

Exactly alternating silarylene-siloxane polymers: 6. Thermal stability and degradation behaviour

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The thermal stability and degradation behaviour of a series of twelve different exactly alternating silarylene-siloxane polymers were investigated by several different methods including thermal gravimetric analysis (t.g.a.) in air and in nitrogen, long term (up to 48 h) high temperature (600° and 900°C) isothermal degradation in nitrogen, and rapid pyrolysis in helium. No weight loss was observed by t.g.a. until about 400°C, and two distinctly different mechanisms were observed, one for degradation in nitrogen (a single step process), and the other in air (a three step process). Under nitrogen, black, insoluble, carbon-hydrogen-silicon containing degradation products were obtained, which were stable in pure oxygen to at least 1100°C. In air, pure SiO₂ was obtained after heating to above 730°C. Isothermal investigations revealed that at temperatures of 600°C and above, weight loss by thermal degradation under a nitrogen atmosphere was completed in less than an hour, and the polymeric products which remained thereafter did not change any further even after 48 h at 900°C.

Keywords Silarylene-siloxane polymers; thermal degradation; thermal gravimetric analysis; thermal stability; degradation behaviour

INTRODUCTION

In the search for high-temperature elastomers which would exhibit useful mechanical properties over a wide range of temperatures and in highly thermo-oxidative environments for extended periods of time, organosiloxane polymers have long been known as good candidates¹. Considerable research efforts have been devoted to their synthesis and evaluation, and these studies have shown that in addition to excellent chemical, mechanical and electrical properties, not common to any other class of polymers, the polysiloxanes are generally characterized by a combination of very low glass transition temperatures, T_g , (as low as -123°C for polydimethylsiloxane) and high thermal stabilities superior to most of the carbon-based polymers^{2,3}.

However, a major limitation of these polymers is their limited long term thermal stability at temperatures above 200°C, primarily caused by degradation by ionic reactions to which their backbone chains are easily susceptible because they are comprised entirely of siloxane units, -Si-O-. Thermal degradation is also facilitated in inert atmospheres by formation of cyclic products, particularly six- and/or eight-membered siloxane rings, which are thermodynamically stable at elevated temperatures and thus will easily form after the initial scission of the siloxane backbone bonds⁴⁻⁶. In oxidative atmospheres, the major

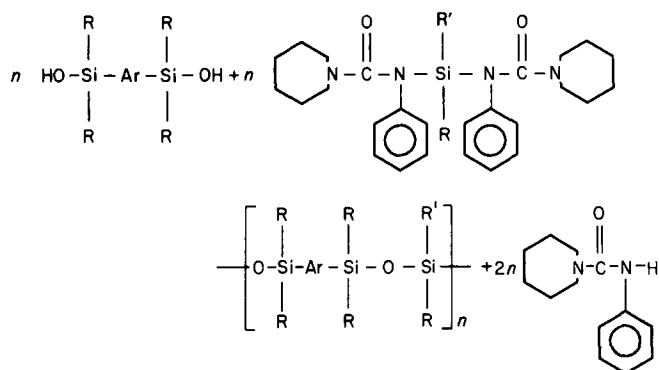
degradation mode is believed to involve formation of free radical centres on the substituent alkyl groups pendant to the main polymer chains, followed by the formation of cross-linked products by coupling reactions of these radicals during propagation of the degradation process⁷.

On the basis of such understanding of the degradation mechanisms occurring in the polysiloxanes, and in order to improve their long-term thermal stability at high temperature while still retaining their very desirable low temperature flexibility, various investigations have been directed toward the preparation of siloxane polymers modified with thermally stable units incorporated either into their main chains or into the pendant groups. Among these, significant attention has been devoted to the use of different aromatic structural units which were expected to successfully prevent formation of the cyclic degradation products when incorporated into the polysiloxane backbone⁸.

Recent and earlier studies in this field^{9,10}, have shown that incorporation of the arylene units in the main chain can produce polymers with a very favourable combination of low temperature flexibility and high thermal stability. These investigations have indicated that the exactly alternating silarylene-siloxane polymers should exhibit the optimum combination of these properties¹¹. Polymers of this type have been prepared in this laboratory¹²⁻¹⁴ by a controlled low-temperature condensation polymerization reaction¹⁵ of arylendisilanol with difunctional, reactive

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bisureidosilanes¹⁶⁻¹⁸ in chlorobenzene solvent, as shown in the following equation:



where R was $-\text{CH}_3$; R' was $-\text{CH}_3$ and/or $-\text{CH}=\text{CH}_2$; and Ar was $p\text{-C}_6\text{H}_4$ and/or $p,p'(\text{C}_6\text{H}_4\text{-O-C}_6\text{H}_4)$; see Table 1 for sample designations. In almost all cases the polymers obtained had number average molecular weights of about 100 000 or higher and exhibited glass transition temperatures which were low enough to be acceptable for good elastomers at room temperature and above^{14,19}.

