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Pyrolysis–Molecular Weight Chromatography–Vapor-Phase Infrared Spectrophotometry: An On-Line System For Analysis of Polymers. III. Thermal Decomposition of Polysulfones and Polystyrene

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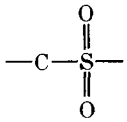
Synopsis

The thermal decomposition of poly(butene-1 sulfone), poly(pentene-1 sulfone), poly(hexene-1 sulfone), poly(styrene sulfone), and polystyrene was investigated in helium at a heating rate of 20°C/min using an experimental system which consists of a programmable pyrolyzer, a thermal conductivity detector, a mass chromatograph, and a vapor-phase infrared spectrophotometer. Poly(butene-1 sulfone), poly(pentene-1 sulfone), and poly(hexene-1 sulfone) displayed two-step decomposition; the primary products of decomposition at both steps were the comonomers (olefin and SO_2). For poly(styrene sulfone), in addition to styrene and SO_2, products with molecular weights corresponding to dimers of styrene were obesrved. Decomposition of this polymer was compared with that of polystyrene, which formed mostly monomer.

INTRODUCTION

The polysulfones examined for this report provided an example of the systematic variation of molecular structure as an aid to characterization of products of thermal degradation using a new experimental pyrolysis system.[1,2] Application of the pyrolysis system to the thermal degradation of polyethylene, polypropylene, and polyisobutylene formed the subject matter of a previous communication.[3]

The structures of the polysulfones which were investigated are shown in Table I. They contain



$$-\mathrm{C}-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{\mathrm{S}}}-$$

in the polymer backbone. The bond dissociation energy for the C—S bond (55–60 kcal/mole) is appreciably lower than for the C—C bond (80–85 kcal/mole) and the C—H bond (90–100 kcal/mole).[4] Consequently, initiation of thermal decomposition in the polysulfones would be expected to occur readily by scission of the C—S bond.

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EXPERIMENTAL

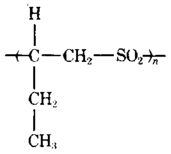
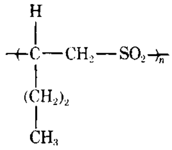
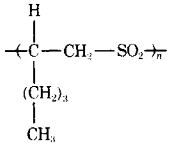
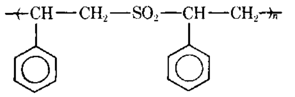
Description of the Pyrolysis System

Details of the experimental system which consists of a programmable pyrolyzer, a thermal conductivity detector, a mass chromatograph, and a fast-scan vapor-phase infrared spectrophotometer have been provided.[1,2]

The thermal conductivity detector permits monitoring the formation of volatile decomposition products and in so doing facilitates their selective trapping. In the mass chromatograph, two independent gas-chromatographic systems using two different carrier gases (such as CO_2 and monochloropentafluoroethane, ClC_2F_5) are coupled through a common injection port. Thus, when a sample is introduced to this instrument, it is split into two approximately equal fractions and analyzed by the matched chromatographic systems. The constituents eluting from the columns are detected by gas density balance detectors which respond to the difference between the molecular weight of the carrier gas and that of solute. The mass chromatograph gives two simultaneous sets of gas-chromatographic peaks. The ratio of a peak in one set to its counterpart in the other is related to the molecular weight of the constituent which is responsible for the particular peaks through

$$M_x = \frac{\left(\frac{A_1}{A_2}\right) K M_{c2} - M_{c1}}{\left(\frac{A_1}{A_2}\right) K - 1}$$

TABLE I
Synthesis of Olefin–SO_2 Copolymers

Polysulfone	Structure	Solvent	Initiator	Temp., °C	Conversion, %
Butene-1	 $-\!\!\left(\mathrm{CH}(\mathrm{CH_2CH_3})-\mathrm{CH_2}-\mathrm{SO_2}\right)_n\!-$	SO_2	AIBN[a]	40–45	41
Pentene-1	 $-\!\!\left(\mathrm{CH}((\mathrm{CH_2})_2\mathrm{CH_3})-\mathrm{CH_2}-\mathrm{SO_2}\right)_n\!-$	SO_2	AIBN	40	56.6
Hexene-1	 $-\!\!\left(\mathrm{CH}((\mathrm{CH_2})_3\mathrm{CH_3})-\mathrm{CH_2}-\mathrm{SO_2}\right)_n\!-$	SO_2	t-BHPO[b]	−30	80
Styrene		SO_2	AIBN	25	57.5

[a] AIBN = Azobisisobutyronitrile.
[b] *t*-BHPO = *t*-Butyl hydroperoxide.

M_x, M_{c_1}, and M_{c_2}, are the molecular weights of the unknown, carrier gas 1, and carrier gas 2, respectively; A_1 and A_2 are the chromatographic peak areas for the unknown constituent, and K is an instrument constant determinable from analyses of samples of known molecular weight. Thus, the mass chromatograph separates constituents in the decomposition mixture and permits computation of their molecular weights. (A theoretical development of the gas density balance and of its operational relationships in the mass chromatograph has been published.[5]) Effluents from the mass chromatograph are further analyzed using a fast-scan vapor-phase infrared spectrophotometer which produces spectra "on the fly" as the vapors elute from the mass chromatograph.

Helium was used, at a flow rate of 20 ml/min, as the carrier gas for the pyrolyzer. Carbon dioxide and monochloropentafluoroethane (du Pont, Freon-115) were the carrier gases used in the mass chromatograph. The two matched chromatographic columns of the mass chromatograph were stainless steel (⅛ in. × 12 ft) packed with 10% silicone gum SE-30 on 60/80 mesh Chromosorb W-AW. The column flow rates were 10 ml/min. The flow rates of the reference gases in the gas density balance detectors were 41 ml/min for Freon-115 and 100 ml/min for CO_2. The temperatures of the thermal conductivity cell, the gas density balance detectors, and the infrared sample cell oven were maintained at 230°, 242°, and 240°C, respectively. The transfer lines from the pyrolyzer to the mass chromatograph and that from the mass chromatograph to the infrared spectrophotometer were maintained at 300° and 240°C, respectively. The gas density balance detector currents were set at 100 mAmp.

Calibration of the mass chromatograph was performed by analyzing a synthetic mixture containing 15 known saturated normal hydrocarbons (C_5 to C_{28}). The instrument constant was evaluated from peak height ratios (Freon-115/CO_2 response ratios) at 5°C/min, which was found suitable for separation of decomposition products. In the molecular weight region below and above the molecular weight of monochloropentafluoroethane (154.46), K was found to be 0.206 and 0.189, respectively.

The infrared unit was coupled with the CO_2 exit of the mass chromatograph.

