Mass Spectral Characterization and Thermal Decomposition Mechanism of Alternating Silarylene–Siloxane Polymers

Alberto Ballistreri and Giorgio Montaudo*

Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania, 95125 Catania, Italy

Robert W. Lenz

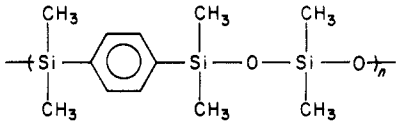
Chemical Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003. *Received September 22, 1983*

ABSTRACT: The thermal decomposition of two alternating silarylene–siloxane polymers was studied by direct pyrolysis into a mass spectrometer. The results indicate that intramolecular exchange reactions occurred during the primary thermal fragmentation processes causing the formation of cyclic compounds. Only part of the thermal fragments had structures corresponding to the repeating unit of the polymers. The remaining pyrolytic products resulted from thermal rearrangement of the silarylene–siloxane polymer chain and had structures different from those of the original polymer repeating units. Both siloxane and *p*-phenylenedisilanol cyclic oligomers were found in the products.

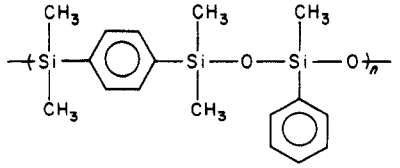
Introduction

We have recently carried out an investigation on the direct pyrolysis–mass spectrometry (DP–MS) of poly(dimethylsiloxane) (PDMS) as part of our longer term investigations on the primary thermal fragmentation processes of condensation polymers.[1] We report here on a similar study on polymers containing an alternating sequence of silarylene–siloxane units.

Polysiloxanes, when heated alone or in the presence of a variety of catalysts, are known to undergo ring–chain equilibration reactions, which involve a series of intramolecular exchange reactions that produce cyclic siloxane oligomers.[2] The presence of a catalyst for the exchange reaction provides a faster equilibration rate but should not alter the identity and the relative amounts of cyclic oligomers formed at the equilibrium. In the present polymer under study, however, the siloxane groups are separated by phenylene rings, so a ring–chain equilibrium of this type may produce thermal fragments having structures different from that of the original polymer. This possibility was found to be the case for the two alternating silphenylene–siloxane polymers, I and II, in the present investigation:



I



II

These polymers were synthesized by reacting the 1,4-phenylenedisilanol monomer with either the dimethylsilyl or the methylphenylsilyl monomers, respectively.[3,4] A detailed investigation of the thermal gravimetric analysis of the former polymer in both air and nitrogen has been reported previously.[5]

In these two polymers, I and II, the three silicon atoms in each repeating unit are not equivalent because only one is linked to two oxygen atoms in the siloxane portion while the other two are linked to an oxygen atom and to a phenyl ring in the silphenylene portion. As a consequence of this molecular arrangement, the effect of the thermal exchange reactions involving Si–O bonds was the formation of volatile thermal fragments containing either pure siloxane or pure phenylenedisilanol units, or various sequences of these two types of units. Hence, these fragments have structures different from that of the repeating unit present in the original polymer. The overall evidence collected here points to a thermal decomposition in which the exchange reactions predominate with the consequent formation of fragments containing either pure siloxane or pure phenylenedisilanol units.

Experimental Section

Direct Pyrolysis–Mass Spectrometry. Mass spectra were recorded on an LKB 9000 S gas–mass spectrometer operated at an electron voltage of 70 or 18 eV, an ion source temperature of 330 °C, and an accelerating voltage of 3.5 kV. The polymers, either pure or containing catalytic amounts of sodium hydroxide, were introduced at the direct inlet and heated at a constant rate of 10 °C/min. The experimental procedure used to obtain mass spectra from polymer samples has been described elsewhere.[6]

Indirect Thermal Decomposition. About 100-mg quantities of polymer I were decomposed in bulk in sealed glass tubes at 250 °C using sodium hydroxide as catalyst. After about 4 h, the mixture obtained was dissolved in toluene and analyzed directly by gas–liquid chromatography.

Gas–Liquid Chromatography. An Erbe Fractovap 2350 gas chromatograph, equipped with FID, was used to analyze the catalyzed thermal decomposition products. A 3.8% UCW-98 on 80/100 Supelcoport column was used for cyclic fraction separation, 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.

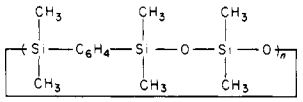
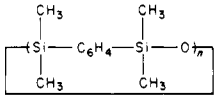
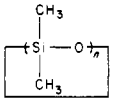
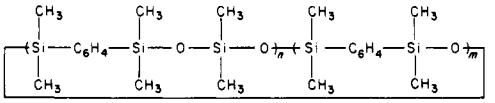
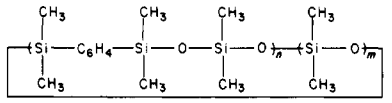
Cyclic Oligomer Standards. Cyclic trimer, tetramer, pentamer, and hexamer dimethylsiloxanes, which were used as standards for GC analysis, were prepared according to procedures in the literature.[1,7]