Table 1 Exactly alternating silarylene-siloxane polymers

Polymer designation	Polymer composition*	
	Ar	R'
I A	I	III
I B	I	(0.95 III + 0.05 IV)
I C	I	(0.925 III + 0.075 IV)
I D	I	IV
II A	II	III
II B	II	(0.95 III + 0.05 IV)
II C	II	(0.925 III + 0.075 IV)
II D	II	IV
III A	(0.5 I + 0.5 II)	III
III B	(0.5 I + 0.5 II)	(0.95 III + 0.05 IV)
III C	(0.5 I + 0.5 II)	(0.925 III + 0.075 IV)
III D	(0.5 I + 0.5 II)	IV

* I: $(p)\text{-C}_6\text{H}_4$; II: $(p,p')\text{-C}_6\text{H}_4\text{-O-C}_6\text{H}_4$; III: $-\text{CH}_3$; IV: $-\text{CH}=\text{CH}_2$

Table 2 T.g.a. in air of exactly alternating silarylene-siloxane polymers*

Polymer	Arylene unit	Vinyl content (%)	Onset of degrad. (°C)	Temp. for 50% wt. loss (°C)	End of degrad. (°C)	Wt. remaining (%)
I A	<i>p</i> -phenylene	0	345	665	735	39.5
I B		5	370	705	730	46
I C		7.5	375	725	730	49.5
I D		100	420	—	725	58.5
II A	<i>p,p'</i> -diphenyl ether	0	335	610	720	26.5
II B		5	370	620	740	32
II C		7.5	410	630	720	35
II D		100	425	675	730	41
III A	50 mol % mixture	0	360	635	730	37
III B		5	390	670	725	40.5
III C		7.5	405	660	720	42
III D		100	420	670	730	46

* Measured at a heating rate of $15^\circ\text{C min}^{-1}$

This report describes the results obtained from investigation of the thermal stabilities and degradation behaviour of these polymers.

EXPERIMENTAL

Thermal gravimetric analyses, t.g.a., of all polymers were performed in air and in nitrogen. A DuPont 950 Thermogravimetric Analyzer in line with a DuPont 900 Thermal Analyzer was used. The sample weights ranged from 10 to 15 mg, and they were heated from 25° to 960°C in all cases at a rate of $15^\circ\text{C min}^{-1}$.

Isothermal degradation experiments were performed in a tubular, electrically heated furnace equipped with a quartz tube with a nitrogen inlet and outlet. Nitrogen was prepurified by passing through a system of in-line columns which contained sulphuric acid, KOH, P_2O_5 and molecular sieves ('Linde' type 3A, 1/6"). Polymer samples of about 100 mg were placed in quartz boats and carefully positioned in the middle of the tube. Before every run the tube was thoroughly purged with nitrogen for 20–30 min at a flow rate of $50\text{--}100\text{ ml N}_2\text{ min}^{-1}$. After this had been accomplished heating was started at the maximum heating rate allowed by the furnace, which was $45^\circ\text{C min}^{-1}$ so that samples were heated from 25° to 900°C in ~ 20 min. After the desired degradation temperature was reached the samples were allowed to degrade 1, 24 and 48 h.

Two polymers (Polymers IA and IIA) were selected for pyrolysis in helium atmosphere. For this, a Chromalytics Multi-Purpose Thermal Analyzer, Model MP-3 was used. The samples were heated from 200° to 800°C at a rate of $16^\circ\text{C min}^{-1}$.