In addition to the thermal conductivity cell response, thermal histories before and during pyrolysis were determined using a thermogravimetric analyzer (du Pont 950) and a differential thermal analyzer (du Pont 900) at 20°C/min heating rate in an atmosphere of flowing nitrogen.

A 5- to 10-mg sample of each polymer was pyrolyzed in helium by program heating at 20°C/min. The response from the thermal conductivity cell during pyrolysis was compared with the results of thermogravimetric and differential thermal analyses. Volatile products formed in the temperature range of 100° to 500°C were trapped and analyzed by the mass chromatograph. These results are shown in Figures 1 through 4 and 6 through 9 and in Tables III through VII.

Synthesis of Poly(olefin Sulfones)

The poly(olefin sulfones) were prepared at temperatures from −30° to 45°C with excess sulfur dioxide (generally ⅓ mole ratio olefin/SO_2) as reaction solvent

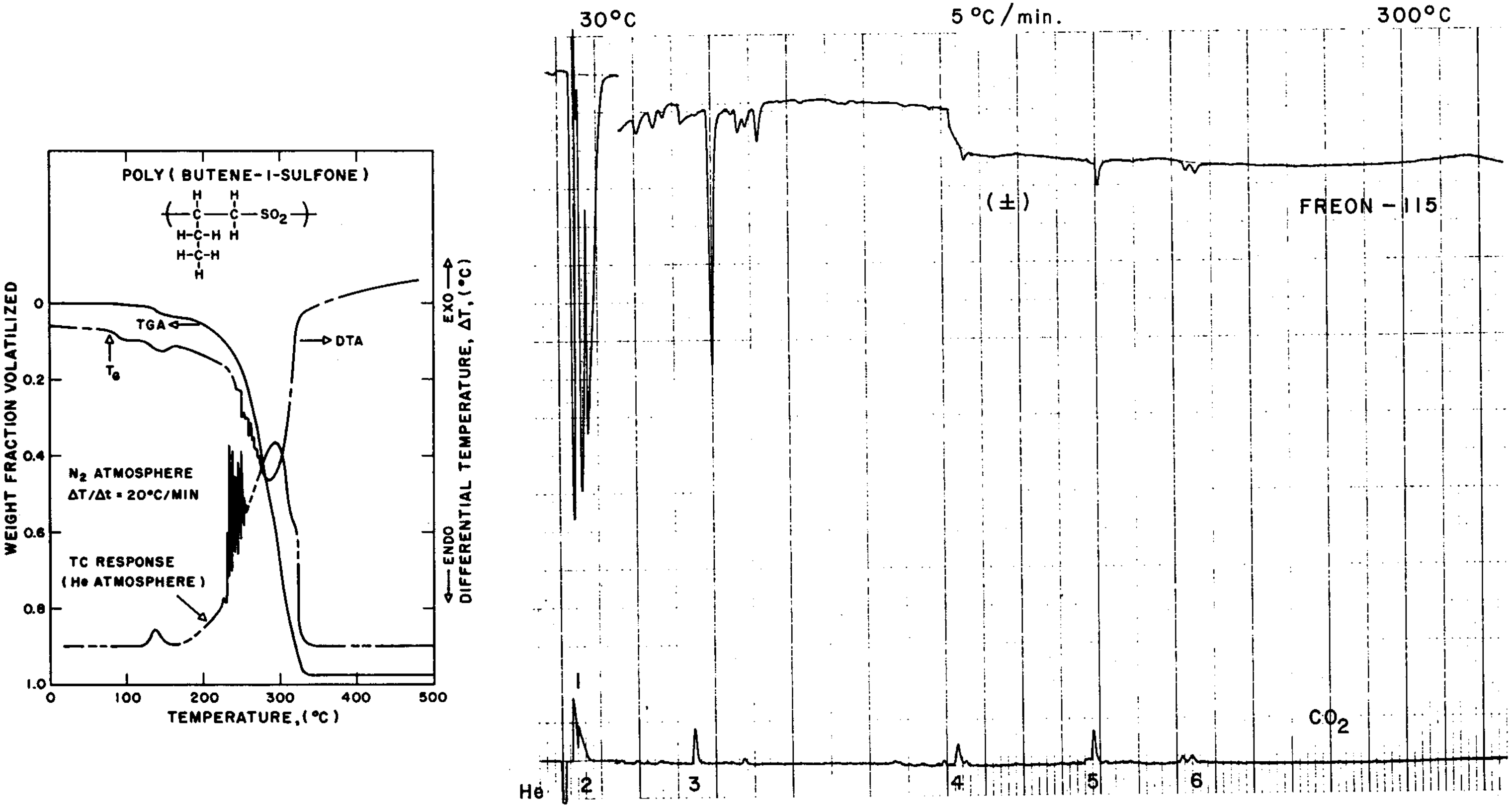


Fig. 1. Left: Thermal history before and during pyrolysis of poly(butene-1 sulfone). Right: Mass chromatogram of pyrolysis products of poly(butene-1 sulfone). Columns (SE-30) were program heated (at 5°C/min) from 30° to 300°C. In both channels, peak attenuations were ×256 for peaks 1 and 2 and ×16 thereafter. The symbol ± indicates the location at which the polarity of the Freon-115 detector was reversed. Molecular weights (calculated from peak height ratios) are tabulated in Table III. (Detector responses for peaks 1 and 2, the major products, were beyond the dynamic range of the detector.)

