describes the application of DP-MS to PDMSi.

It is well-known that PDMSi thermally decomposes via an intramolecular exchange process.[10-14] As with many other polysiloxanes, PDMSi equilibrates under the influence of a catalyst to produce a thermodynamically controlled distribution of ring and chain molecules.[10] Previous studies have focused attention on the ring-chain equilibration reactions, i.e. on the product distribution in thermally or catalytically equilibrated samples.[10] However, conversion to cyclic oligomers also occurs under gradual heating (dynamic) conditions, which are typically realized in thermogravimetric analysis and in DP-MS. Our study provides an estimate of the cyclic distribution products obtained by decomposing PDMSi under nonequilibrium conditions.

Our results show that, as often found with several polymers,[10,15,16] PDMSi contains a mixture of cyclic oligomers, formed together with the high polymer in the synthesis. These cyclic oligomers are the same that are produced in the thermal decomposition process.

In fact, the simultaneous detection and identification of the oligomers contained in the polymer was obtained at relatively low temperatures, while PDMSi pyrolyzed at higher temperatures.

Experimental Section

Materials. Linear PDMSi was obtained from different sources, including Dow Corning, General Electric, Union Carbide, and Aldrich Chemical Co. All these samples yielded identical pyrolysis product distributions, in agreement with previous literature studies, which established that the decomposition mechanism is independent of molecular weight.[11]

Mass spectra and the data presented in this study refer to a high-purity sample terminated with trimethylsiloxy groups obtained from Aldrich Chemical Co. Viscosity at 25 °C, 60 000 cSt.

Cyclic (trimer, tetramer, pentamer, and hexamer) dimethylsiloxanes were prepared according to the literature[17] and their purity was checked by gas chromatography.

Mass Spectrometry. Mass spectra were recorded on an LKB 9000 S mass spectrometer operated at an electron voltage of 70 or 18 eV, an ion source temperature of 330 °C, and an ion accelerating voltage of 3.5 kV.

PDMSi, pure or containing NaOH, was introduced by the direct inlet and heated at a constant heating rate of 10 °C/min. The experimental procedure used to obtain mass spectra from polymer samples is described elsewhere.[1]

Gas Chromatography. A Carlo Erba Fractovap 2350 gas chromatograph, equipped with FID, was used. A 3.8% UCW-98 on 80/100 Supelcoport column was used for cyclic fraction separations with a temperature program allowing 15 °C/min heating rates from 50 to 150 °C. The flow rate of nitrogen gas was 50 mL/min.

Thermogravimetry. Thermal analysis was performed with a Perkin-Elmer TGS/2 apparatus under a nitrogen atmosphere (60 mL/min), using a heating rate of 10 °C/min.

Results and Discussion

The mass spectrum of PDMSi, taken at 18 eV and a probe temperature of 470 °C, is reported in Figure 1. A large number of peaks appear in the spectrum up to about m/z 700.

When compared with the spectrum recorded at 70 eV (omitted here for brevity), the low electron energy mass spectrum shows a sharp increase in the relative intensities of peaks corresponding to m/z values of 207 + 74(n), with n = 0, 1, 2, ..., 10 (Scheme I). This increment of intensity is a strong indication that these peaks derive from cyclic oligomers formed in the thermal decomposition process.