RESULTS AND DISCUSSION

Thermal gravimetric analysis

The results obtained from t.g.a. investigations are shown in Tables 2 and 3 and in Figures 1–6. Included in Table 3 are comparable data for the t.g.a. analysis of polydimethylsiloxane⁶. It can be seen from these data that the polymer degradation mechanisms were entirely different in air (Figures 1–3) and in nitrogen (Figures 4–6), so that while decomposition by a single-step process apparently occurred in nitrogen, in air a three-step process appeared to be involved. In almost all cases

Table 3 T.g.a. in nitrogen of exactly alternating silarylene-siloxane polymers*

Polymer	Arylene unit	Vinyl content (%)	Onset of degrad. (°C)	Temp. for 50% wt. loss (°C)	End of degrad. (°C)	Wt. remaining (%)
I A	<i>p</i> -phenylene	0	400	545	660	30.5
I B		5	360	580	670	41
I C		7.5	420	—	680	51
I D		100	450	—	690	75
II A	<i>p,p'</i> -diphenyl ether	0	470	520	650	33
II B		5	420	590	690	38.5
II C		7.5	465	600	720	43
II D		100	490	—	740	66.5
III A	50 mol % mixture	0	390	530	750	31.5
III B		5	430	620	760	40.5
III C		7.5	420	625	770	42.5
III D	polydimethylsiloxane†	100	415	—	785	59
		0	290	445	600	25

* Measured at a heating rate of 15°C min⁻¹

† From reference 10

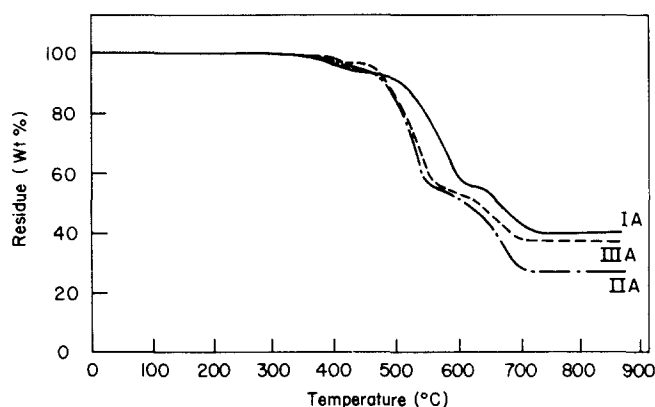


Figure 1 T.g.a. thermogram in air for silarylene-dimethylsiloxane polymers containing the following silarylene units: IA: *p*-phenylene; IIA: *p,p'*-diphenyl ether; IIIA: 50 mol% mixture

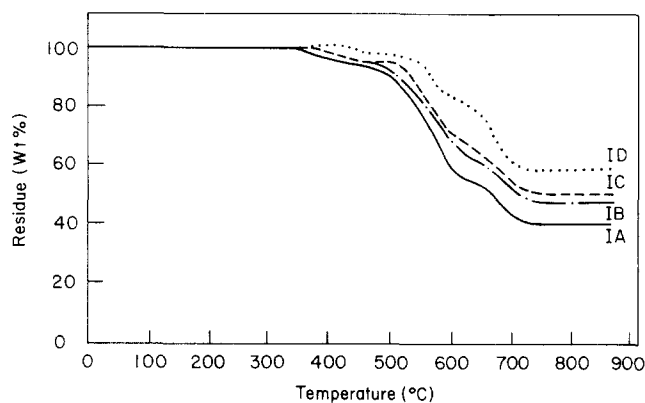


Figure 3 T.g.a. thermogram in air for silarylene-siloxane polymers containing *p*-phenylene units and the following amount of methylvinylsiloxane units: IA: 0%; IB: 5%; IC: 7.5%; ID: 100%

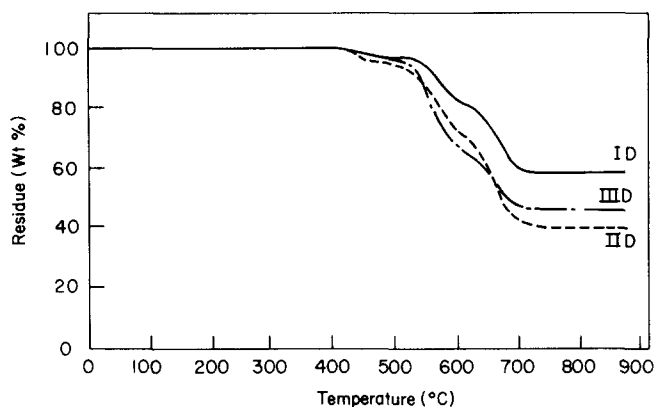


Figure 2 T.g.a. thermogram in air for silarylene-methylvinylsiloxane polymers containing the following arylene units: ID: *p*-phenylene; IID: *p,p'*-diphenyl ether; IIID: 50 mol% mixture