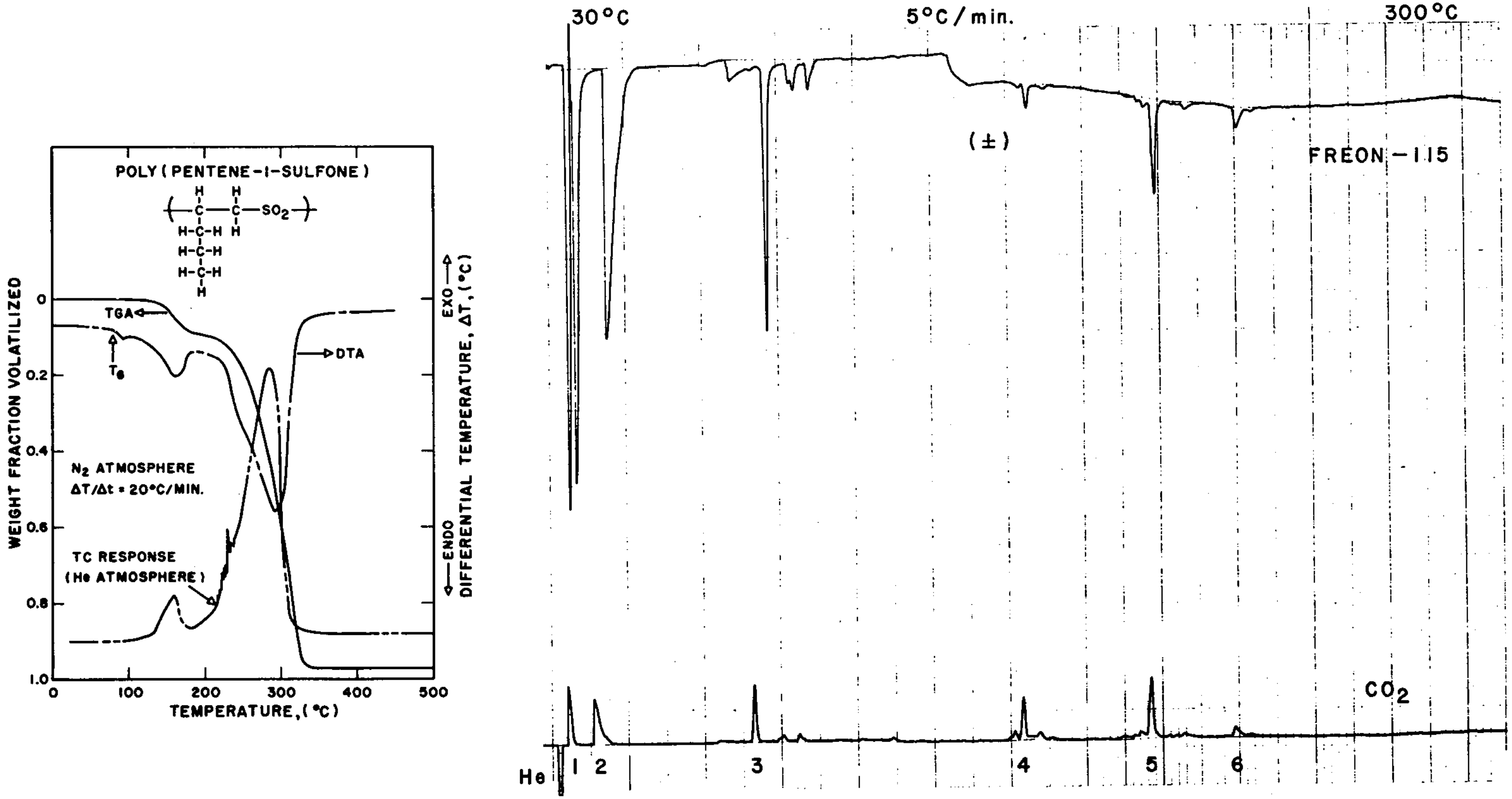


Fig. 2. Left: Thermal history before and during pyrolysis of poly(pentene-1 sulfone). Right: Mass chromatogram of pyrolysis products of poly(pentene-1 sulfone). Columns (SE-30) were program heated (at 5°C/min) from 30° to 300°C. In both channels, peak attenuations were ×256 for peaks 1 and 2 and ×16 thereafter. The symbol ± indicates the location at which the polarity of the Freon-115 detector was reversed. Molecular weights (calculated from peak height ratios) are tabulated in Table IV. (Detector responses for peaks 1 and 2, the major products, were beyond the dynamic range of the detector.)

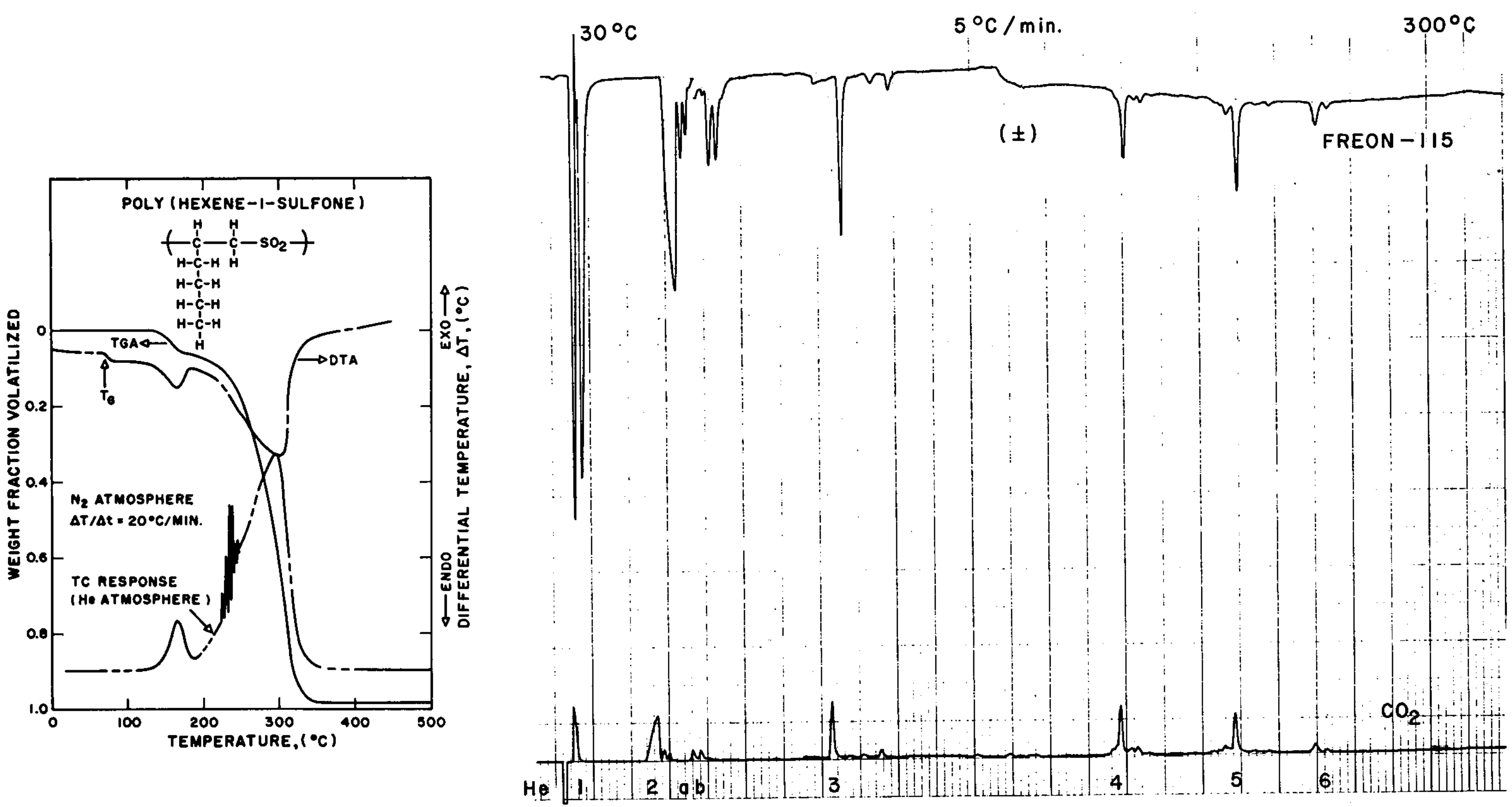


Fig. 3. Left: Thermal history before and during pyrolysis of poly(hexene-1 sulfone). Right: Mass chromatogram of pyrolysis products of poly(hexene-1 sulfone). Columns (SE-30) were program heated (at 5°C/min) from 30° to 300°C. In both channels, peak attenuations were ×256 for peaks 1 and 2 and ×16 thereafter. The symbol ± indicates the location at which the polarity of the Freon-115 detector was reversed. Molecular weights (calculated from peak height ratios) are tabulated in Table V. (Detector responses for peaks 1 and 2, the major products, were beyond the dynamic range of the detector.)