Results and Discussion

Polymer I. The mass spectrum of the volatile products obtained from polymer I, decomposed in the spectrometer at a probe temperature of 470 °C and 18 eV to minimize the EI fragmentation, is shown in Figure 1. The spectrum is characterized by the presence of EI fragments derived from the cyclic compounds formed in the primary thermal decomposition process through intramolecular Si–O exchange reactions. The molecular weights of these compounds are compiled in Table I as m/z values. As in the case of PDMS,[1] the cyclic compounds of Table I that were

0024-9297/84/2217-1848$01.50/0

Table I
Cyclic Compounds Formed in the Thermal Degradation of Polymer I

	(M^+)	$(M^+ - 15)$
		
$n = 2$	564	549
$n = 3$	846	831
		
$n = 2$	416	401
$n = 3$	624	609
$n = 4$	832	817
		
$n = 3$	222	207
$n = 4$	296	281
$n = 5$	370	355
$n = 6$	444	429
$n = 7$	518	503
		
$n = 1, m = 1$	490	475
$n = 1, m = 2$	698	683
$n = 1, m = 3$	906	891
$n = 2, m = 1$	772	757
$n = 2, m = 2$	980	965
		
$n = 2, m = 2$	430	415
$n = 1, m = 3$	504	489
$n = 1, m = 4$	578	563
$n = 1, m = 5$	652	637
$n = 2, m = 1$	638	623
$n = 2, m = 2$	712	697
$n = 3, m = 1$	920	905

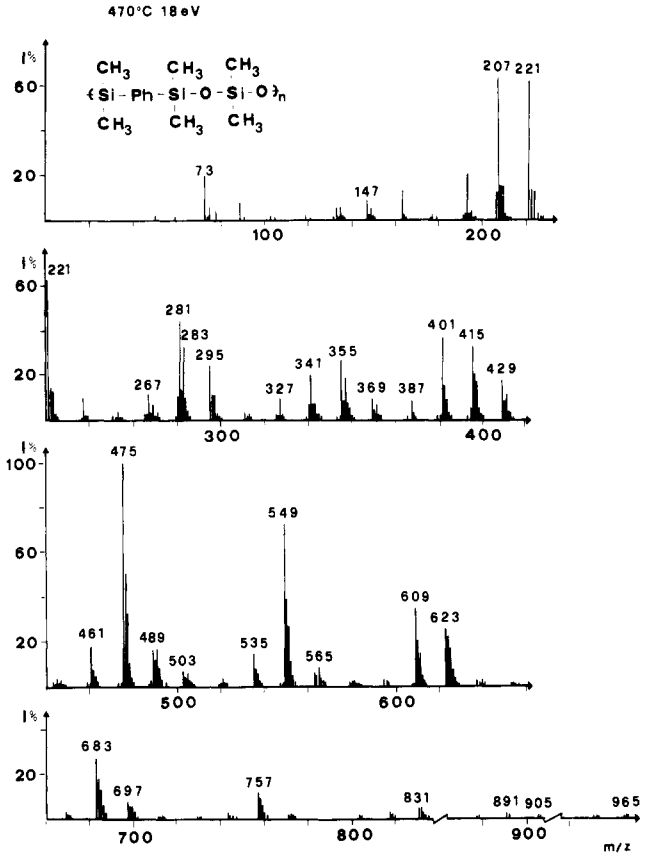


Figure 1. Mass spectrum (18 eV) of polymer I decomposed at 470 °C.

formed thermally either lose a methyl group by EI or rearrange to open-chain fragments, which undergo further fragmentation by EI, as outlined in Figure 2.

Remarkably, all of the peaks appearing in the spectrum in Figure 1 can be identified by use of Table I and Figure 1, and only two of the fragment ions, those at m/z 549 and 831 in Figure 1, have structures corresponding to the repeating unit of polymer I. The remaining fragments reported in Table I are formed by thermal rearrangement of the silarylene–siloxane polymer chain, and these have structures different from that of the original repeating unit. As a result, fragments having a mixed silarylene–siloxane structure, as well as both pure dimethylsiloxane and *p*-phenylenedisilanol cyclic oligomers, were found as shown in Table I.

The EI fragmentation processes of the cyclic compounds formed thermally are summarized in Figure 2. The methyl group loss and tetramethylsiloxane (m/z 88) loss are analogous to those observed in PDMS.[2] The methyl shift rearrangement can occur here onto either one of the nonequivalent silicon atoms of the polymer chain, thus generating a number of different possibilities as shown in Figure 2. Sometimes the isotopic pattern of cyclic fragments (for example, m/z 623 and 831) is altered because the M + 1 or M + 2 peaks are often coincident with either the molecular ions of cyclic fragments (for example, m/z 624 and 832) or with EI fragments of other compounds of higher mass (see Figure 2).