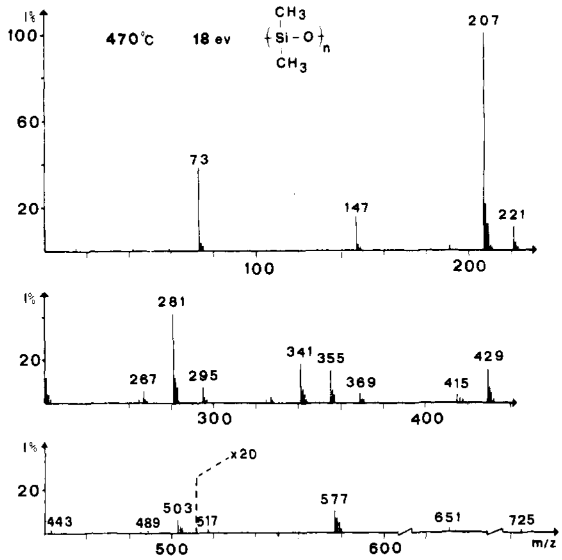
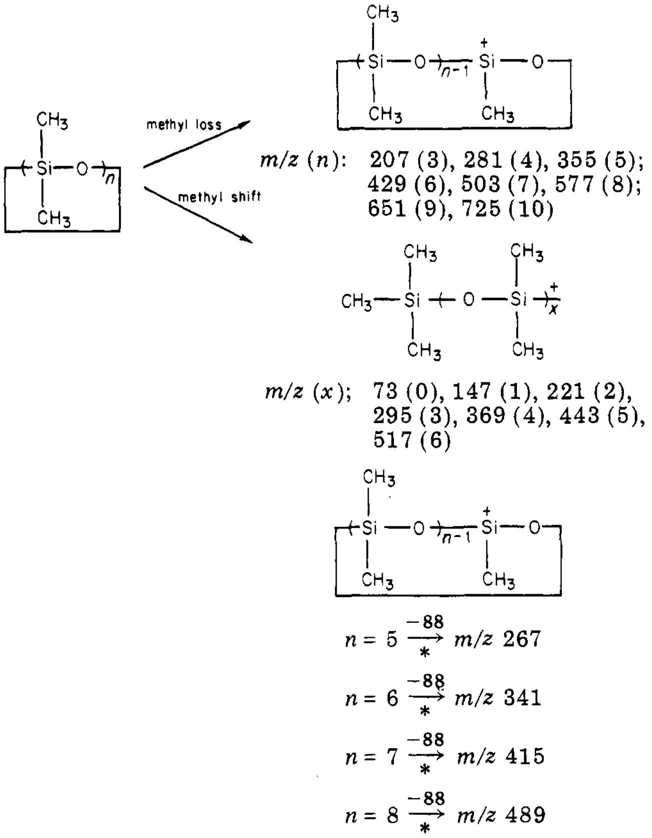


Figure 1. Mass spectrum (18 eV) of PDMSi at 470 °C.

Scheme I[a]
Electron Impact Fragmentation for the Cyclic Oligomers Formed by Thermal Degradation of PDMSi



[a] Asterisks indicate transitions substantiated by metastable peaks.

Actually, the cyclic oligomers formed in the primary thermal fragmentation reaction are not seen in the spectrum since they lose a methyl group by EI or form open-chain fragments through a methyl shift rearrangement involving the transfer of a methyl group from a neighboring Si atom to form a terminal trimethylsilyl group (Scheme I).

The latter series of fragments appears in the spectrum at m/z values of 73 + 74(n), with n = 0, 1, 2. ..., 6.

The two EI fragmentation processes described in Scheme I account for all peaks appearing in Figure 1 except a series of four peaks at m/z 267, 341, 415, and 489.

Table I
Distribution of Cyclic Products Generated in the Thermal Degradation of PDMSi[a]

	equil conditions[12]	dynamic TGA expts[13]	flash pyrolysis[14]	DP-MS pure PDMSi[b]	DP-MS PDMSi + NaOH[c]
$n = 3$	1.7	185.9	277.8	243.9	149.2
$n = 4$	100	100	100	100	100
$n = 5$	61	41.1	36	35.6	28.8
$n = 6$	18.5	46.3	22.2	37.6	49.1
$n = 7$	3.8	30.7	16.6	13.1	15.4
$n = 8$	2.5			1.1	0.5
$n = 9$	1.7			0.2	0.1

[a] Contribution of octamethylcyclotetrasiloxane arbitrarily assigned a value of 100. [b] Peak intensities from mass spectrum at 470 °C of pure PDMSi. [c] Peak intensities from mass spectrum at 350 °C of PDMSi containing NaOH.

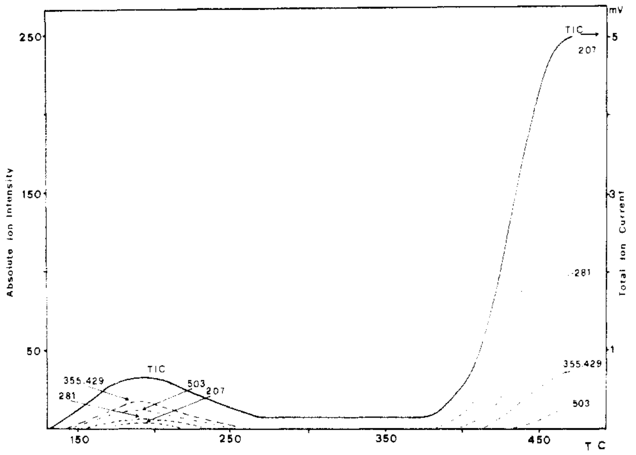


Figure 2. Total ion current (TIC) curve and mass fragmentograms of decomposition products for PDMSi.