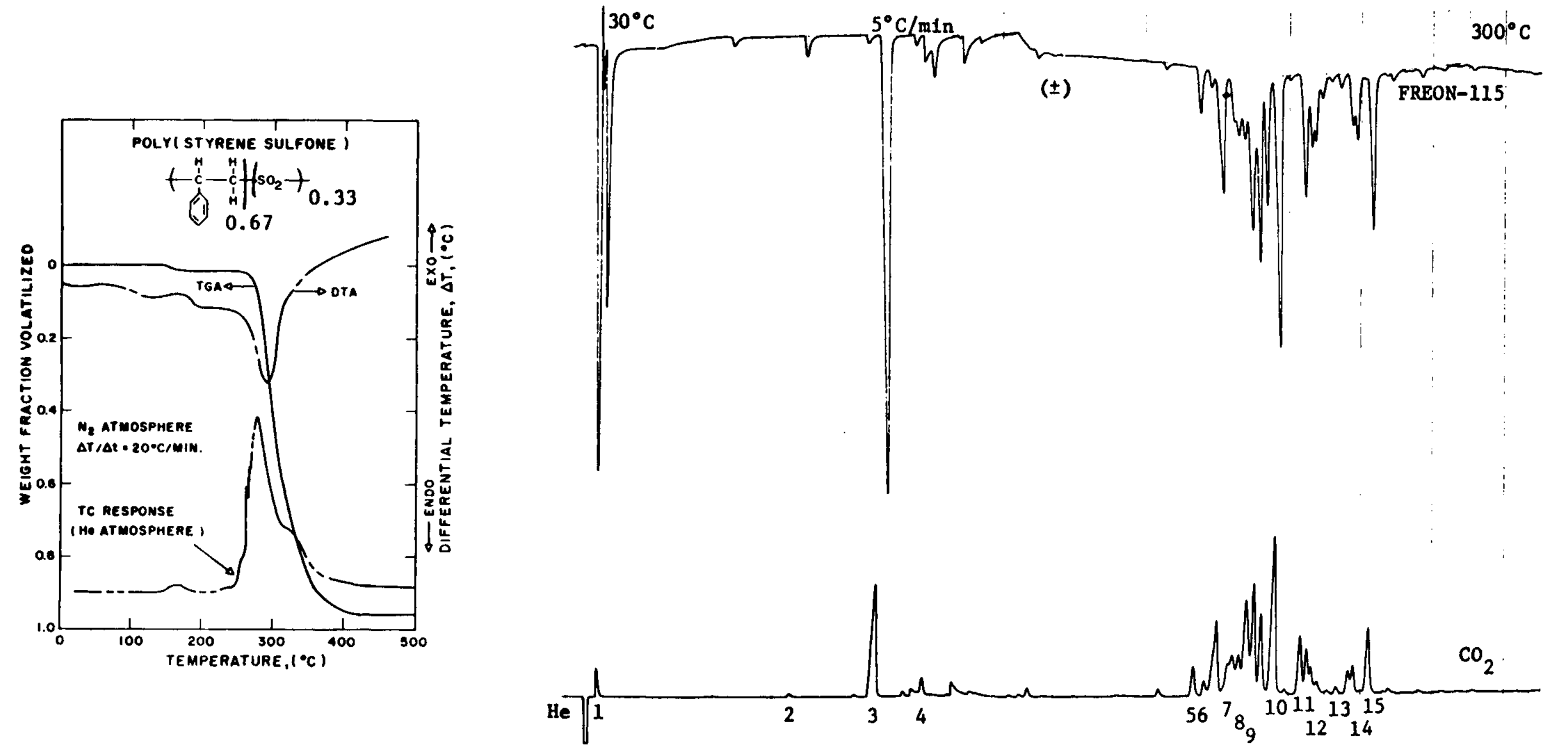


Fig. 4. Left: Thermal history before and during pyrolysis of poly(styrene sulfone). Right: Mass chromatogram of pyrolysis products of poly(styrene sulfone). Columns (SE-30) were program heated (at 5°C/min) from 30° to 300°C. In both channels, peak attenuations were ×256 (peak 1), ×32 (peaks 2 and 3), and ×16 thereafter. The symbol ± indicates the location at which the polarity of the Freon-115 detector was reversed. Molecular weights (calculated from peak height ratios) are tabulated in Table VI. (Detector response for peak 1 was beyond the dynamic range of the detector.)

TABLE II
Molecular Weight Characteristics of Olefin–SO_2 Copolymers

Polysulfone	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_v$	$[\eta]$, dl/g
Butene-1	528,100	76,400	6.91	1,080,000	0.78[a]
Pentene-1	—	—	—	—	1.49[a]
Hexene-1	560,300	270,700	2.07	611,500	1.00[b]
Styrene	675,100	119,500	5.65	366,000	1.01[c]

[a] Acetone solvent at 25°C.
[b] Benzene solvent at 25°C.
[c] Chloroform solvent at 25°C.

and *t*-butyl hydroperoxide or azobisisobutyronitrile as the initiator (see Table I). Olefins (>99% purity) were reacted without further purification with anhydrous sulfur dioxide in a 1-liter stainless steel Parr stirring-type autoclave after flushing the vessel with nitrogen. All polymerizations were carried out from 15 to 24 hr. Work-up of the polymer reactions involved allowing excess sulfur dioxide (which evolved on warming) to pass through a caustic scrubber, dissolving the polymers in appropriate solvents, and precipitating the products from cold hexane or methyl alcohol with high-speed agitation. Repeated precipitations were used to obtain polymers of high purity. The products were dried 24–48 hr at 45–50°C under vacuum.

The isolated polymers were white powders. Elemental analysis supported a 1/1 olefin/SO_2 ratio for the butene-1, pentene-1, and hexene-1 polysulfones and a 2/1 composition for poly(styrene sulfone). IR and NMR spectra were consistent with the assigned structures (Table I).