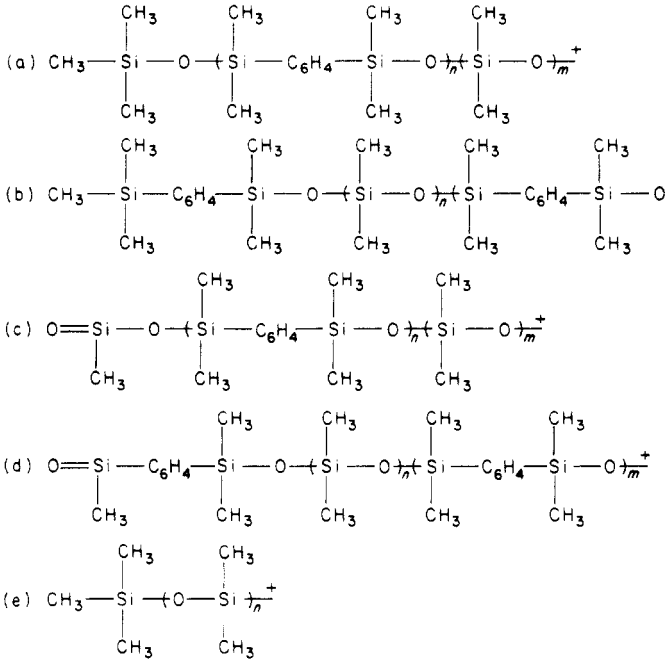
Inspection of the total ion current (TIC) curve corresponding to polymer I in Figure 3 reveals that this sample, before degradation, contained a mixture of low molecular weight compounds, which formed together with the high polymer in the synthesis of the polymer. The possible presence of such cyclic oligomers had been previously inferred from the GPC analysis of the polymers found.[3] These compounds distilled under the high vacuum of the MS when a probe temperature 100–250 °C was reached, while the decomposition of the polymer started at about 400 °C. The mass fragmentograms in Figure 3 of the single ions show that their intensities reached a maximum at about 160 °C, and their m/z values correspond to those of the cyclic fragments in Figure 1.

In Figure 4 is reported the spectrum of these low molecular compounds taken at a probe temperature of 150 °C and at 18 eV. The most intense peak in the spectrum at m/z 549 corresponds to the alternating silarylene–siloxane cyclic dimer of Table I. However, compounds containing nonalternating silarylene–siloxane sequences are also present at m/z 401, 475, and 623, together with small amounts of cyclic dimethylsiloxanes at m/z 207, 281, 355, and 429.

cyclic compounds $\xrightarrow{-15}$ cyclic fragments[a] $\xrightarrow{-88}$ m/z: 877, 803, 743, 729, 669, 595, 535, 521, 461, 387, 341, 327, 313, 267

(methyl shift)

fragments a-e



(a) m/z (n, m): 89 (0, 0), 297 (1, 0), 371 (1, 1), 579 (2, 1), 653 (2, 2)

(b) m/z (n, m): 223 (0, 0), 297 (1, 0), 505 (1, 1), 579 (2, 1)

(c) m/z (n, m): 75 (0, 0), 283 (1, 0), 357 (1, 1), 565 (2, 1), 639 (2, 2)

(d) m/z (n, m): 209 (0, 0), 283 (1, 0), 491 (1, 1), 565 (2, 1), 773 (2, 2)

(e) m/z (n): 73 (0), 147 (1), 221 (2), 295 (3), 369 (4)

[a] Cyclic fragments are identified in Table I.

Figure 2. Electron impact fragmentation of the cyclic compounds formed by the thermal degradation of polymer I.

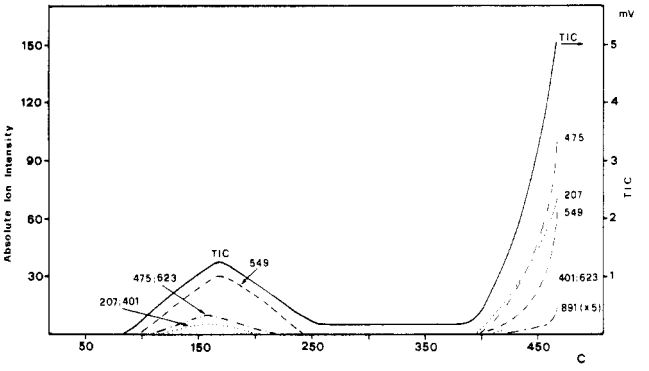


Figure 3. Total ion current (TIC) curve and mass fragmentograms of decomposition products for polymer I.

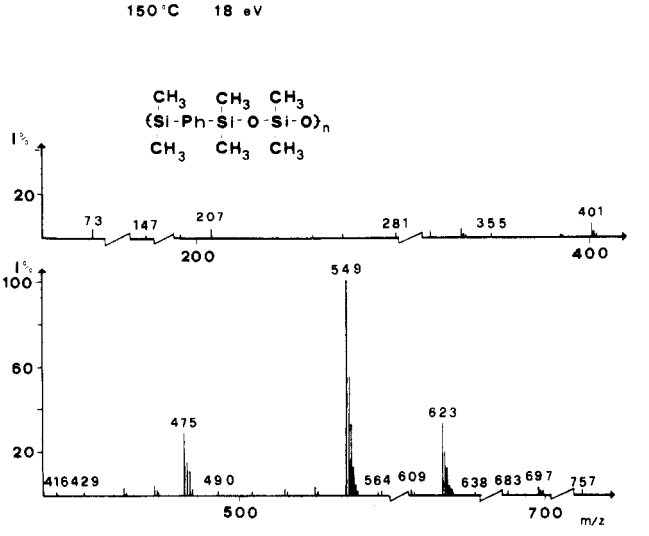


Figure 4. Mass spectrum (18 eV) of cyclic oligomers contained in polymer I at 150 °C.