The latter derive from cyclic fragments through EI rearrangement occurring with loss of tetramethylsilane (m/z 88), as illustrated in Scheme I. These transitions are supported by the presence of strong metastable peaks. In order to substantiate our interpretation, authentic samples of dimethylsiloxane cyclic trimer, tetramer, pentamer, and hexamer were prepared and the mass spectra recorded at 18 eV. Molecular ions corresponding to the cyclic siloxanes were found to be nearly absent in the spectra, and the highest mass found in each spectrum corresponds to the loss of a methyl group from the parent ion. These results are in agreement with the literature.[14,18]

Inspection of the total ion current (TIC) curve relative to PDMSi (Figure 2) reveals that the PDMSi sample contains a mixture of oligomers, formed together with the high polymer in the synthesis. These compounds distill in the high vacuum of the mass spectrometer already at probe temperatures of 150–250 °C, while the decomposition of the polymer starts around 400 °C. Mass fragmentograms (Figure 2) of the single ions show that the intensities reach a maximum around 190 °C; their m/z values correspond to those of the cyclic fragments in Scheme I. The TIC curve in Figure 2 shows furthermore that the thermal decomposition of PDMSi starts at 400 °C but reaches its maximum beyond our probe temperature limit (about 500 °C). This fact is confirmed by the differential thermogravimetric (DTG) curve reported in Figure 3, showing that PDMSi reaches its maximum PDT at about 600 °C. The addition of a catalyst (NaOH) lowers the PDT to about 300 °C (Figure 3). The TIC curve relative to the catalyzed thermal decomposition of PDMSi is reported in Figure 4.

It can be noted that, while the volatilization temperature of the preexisting oligomers remains unaffected, the thermal decomposition of PDMSi in the mass spectrometer undergoes strong anticipation, and the TIC maximum occurs at about 325 °C, in good agreement with DTG.

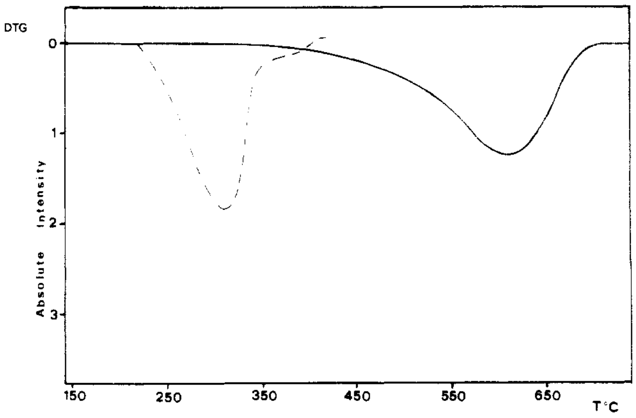


Figure 3. Differential thermogravimetric curves of PDMSi: (—) pure; (---) containing NaOH.

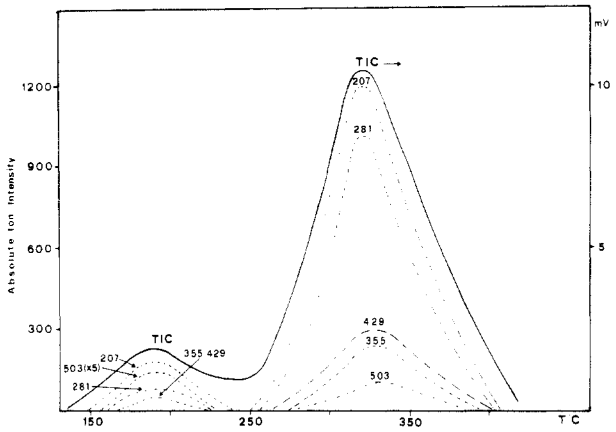


Figure 4. Total ion current (TIC) curve and mass fragmentograms of decomposition products for PDMSi containing NaOH.

Remarkably, the mass fragmentograms in Figure 4 show no sensible changes in the relative intensities of the peaks with respect to the thermal decomposition of the catalyst-free PDMSi (Figure 2). This implies that the catalysis induces only a lowering in the decomposition temperature without altering the relative amounts of cyclic oligomers formed.