Molecular weight distributions and molecular weight averages (number and weight averages) were obtained with a modified Waters Associates GPC 200 gel permeation chromatograph (Table II). The chromatograph was run at ambient temperatures. Polymer solutions of 0.10% to 0.15% w/v concentration were prepared in chloroform stabilized with Ionol (125 mg/l.) (Shell Chemical Antioxidant No. 29, di-*t*-butylcresol). The solutions were filtered through a 1.5-μ Millipore filter prior to their injection into the chromatograph. These precautions were necessary to prevent plugging of the chromatograph columns.[6] Flow rates of 1ml/min $CHCl_3$ were used through the columns packed with 10^6, 10^5, 10^4, 10^3, 250, and 50 Å polystyrene. $\bar{M}_w$ and $\bar{M}_n$ values corresponding to chain-extended molecular sizes based on polystyrene were determined by a computer-programmed analysis of the chromatograms.

TABLE III
Decomposition Products of Poly(butene-1 Sulfone)

Peak no.	A_1/A_2[a]	Calculated MW	Compound with comparable MW Structure (MW)
1			sulfur dioxide (64)
2			butene $[C_4^=]$ (56)
3	−7.32	88.3	$[C_4^=][S]$ (88)
4	−0.5	144.1	$[C_4^=]_2[S]$ (144)
5	0.75	173.8	$[C_4^=]_2[S][O]_2$ or $[C_4^=]_2[S]_2$ (176)
6	1.27	189.3	$[C_4^=]_2[S][O]_3$ or $[C_4^=]_2[S]_2[O]$ (192)

[a] Response ratio, Freon-115/CO_2.

TABLE IV
Decomposition Products of Poly(pentene-1 Sulfone)

Peak no.	A_1/A_2[a]	Calculated MW	Compound with comparable MW Structure (MW)
1			sulfur dioxide (64)
2			pentene $[C_5^=]$ (70)
3	−4.75	99.9	$[C_5^=][S]$ (102)
4	0.56	167.5	$[C_5^=]_2[S]$ (172)
5	1.56	200.6	$[C_5^=]_2[S][O]_2$ or $[C_5^=]_2[S]_2$ (204)
6	1.88	215.3	$[C_5^=]_2[S][O]_3$ or $[C_5^=]_2[S]_2[O]$ (220)

[a] Response ratio, Freon-115/CO_2.

Intrinsic viscosities (dl/g) (Table II) were measured at 25°C with a Bausch and Lomb Fica "Viscomatic" automatic viscometer. Viscosity-average molecular weight calculations ($\bar{M}_v$) were made using the K and a values for the Mark-Houwink equation reported for these polysulfones.[7,8]

RESULTS AND DISCUSSION

Aliphatic Polysulfones

The major products of pyrolysis of poly(butene-1 sulfone), poly(pentene-1 sulfone), and poly(hexene-1 sulfone) were sulfur dioxide and the respective olefins. The vapor-phase infrared spectra of these major constituents, taken as they eluted from the CO_2 channel of the mass chromatograph, are shown in Figure 5 (which includes the spectrum of CO_2 for purposes of comparison).

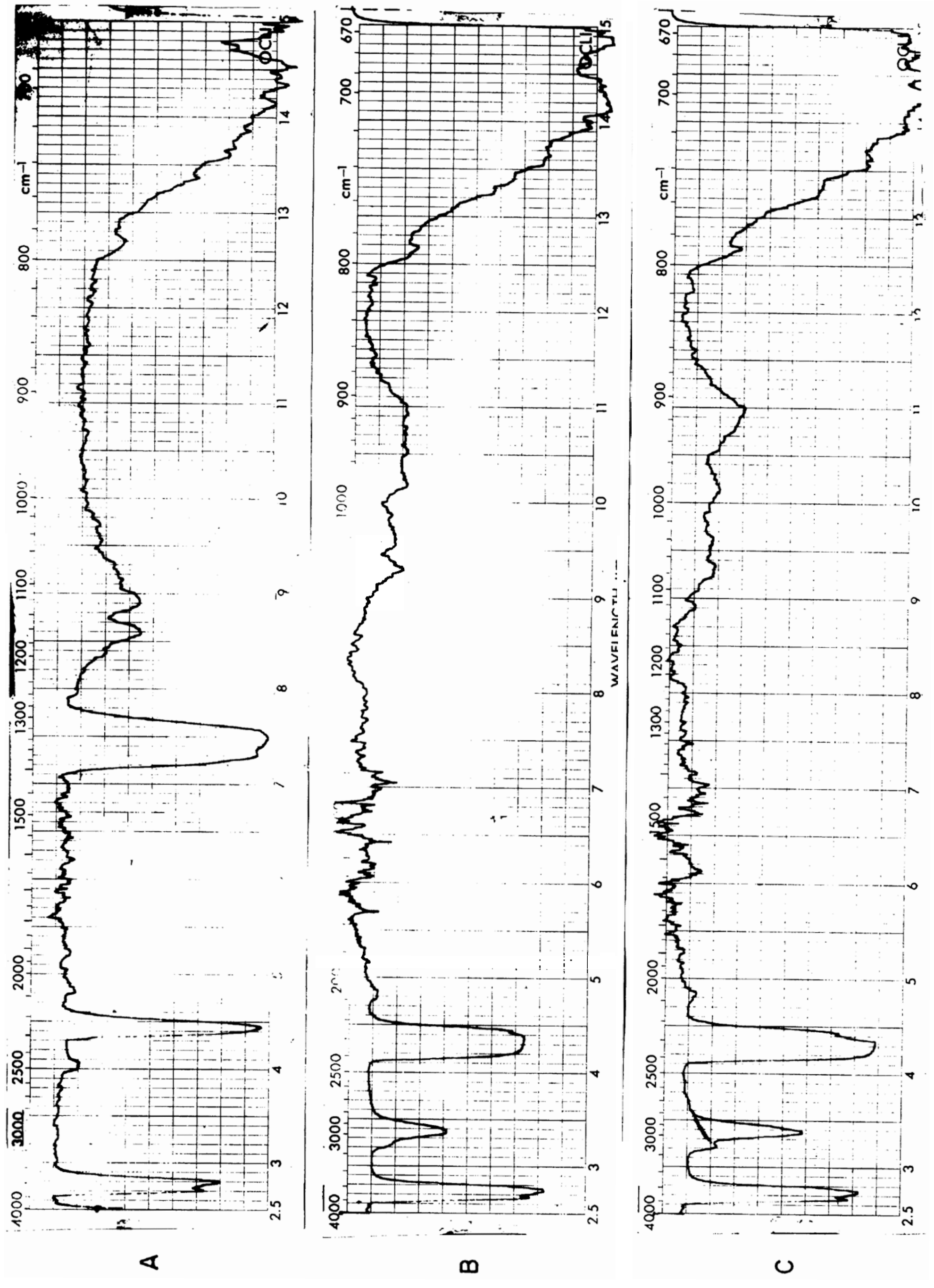
That the main decomposition products from sulfone polymers are sulfur dioxide and olefin has been reported for different pyrolysis conditions.[9,10] However, the chromatograms (Figs. 1–3) of poly(butene-1 sulfone), poly(pentene-1 sulfone), and poly(hexene-1 sulfone) reveal, in addition to sulfur dioxide and the olefins (peaks 1 and 2), four additional constituents in relatively small amounts (peaks 3, 4, 5, and 6) that have not been reported previously. They are characteristic of each pyrogram and follow an interesting pattern.