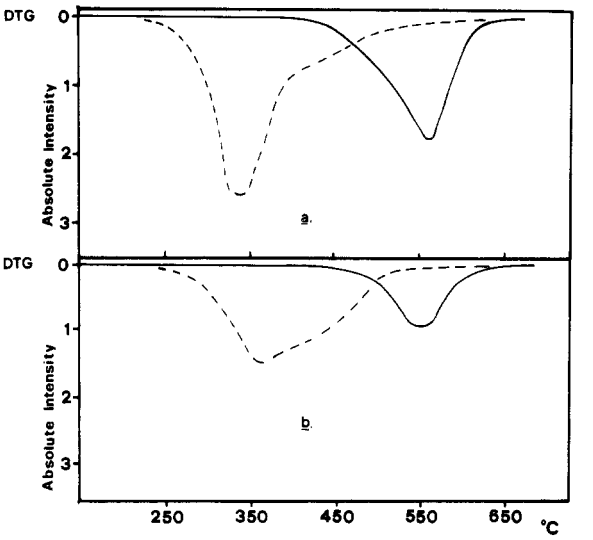


Figure 5. Differential thermogravimetric curves (DTG) for polymer I (a) and polymer II (b), either pure (—) or containing sodium hydroxide catalyst (- - -).

In the spectrum in Figure 4 are detectable also the molecular ions corresponding to the most intense cyclic fragments at m/z 416, 490, 564, and 638. The presence of these compounds indicates that either the alternating polymer was subjected to a rearrangement process during the polymerization reaction or a nonalternating silarylene–siloxane sequence was formed directly in the polymer, but the latter is unlikely on the basis of the results from our previous work.[3,4]

The TIC curve in Figure 3 shows, furthermore, that the thermal decomposition of polymer I started at 400 °C but reached its maximum beyond the probe temperature limit of about 500 °C. This fact is confirmed in the differential thermogravimetric (DTG) curve reported in Figure 5a,

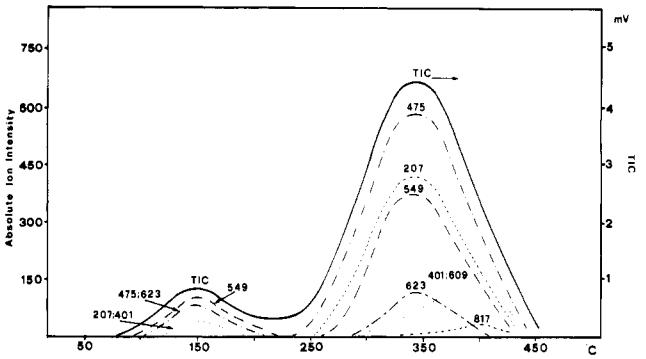


Figure 6. Total ion current curve and mass fragmentograms of decomposition products of polymer I containing sodium hydroxide.

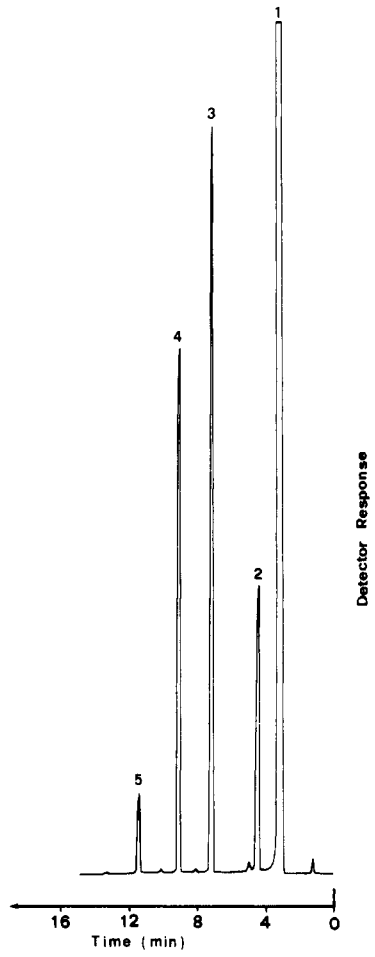


Figure 7. Gas chromatogram of the most volatile products from the catalyzed decomposition of polymer I: (1) toluene; (2) hexamethylcyclotrisiloxane; (3) octamethylcyclotetrasiloxane; (4) decamethylcyclopentasiloxane; (5) dodecamethylcyclohexasiloxane.

which shows that polymer I reached its maximum decomposition rate at a temperature, PDT, of aboout 550 °C. The addition of a catalyst, sodium hydroxide, lowered the PDT to about 350 °C, as shown in Figure 5a.

As reported elsewhere,[5] polymer I was also analyzed by thermal gravimetric analysis (TGA) under nitrogen. TGA also revealed that the polymer began to degrade at about 400 °C, and a constant maximum rate of weight loss occurred over the temperature range from about 480 to 560 °C. Weight loss ceased at about 600 °C, by which point the polymer had lost 70% of its initial weight, but the residue still contained substantial amounts of carbon, 41.8%, and hydrogen, 1.3%. The composition of the residue was not determined, but these results are consistent with the present observation of the elimination of cyclic dimethylsiloxane oligomers.