In order to estimate the distribution of cyclic products obtained by DP–MS of PDMSi, we have performed parallel MS and GC determinations of cyclic siloxane mixtures of known compositions.

In Figure 5 are reported mass spectrum peak intensities ($M^+ - 15$) vs. chromatographic peak areas corresponding to each cyclic compound present in these mixtures. A fairly good correlation is obtained.

In Table I our results are compared to those of other authors, obtained under equilibrium[12] and nonequilibrium[13,14] conditions.

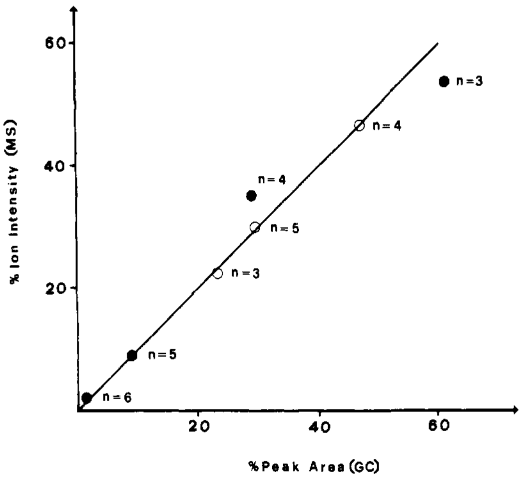


Figure 5. Percent ion intensity (MS) vs. percent peak area (GC) for each cyclic dimethylsiloxane present in two mixtures (○): $n = 3$ (24%), $n = 4$ (48%), $n = 5$ (28%); (●): $n = 3$ (62%), $n = 4$ (28%), $n = 5$ (9%), $n = 6$ (1%).

It is interesting to note that the product distribution obtained by DP–MS is similar to that observed in flash pyrolysis[14] and TGA[13] experiments.

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Registry No. NaOH, 1310-73-2.

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Thermal Degradation of the Blend Poly(2,6-dimethyl-1,4-phenylene oxide)–Polystyrene

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ABSTRACT: Thermal decomposition of blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with polystyrene (PS) and graft copolymers of PS with PPO under vacuum or in an inert atmosphere in the temperature range 320–380 °C has been examined. The overall character of the process has been investigated by using nonisothermal techniques such as thermogravimetric analysis and thermal volatilization analysis. It has been shown that polystyrene is stabilized in the presence of PPO and that the temperature of the maximum rate of PS decomposition is shifted toward higher temperatures. More precise analysis of the composition of degradation products and the shape of isothermal thermogravimetric curves indicate the following elementary steps of PS decomposition in the presence of PPO: initiation by random scission, propagation by unzipping and intramolecular chain transfer, and first-order termination. Phase structure of the blend and the abundance of labile PPO protons eliminate the process of intermolecular chain transfer. It has also been shown that the presence of PPO interferes with the process of intramolecular hydrogen transfer.

1. Introduction

Thermal decomposition of a polymer blend is not, in general, the superposition of the processes of degradation of its pure components. Several publications have been devoted to studies of the interactions between degrading components of polymer blends, for example, for the following systems: poly(methyl methacrylate)–poly(vinyl chloride),[1] polystyrene–poly(vinyl chloride),[2] polystyrene–poly(α-methylstyrene),[3] and polystyrene–poly(ethylene glycol).[4] Blends of poly(2,6-dimethyl-1,4-phenylene oxide) with polystyrene are of particular intrest due to their complete homogeneity[5] and broad commercial use. Thermal degradation of this system has not been examined so far. The aim of this paper is to investigate the observed stabilization effect of polystyrene in mixtures with PPO during thermal degradation.

2. Experimental Section

2.1. Materials. The two samples of polystyrene used throughout this work were prepared in a free radical polymerization (sample 1: $M_v = 172000$, $M_n = 100000$, $M_v/M_n = 1.72$; sample 2: $M_v = 840000$, $M_n = 450000$, $M_v/M_n = 1.87$). M_v molecular weights were determined by the use of a viscosimetric method in toluene (25 °C, $K = 1.16 \times 10^{-4}$, $a = 0.72^{6}$). M_n molecular weights were determined by membrane osmometry. The molecular weight distribution of these samples is, thus, intermediate between "the most probable" and that resulting from termination by recombination.

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