For comparison, the CO_2 channel of each of the mass chromatograms of the pyrolysis products of these polymers is reproduced in Figure 6. As seen in this figure, in going from one chromatogram to the next, except for the SO_2 peak, the location of the other peaks (peaks 2 through 6) shifts to higher retention times.

TABLE V
Decomposition Products of Poly(hexene-1 Sulfone)

Peak no.	A_1/A_2[a]	Calculated MW	Compound with comparable MW Structure (MW)
1			sulfur dioxide (64)
2			hexene $[C_6^=]$ (84)
a	−7.53	87.3	hexane (86)
b	−7.62	86.9	
3	−2.85	113.6	$[C_6^=][S]$ (116)
4	1.41	194.6	$[C_6^=]_2[S]$ (200)
5	2.21	233.6	$[C_6^=]_2[S][O]_2$ or $[C_6^=]_2[S]_2$ (232)
6	2.4	246.1	$[C_6^=]_2[S][O]_3$ or $[C_6^=]_2[S]_2[O]$ (248)

[a] Response ratio, Freon-115/CO_2.


A
B
C
cm−1
4000
3000
2500
2000
1500
1300
1200
1100
1000
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2.5
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14
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OCL
WAVELENGTH

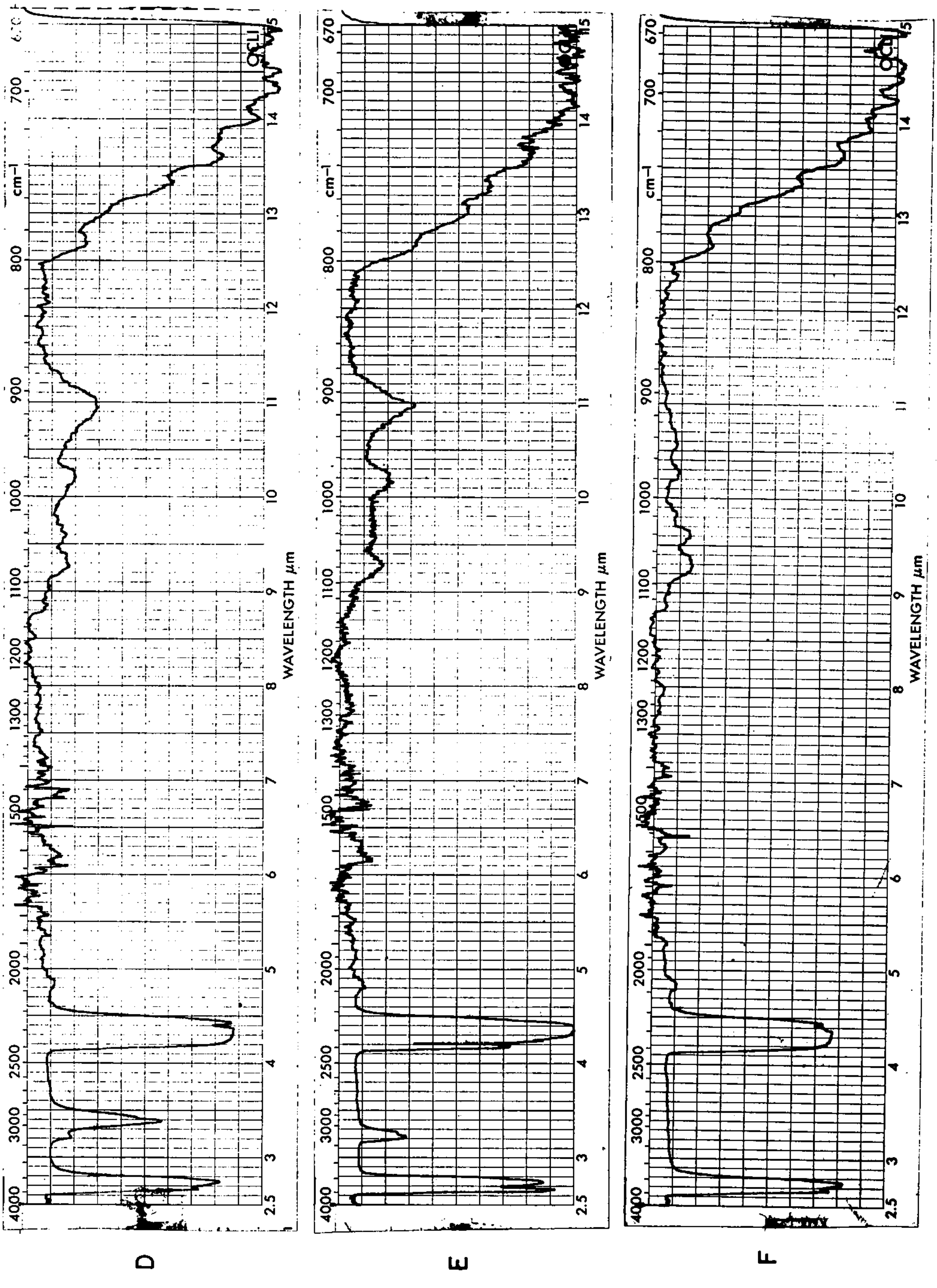
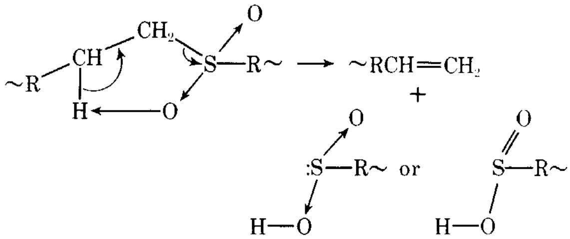


Fig. 5. Vapor-phase infrared spectra in CO_2 carrier gas of the major products of pyrolysis of the sulfone polymers: A, peak 1 in Figs. 1–4 (sulfur dioxide); B, peak 2 in Fig. 1 (1-butene); C, peak 2 in Fig. 2 (1-pentene); D, peak 2 in Fig. 3 (1-hexene); E, peak 3 in Fig. 4 (styrene); F, CO_2 carrier gas (included for comparison). (The spectra are 6-sec scans, except for E, which is a 30-sec scan.)