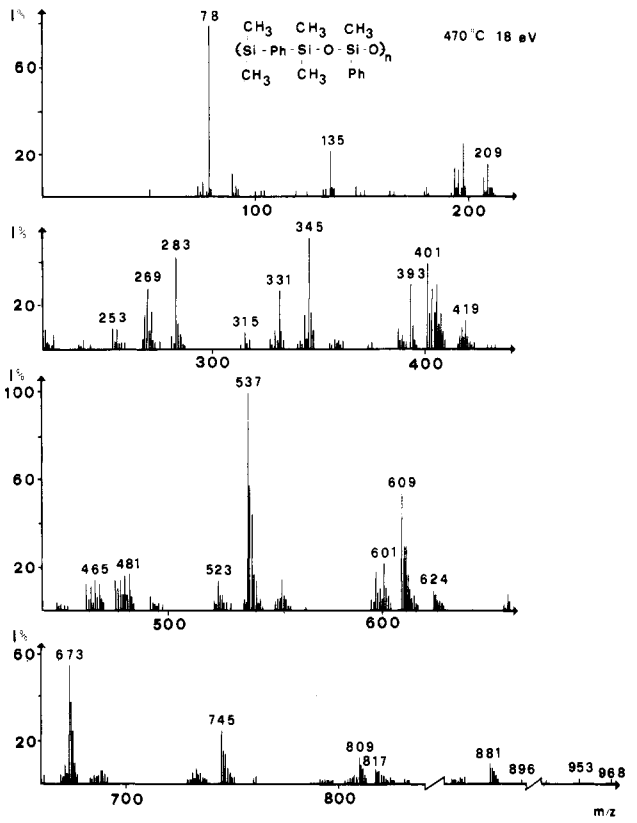


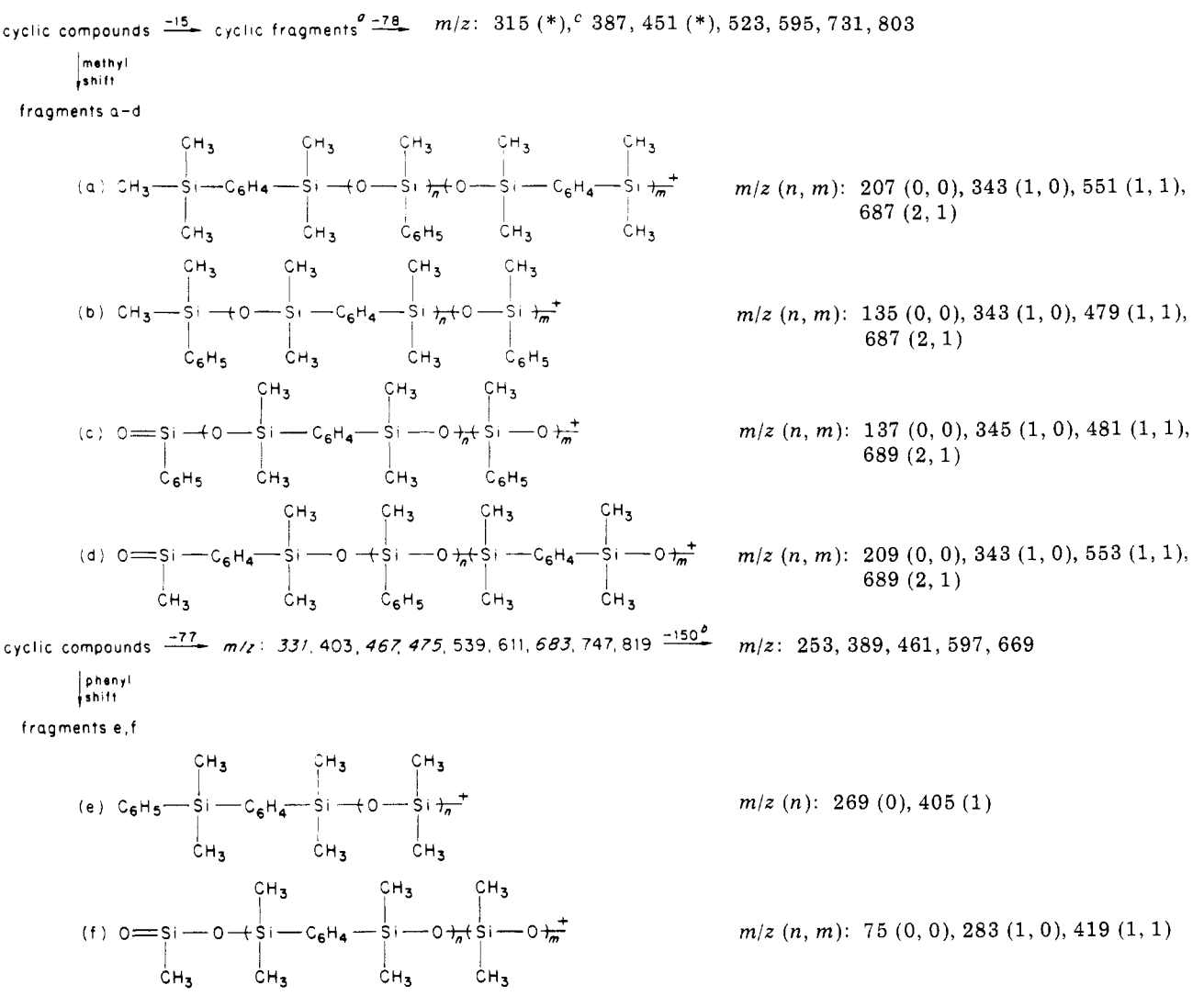
Figure 8. Mass spectrum (18 eV) of polymer II at 470 °C.