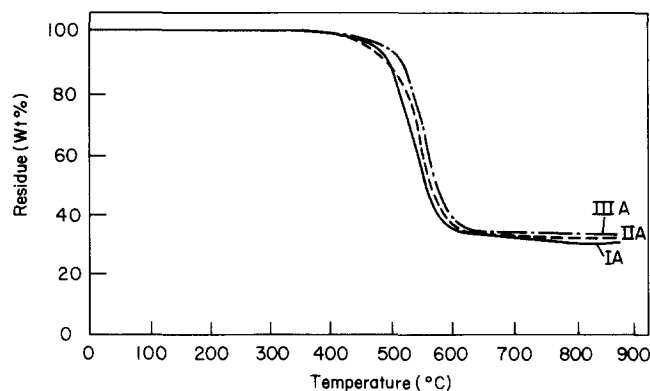


Figure 4 T.g.a. thermogram in nitrogen for silarylene-dimethylsiloxane polymers containing the following silarylene units: IA: *p*-phenylene; IIA: *p,p'*-diphenyl ether; IIIA: 50 mol% mixture

degradation started at lower temperatures in air than in nitrogen. This result was most prominent for the Group II polymers which contained *p,p'*-diphenyl ether units, so that, for example, the temperature difference between the onset of degradation in nitrogen and in air was as great as 135°C for Polymer IIA. However, with the exception of

the polymers which contained methylvinylsiloxy groups (Polymers IID and IIID) and Polymer IC, a 50% weight loss was achieved at lower temperatures in nitrogen atmosphere than in air.

Vinyl substituted polymers were more stable than the dimethylsiloxane polymers and resistance to thermal

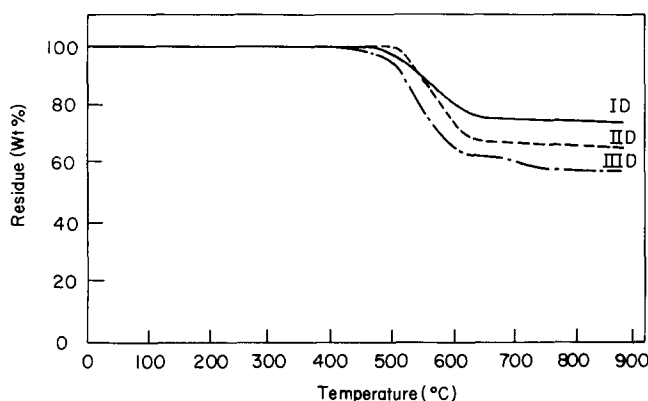


Figure 5 T.g.a. thermogram in nitrogen for silarylene-methylvinylsiloxane polymers containing the following silarylene units: ID: *p*-phenylene; IID: *p,p'*-diphenyl ether; IIID: 50 mol% mixture

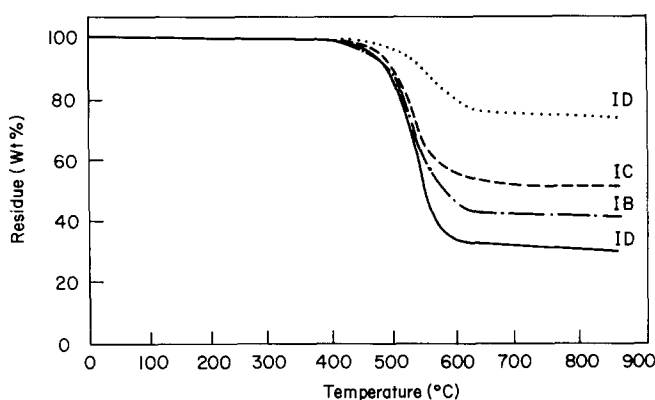


Figure 6 T.g.a. thermogram in nitrogen for silarylene-siloxane polymers containing *p*-phenylene units and the following amount of methylvinylsiloxane units: IA: 0%; IB: 5%; IC: 7.5%; ID: 100%

degradation apparently increased with increasing vinyl content as seen in Figures 3 and 6 for degradation in air and nitrogen, respectively.

In nitrogen, polymers containing *p,p'*-diphenyl ether units showed increased stabilities as compared to those containing *p*-phenylene units, and while the copolymers which contained the 50 mol% mixture of these two structural groups showed an intermediate behaviour between those of the two homopolymers, the situation was reversed in air, as seen by comparing Figures 1 and 2 and Figures 4 and 5, respectively.