Furthermore, it is interesting to note the incremental increases in the molecular weights in going from peak 3 to peak 4, from 4 to 5, and from 5 to 6. In each chromatogram, the following trends are present: (1) The difference between the molecular weights of constituents 3 and 2 is equal to 32. (2) The difference between the molecular weights of constituents 4 and 3 is equal to the molecular weight of constituent 2. (3) The difference between the molecular weights of constituents 5 and 4 is 32. (4) The difference in molecular weights between constituents 6 and 5 is 16.

Since the atomic weights of sulfur and oxygen are 32 and 16, respectively, some compositional possibilities for the constituents which are revealed by peaks 3 through 6 are provided in Tables III–V.

Studies on the thermal decomposition of polysulfones of the type $\left[(CH_2)_m SO_2 \right]_n$, where $m = 4, 6$, and 8, at 275°C under reduced pressure show that the volatile decomposition products from these polymers consist of large proportions of sulfur dioxide and unsaturated hydrocarbons, and minor proportions of water, hydrogen, and carbon dioxide.[11] Their formation was explained according to a mechanism whereby the initiation of decomposition involves a β-elimination reaction of the type

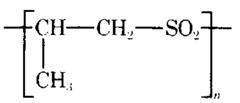


The sulfinic acids then decompose to give radicals and sulfur dioxide:

$$\sim\!RSOOH \rightarrow \sim\!R\cdot + SO_2 + H\cdot$$

The final products presumably form by reaction of these radicals with polymer chains via intra- and intermolecular hydrogen transfer processes.

This type of initiation, along with direct cleavage of the C—S bond, may also be operative in the present system and account for the major products. However, it is not easy to deduce mechanisms that account for the formation of products with the compositions proposed for the constituents corresponding to peaks 3 to 6 (Fig. 6, Tables III–V). Their formation must involve a number of steps, one step possibly being some destruction of SO_2 in the presence of free radicals. The possibility of destruction of SO_2 was also noted in a study[12] of the thermal decomposition in nitrogen at 280°–290°C of poly(propylene sulfone):



$$\left[\begin{array}{l} CH-CH_2-SO_2 \\ | \\ CH_3 \end{array}\right]_n$$

which is an example of the type of aliphatic polysulfone studied herein.

An examination of the results of thermogravimetric and differential thermal analyses as well as the responses of the thermal conductivity cell during pyrolysis indicates that the sulfone polymers undergo a two-step degradation process, initial degradation occurring in the temperature range 100° to 200°C and major degradation taking place at higher temperatures.

The present experimental system is well suited for selective trapping of volatile

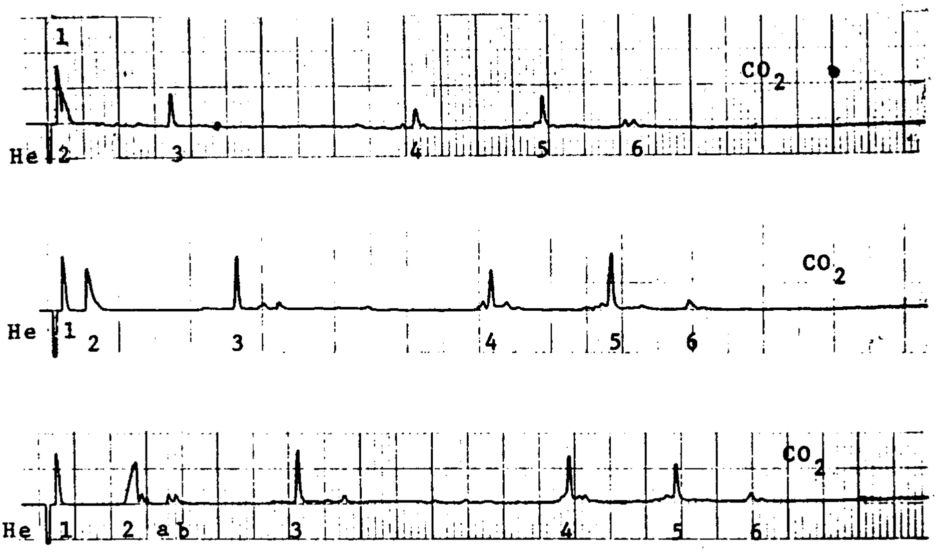
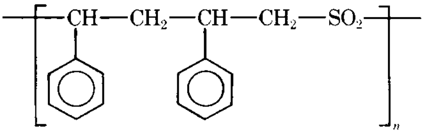


Fig. 6. Comparison of the CO_2 channel of the mass chromatogram of pyrolysis products of poly(butene-1 sulfone) (top), poly(pentene-1 sulfone) (middle), and poly(hexene-1 sulfone) (bottom). (See Figs 1 through 3 for other details.)

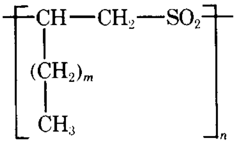
decomposition products which form in different temperature intervals. Figure 7 presents a comparison of the products of pyrolysis formed in the temperature range of 100° to 500°C with the products of pyrolysis formed in the initial decomposition stage 100° to 250°C from poly(pentene-1 sulfone), poly(hexene-1 sulfone), and poly(styrene sulfone). Only sulfur dioxide and the olefin are formed in the initial degradation regime of the aliphatic polysulfones. For poly(styrene sulfone), the initial weight loss is small (compare Fig. 4 with Figs. 1–3), and no sulfur dioxide, styrene, or other characteristic constituents could be detailed (see Fig. 7).

Poly(styrene Sulfone)

The thermal breakdown pattern for poly(styrene sulfone) is displayed in Figure 4. In the complexity of the mass chromatogram, this polymer differs markedly from the other polysulfones. Products with molecular weights in the range of dimers of styrene are observed in addition to the characteristic sulfur dioxide and styrene peaks. The different behavior of poly(styrene sulfone) in comparison with other polysulfones can be attributed in part to the styrene-to-sulfur dioxide mole ratio being 2/1, whereas the ratio in the other polysulfones was 1/1. The observation that no trimers of styrene are formed upon degradation of poly(styrene sulfone) and that no dimers of olefins are detected among the decomposition products of the other polysulfones indicates that



and



$$\left[-CH(-(CH_2)_m-CH_3)-CH_2-SO_2-\right]_n$$

are the repeat units of these polysulfones, respectively, (see Table I).