The TIC curve relative to the catalyzed thermal decomposition of polymer I is reported in Figure 6. It can be noted that, while the volatilization temperature of the preexisting oligomers remained unaffected, the thermal decomposition of polymer I in the mass spectrometer occurred at a considerably lower temperature and the TIC maximum occurred at about 350 °C, in good agreement with the DTG results.

By comparing the mass fragmentograms of the fragments generated in the uncatalyzed (Figure 3) and catalyzed (Figure 6) pyrolysis of polymer I, one can note that the relative ion intensities are similar. Therefore, the catalyst did not influence the distribution of the pyrolysis products, but it only increased the pyrolysis rate, as would be expected for a true catalyst.

Additional evidence for the formation of the cyclic compounds reported in Table I was sought by performing the pyrolysis of polymer I isothermally in sealed tubes and then analyzing the pyrolysis products by GC. In Figure 7 is shown the GC tracing of the mixture of the most volatile compounds formed in these experiments. The five peaks shown in Figure 7 were identified as cyclic siloxanes by comparison with authentic samples[1] using the GC enhancement method and by GC–MS. The complete GC analysis of the complex mixture of compounds generated in the sealed-tube pyrolysis was not performed.

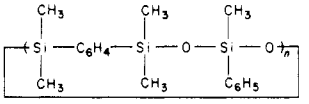
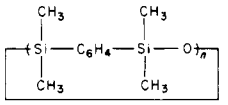
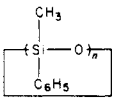
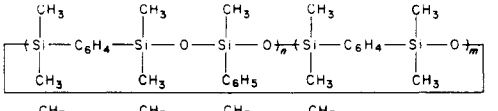
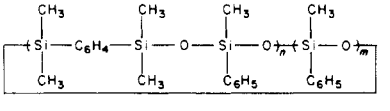
Polymer II. The mass spectrum of polymer II, taken at a probe temperature of 470 °C at 18 eV, is reported in Figure 8. The spectrum is characterized by EI fragments, which were derived from the cyclic compounds formed in the primary thermal decomposition process through intramolecular Si–O exchange reactions are compiled in Table II. Only the fragment ion at m/z 673 in Figure 8 has a structure corresponding to the repeating unit of polymer II. The remaining fragments listed in Table II resulted from thermal rearrangement processes analogous



[a] Cyclic fragments are identified in Table II. [b] Peaks italicized cannot give the 150 loss. [c] Asterisks indicate transitions substantiated by metastable peaks.

Figure 9. Electron impact fragmentation of the cyclic compounds formed by the thermal degradation of polymer II.

Table II
Cyclic Compounds Formed in the Thermal Degradation of Polymer II

		(M^+)	$(M^+ - 15)$
	$n = 2$	688	673
	$n = 2$	416	401
	$n = 3$	624	609
	$n = 4$	832	817
	$n = 3$	408	393
	$n = 4$	544	529
	$n = 1, m = 1$	552	537
	$n = 1, m = 1$	760	745
	$n = 1, m = 3$	968	953
	$n = 2, m = 1$	896	881
	$n = 1, m = 1$	480	465
	$n = 1, m = 2$	616	601
	$n = 1, m = 1$	824	809

to those described for polymer I.

In Figure 9 are summarized the EI fragmentation processes of the cyclic compounds formed thermally. The methyl group loss and methyl shift occurred as described above, but no tetramethylsiloxane loss was observed in this polymer, although the occurrence of a transition with loss of benzene (m/z 78) was substantiated by the presence of metastable peaks. Phenyl loss and phenyl shift reactions

are observable in the data, and the loss of trimethylphenylsiloxane (m/z 150) occurred in this case.

Again, all of the peaks appearing in the spectrum in Figure 8 are identified in Table II and Figure 9. The presence of several fragments with the same mass is again responsible for the altered isotopic pattern of some clusters of peaks.

Analogous to polymer I, polymer II also contained a mixture of low molecular weight compounds, which formed together with the high polymer in its synthesis, as seen in Figure 10. Mass fragmentograms of the single ions show that m/z values correspond to those of the cyclic fragments in Figure 8. However, they distilled over a wide range of temperature (80–250 °C), so that the relative intensities of these fragments changed in the spectra with the probe temperature as seen in Figures 11 and 12, respectively. The most intense peak at m/z 673 in Figure 8 corresponds to the exactly alternating silarylene–siloxane cyclic dimer of Table II. However, compounds containing nonalternating sequences were also quite abundant. By comparing the spectra in Figures 11 and 12 with those recorded at 70 eV, one can see a sharp increase in the relative intensities of peaks corresponding to cyclic fragments. In these spectra are detectable also the molecular ions at m/z 624, 688, 824, and 986, corresponding to the most intense cyclic fragments. For polymer II also, the presence of these compounds indicates that the alternating polymer probably underwent a degradative rearrangement process in the polymerization reaction.