During the degradation in air the polymers lost all of their organic groups and silicon dioxide remained in all cases as the final product at temperatures above 730°C.

Composition of the degradation products

Elemental analyses of the degradation residues were obtained after every stage of degradation in air and after the final degradation stage in both atmospheres. The results obtained for representative samples are listed and compared with the elemental composition of the original polymers in Table 5. For the degradation reactions in nitrogen, it can be seen from this Table that the changes in carbon contents between the original polymers and degradation products were never greater than 10%.

Changes in the silicon content were even smaller (3-4%) and proceeded in the opposite direction. In addition to this result, even after heating the samples at temperatures up to 960°C, there was still 1-2% of hydrogen left in the degradation products. At that temperature the degradation products appeared black and were insoluble in many of the commonly used solvents including tetrahydrofuran, chloroform, acetone, benzene or toluene.

The first step of the degradation in air was characterized by only a small weight loss, which in no case exceeded 5 wt% (Table 4). The major losses occurred during the second and third steps, and their magnitudes were influenced by the content of vinyl groups present in the polymer. In the second step the amount of volatile products apparently decreased with increasing vinyl content of the polymer, but the situation was reversed in the third step.

Elemental analysis of the residues showed that the first step of the degradation in air (up to 450°C) was characterized by about a 20% decrease in carbon content, a very small decrease in hydrogen content (not more than 5% of the original content) and a significant gain in oxygen content (the originally present amount of oxygen was roughly doubled). This behaviour was observed in all samples investigated, and it was most probably caused by the splitting off of -CH₃ with formation of crosslinks by oxygen bridges.

In the second step of the thermal degradation in air, both types of alternating silarylene-siloxane polymers lost about 50% of the carbon and about 50% of the hydrogen contents that remained after the completion of the first degradation step. This second step, which was in all cases completed at temperatures of about 600°-620°C, was also characterized by losses of silicon and oxygen which varied from the polymers containing *p*-phenylene to those containing *p,p'*-diphenyl ether units, so that while Polymer IA lost about 40% of Si and about 10% of O which remained after the first step, the corresponding losses in Polymer IIA were 20% in Si and 35% in O. This result most probably indicates that formation of the volatile organosilicon degradation products occurred during this second step.

The third step of thermo-oxidative degradation was characterized in all cases by complete removal of the

Table 4 Three steps of degradation in air of exactly alternating silarylene-siloxane polymers

Polymer	First step, wt. loss (%)	Second step, wt. loss (%)	Third step, wt. loss (%)	Wt. remaining (%)
I A	4.6	38.6	17.3	39.5
I B	4.9	32.2	16.9	46
I C	4.8	25.0	20.7	49.5
I D	3.2	12.0	26.3	58.5
II A	4.8	39.0	29.7	26.5
II B	4.8	35.0	28.2	32
II C	4.9	34.4	25.7	35
II D	4.8	19.1	35.1	41
III A	3.0	39.6	20.4	37
III B	4.8	36.8	17.9	40.5
III C	4.0	23.8	30.2	42
III D	2.0	22.4	29.6	46

Table 5 Comparison between the elemental compositions of degradation products^a and original polymers

Polymer	Original polymers				Degradation products			
	%C	%Si	%H	%O	in N ₂ ^b		in air ^c	
					%C	%Si	%H	%Si ^d
I A	50.2	30.0	8.4	11.5	41.8	27.4	1.3	45.5
I D	52.0	28.7	7.3	12.1	41.5	30.1	1.3	44.8
II A	56.0	23.1	6.8	14.1	44.0	25.0	—	48.0
II C	57.6	22.9	7.0	12.5	48.0	26.0	—	47.0
II D	59.4	21.7	6.7	12.2	47.0	25.0	—	47.0
III A	54.9	25.3	7.6	12.2	50.0	28.7	1.7	42.0

^a All the products were heated to 960°C

^b No detectable amounts of nitrogen could be found in any of the samples

^c No detectable amounts of carbon could be found in any of the samples

^d %Si in SiO₂ is 46.7

Table 6 Long term isothermal degradation in nitrogen of exactly alternating silarylene-siloxane polymers

Polymer	Temperature (°C)	Time (h)	Wt. loss (%)	T.g.a. wt. loss (%)
IA	600	1	68	69.5
		24	70	
		48	70	
	900	1	68.9	
		24	71	
		48	71	
IC	600	1	48	49
		24	49	
		48	50	
	900	1	48	
		24	49.8	
		48	50.9	
ID	600	1	24	25
		24	25	
		48	26	
	900	1	25	
		24	24	
		48	25	
IID	600	1	28.9	33.5
		24	33	
		48	33.9	
	900	1	30	
		24	33	
		48	33	
IIID	600	1	37.9	41
		24	40	
		48	42	
	900	1	39	
		24	41	
		48	43	

* From t.g.a. data of Table 3

remaining organic content. While the amount of silicon did not change during this third step, there was some gain in the oxygen content. This conversion ended at temperatures above 720°C to leave pure SiO₂ as the final degradation product, and the yield increased with increasing vinyl content.