The DTG curve of polymer II shows a PDT of about 550 °C, and the addition of a catalyst, sodium hydroxide, again lowered the PDT to about 350 °C, as seen in Figure 5b. The TIC curve relative to the catalyzed thermal decomposition of polymer II is reported in Figure 13. It can be noted that there was a substantial decrease in the temperature of the TIC maximum, which occurred at about 350 °C, in good agreement with DTG results. However, contrary to the behavior of polymer I, the ion intensities relative to fragments generated in the uncatalyzed and catalyzed pyrolysis of polymer II were quite different as seen in Figures 10 and 13. In fact, the most intense

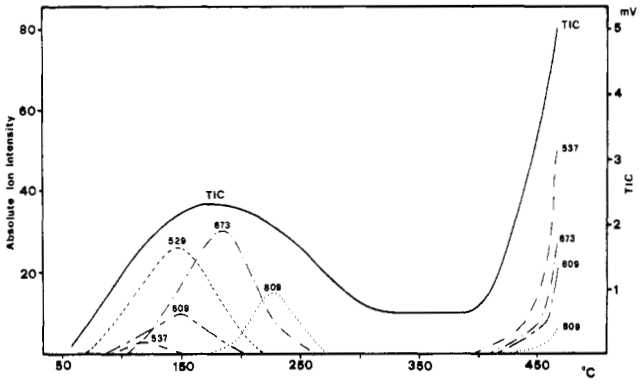


Figure 10. Total ion current curve and mass fragmentograms of decomposition products for polymer II.

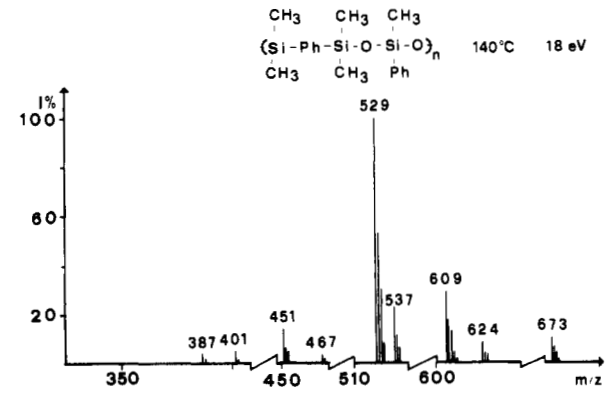


Figure 11. Mass spectrum (18 eV) of cyclic oligomers contained in polymer II at 140 °C.

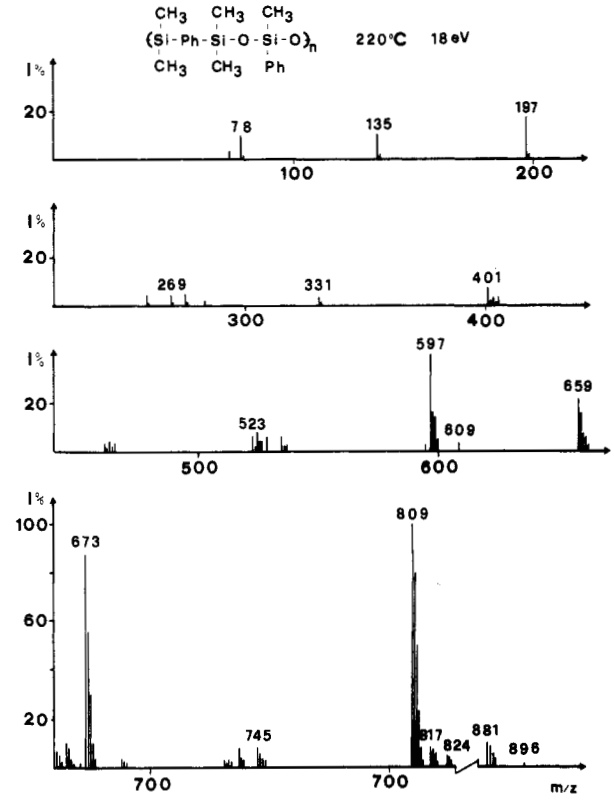
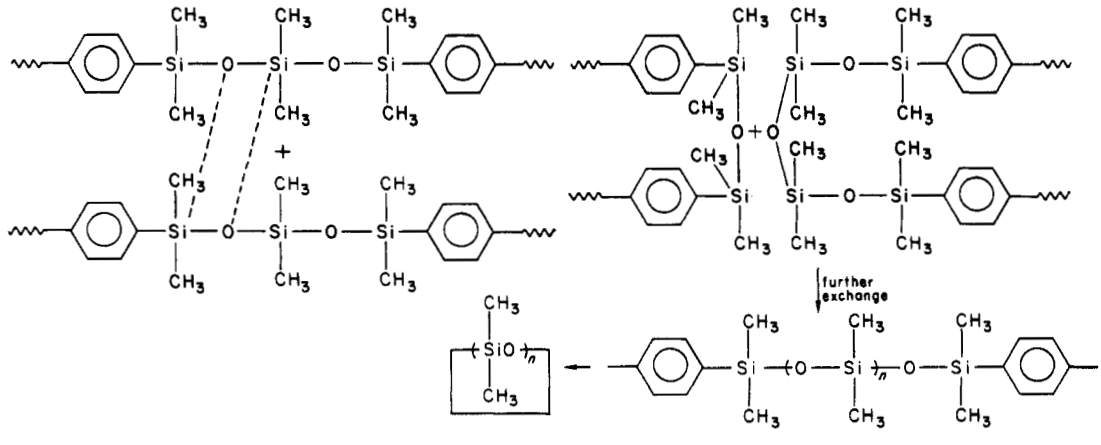


Figure 12. Mass spectrum (18 eV) of cyclic oligomers contained in polymer II at 220 °C.

Scheme I



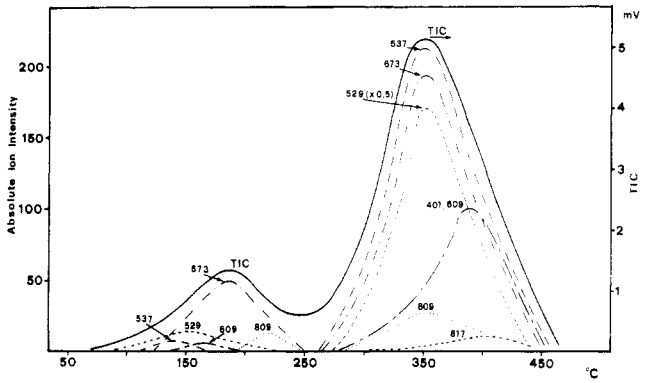


Figure 13. Total ion current curve and mass fragmentograms of decomposition products for polymer II containing sodium hydroxide.

fragment in Figure 13, at m/z 529, corresponds to the phenylmethylsiloxane cyclic trimer of Table II. This results indicates that sodium hydroxide is influencing the distribution of the pyrolytic products as well as the rate in this case.

Conclusion

The mass spectral characterization of two alternating silarylene–siloxane polymers has enabeled the elucidation of the thermal decomposition mechanism of these polymers. The overall evidence points to the occurrence of primary thermal fragmentation processes in which exchange reactions occur, with the consequent formation of cyclic oligomer, as shown in Scheme I.

As suggested by this mechanism, the polymers may undergo severe rearrangements in the thermal decomposition process, and as a result, thermal fragments with structures different from those of the repeating unit of the original polymer can be formed. This unusual mechanism results from the presence of nonequivalent silicon atoms in the repeating units of these polymers. As a consequence, the result of the proposed thermal exchange reactions, involving exchange of Si–O bonds, was the production of fragments containing equivalent species of products. To our knowledge, this may be a unique observation that such a rearrangement can occur.

Acknowledgment. Financial support from the Italian Ministry of Public Education and from the U.S. Office of Naval Research is gratefully acknowledged.

Registry No. I, 41205-84-9; II, 60291-47-6.

References and Notes

(1) A. Ballistreri, D. Garozzo, and G. Montaudo, *Macromolecules*, **17**, 1312 (1984).
(2) J. A. Semlyen, *Adv. Polym. Sci.*, **21**, 41 (1976).
(3) P. R. Dvornic and R. W. Lenz, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 593, 951 (1982).
(4) Y. Lai, P. R. Dvornic, and R. W. Lenz, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 2277 (1982).
(5) P. R. Dvornic and R. W. Lenz, *Polymer*, **24**, 763 (1983).
(6) S. Foti and G. Montaudo, in "Analysis of Polymer Systems", L. S. Bark and N. S. Allen, Eds., Applied Science Publishers, London, 1982, p 103.
(7) M. J. Hunter, J. F. Hyde, E. L. Warrick, and H. J. Fletcher, *J. Am. Chem. Soc.*, **68**, 667 (1946).

Penetration Function and Second Virial Coefficient for Linear and Regular Star Polymers

Jack F. Douglas and Karl F. Freed*

The James Franck Institute and the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. *Received September 16, 1983*

ABSTRACT: The penetration function and second virial coefficient are calculated for linear and regular star polymers to second order in $\epsilon = 4 - d$, where d is the spatial dimension. The predicted value of the penetration function in a good solvent increases monotonically with the number of arms. Theory and experiment are in reasonable agreement up to six or eight arms, where the experimental increase in Ψ^* saturates. These experiments suggest that the theoretical model with two-body excluded volume is inappropriate to describe stars having more than six branches because of the higher segment densities in the star center. We provide the interrelationships necessary for the comparison of the renormalization group (RG) theory to experiment and other theories. These relationships emerge by transforming the RG theoretical results for polymer observables into several analytic forms involving different scaling variables. A new representation, which we call the "renormalized two-parameter theory", is introduced that should be convenient and familiar for experimentalists because the notation is very similar to that of the two-parameter (TP) theory. Expressions for α_R, α_S, Ψ, and h are given for the regular star and linear polymers in terms of this notation, and a method is described for converting ordinary TP theory calculations in three dimensions to this RG representation. For illustrative purposes, we calculate α_S and Ψ for a ring based on well-known TP expansions. The results are compared with experimental and Monte Carlo data. A general expression for Ψ is given that holds for linear, ring, regular star, and regular comb polymers.

I. Introduction

Renormalization group (RG) methods provide a valuable approach to the description of excluded volume effects in polymer systems. The early RG treatments are based on the analogy between the critical properties of magnets and the properties of polymers with excluded volume.[1-4] However, the analogy model has the disadvantage of being abstract, and problems more complicated than the linear polymer at infinite dilution become increasingly cumbersome in this formulation. More physically transparent and powerful direct RG methods have been developed which take advantage of the field theory techniques used in the analogy model.[5-9]

The chain conformation space method, which we employ, offers a number of advantages over other direct renormalization methods. The method is computationally

0024-9297/84/2217-1854$01.50/0