Isothermal degradation in nitrogen

In order to investigate long term thermal degradation behaviour of these exactly alternating silarylene-siloxane polymers, selected samples (Polymers: IA, IC, ID, IID and

IIID) were exposed to 1, 24 and 48 h long heating at temperatures of 600° and 900°C in nitrogen atmosphere, and the results obtained are shown and compared with the corresponding t.g.a. data in Table 6.

Very good agreement between the results obtained from the two degradation procedures can be seen by a comparison of the data in Table 6 with that in Table 3, and in all cases practically the same amount of polymer remained undegraded in isothermal degradation as in the t.g.a. experiments. Also, these results indicate that above 600°C no significant degradation occurred even during extended heating periods of 24 or 48 h, so that only 1% additional weight loss was observed. Essentially the same conclusion holds for the effect of time at constant temperature. With the exception of Polymer IID at 600°C and Polymer IIID, the further weight loss after 1 h heating periods in no case exceeded 3%. The highest weight loss of 5% was observed in the case of Polymer IID at 600°C.

These results indicate that exactly alternating silarylene-siloxane polymers undergo relatively rapid thermal degradation in nitrogen up to 600°C during less than 1 h at constant temperature, but the black and insoluble degradation products remain thermally stable for extended periods of time even at temperatures as high as 900°C. Indeed, all attempts to obtain the elemental analyses of these isothermal degradation products failed because the samples would not undergo oxidation even when heated up to 1100°C in pure oxygen.

Pyrolysis

The rate at which volatile products formed during the thermal degradation of exactly alternating silarylene-siloxane polymers in inert atmosphere was investigated by pyrolysing selected samples in helium. The results obtained for Polymer IA are shown in Figure 7.

The good agreement with the data obtained by t.g.a. experiments can be seen by comparing Figure 7 with Figure 4 and Table 3. In both cases, the degradation began at 400°C and ended at about 650°C. The maximum rate of the production of volatile products was achieved at 520°C, which was about 25°C below the temperature at which 50% of the weight was lost (Table 3), but this temperature correlated very well with the inflexion point in the t.g.a. thermogram (Figure 4). This result indicates that the mechanisms of thermal degradation are the same in nitrogen and helium atmosphere.

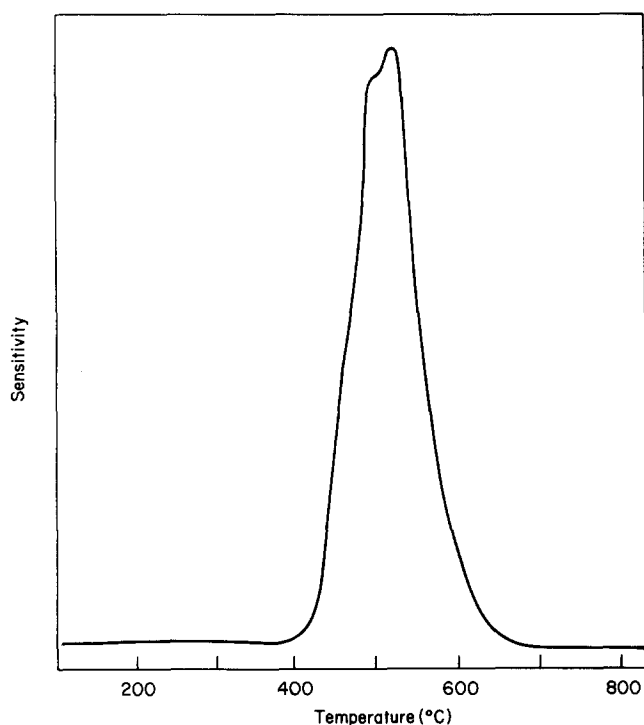


Figure 7 Formation of volatile degradation products during the pyrolysis of Polymer IA

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