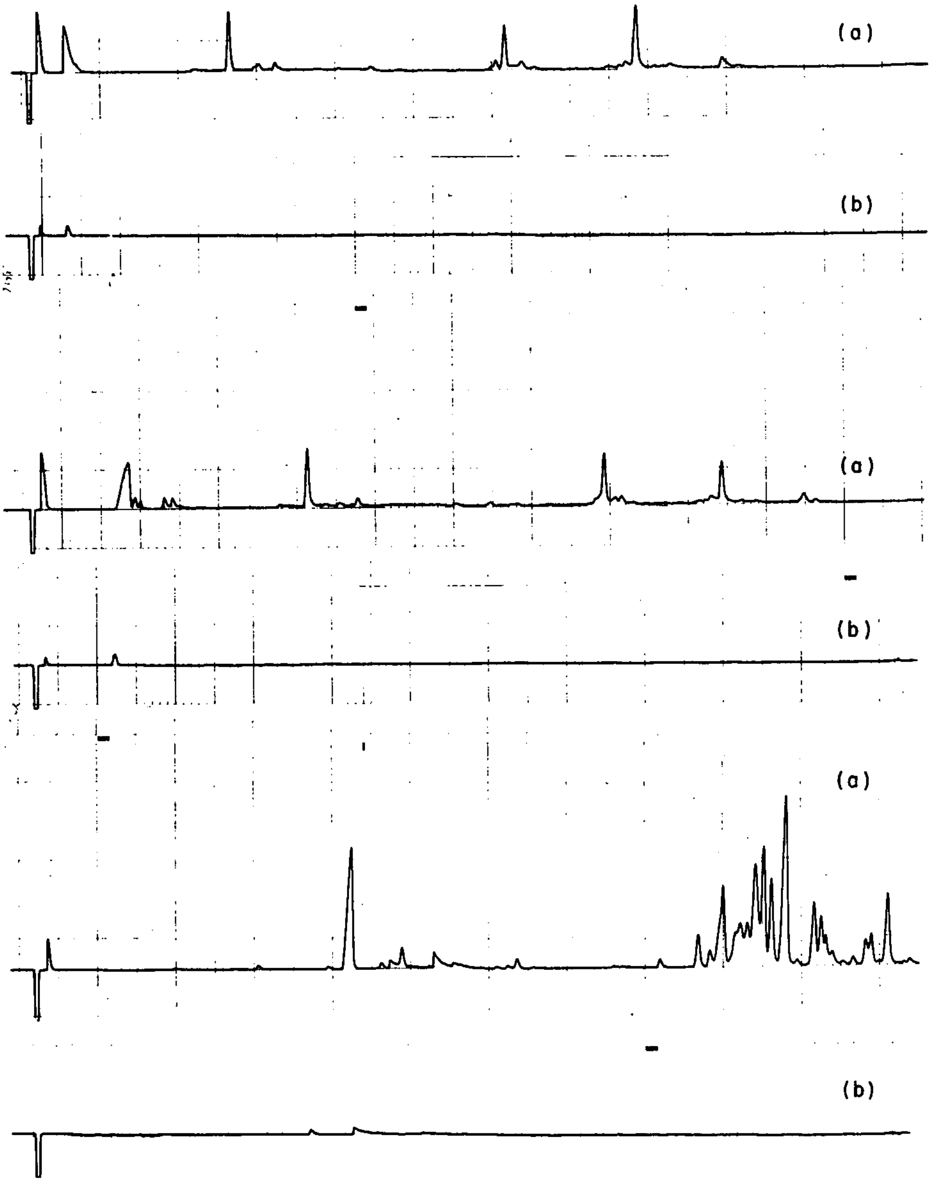


Fig. 7. Comparison of products of pyrolysis formed in the temperature range of 100° to 500°C (a), with the products of pyrolysis formed in the initial decomposition stage 100° to 250°C (b), for poly(pentene-1 sulfone) (top), poly(hexene-1 sulfone) (middle), and poly(styrene sulfone) (bottom). Only the CO_2 channels of the mass-chromatographic analyses are presented. (See also Figs. 2 through 4).

In a previous study,[13] two samples of poly(styrene sulfone), one with composition 2/1 and the other with 1/1 for the ratio styrene/SO_2, were pyrolyzed using a filament pyrolyzer at 600°C and also at 890°C. The constituents were analyzed by gas chromatography. Whereas the products of decomposition from the 1/1 sample were simply SO_2 and styrene, the 2/1 sample gave additional fragments derived from styrene dimers. The chromatogram reported for the 2/1 sample

TABLE VI
Decomposition Products of Poly(styrene Sulfone)

Peak no.	A_1/A_2[a]	Calculated MW	Compound with comparable MW Structure (MW)
1			sulfur dioxide (64)
2	−6.0	93.4	toluene (92)
3	−4.04	104.3	styrene (104)
4	−2.19	120.1	α-methylstyrene (118)
5	1.46	196.6	1,3-diphenylpropane (196)
6	1.54	199.8	
7	1.62	203.2	2,4-diphenyl-1-butene (208)
8	1.67	205.4	
9	1.60	202.4	
10	1.71	207.2	
11	2.10	227.1	
12	1.60	202.4	
13	2.26	236.8	
14	2.19	238.7	
15	2.33	241.3	$[\phi C\text{-}C\text{-}C\phi\text{-}C^{=}][S]$ (240)

[a] Response ratio, Freon-115/CO_2.

is similar to that shown in Figure 4. The same trends were also observed for pyrolysis at 350°C in the vacuum chamber of a field ion mass spectrometer.[10,14] From the 2/1 sample, in addition to light gases, sulfur dioxide, and styrene, fragments with mass numbers 118, 196, 204, 205, 206, 207, 208, 209, 215, 236, and 239 were observed. The fragments with mass numbers 204, 206, 208, and 236 were of higher intensity. These are in good agreement with the molecular weights calculated from Figure 4 (see Table VI). These high molecular weight fragments must have formed from the styrene–styrene segments of the chain. It is, therefore, a natural extension to study the thermal degradation of a homopolymer of styrene. This is discussed in the next section.

Polystyrene

A sample of polystyrene (atactic, $\bar{M}_w$ = 310,000, $\bar{M}_w/\bar{M}_n$ = 1.78) was pyrolyzed at 20°C/min heating rate from room temperature, and the fragments generated in the temperature range of 300° to 600°C were trapped and analyzed by the mass chromatograph. The results are shown in Figure 8 and Table VII.

As in the case of polyolefins,[3,15] the shape of the chromatogram is suggestive of a homologous series of compounds. Indeed, constituents with molecular weights comparable to those of monomer, dimers, and trimers of styrene are observed. The large proportion of styrene formed indicates that depolymerization is the major process of decomposition in polystyrene.

A free-radical mechanism of decomposition has been shown[15] to predict constituents with molecular weights comparable to those calculated for the additional peaks observed in Figure 8. The constituents with molecular weights around 208 correspond to the dimers of styrene. At least four different dimers are observed in Figure 8. In a previous study employing capillary gas-chromatographic columns, about 20 compounds of the formula $C_{16}H_{16}$ (dimeric styrene of molecular weight 208) were detected.[16] In another study[10] using a mass

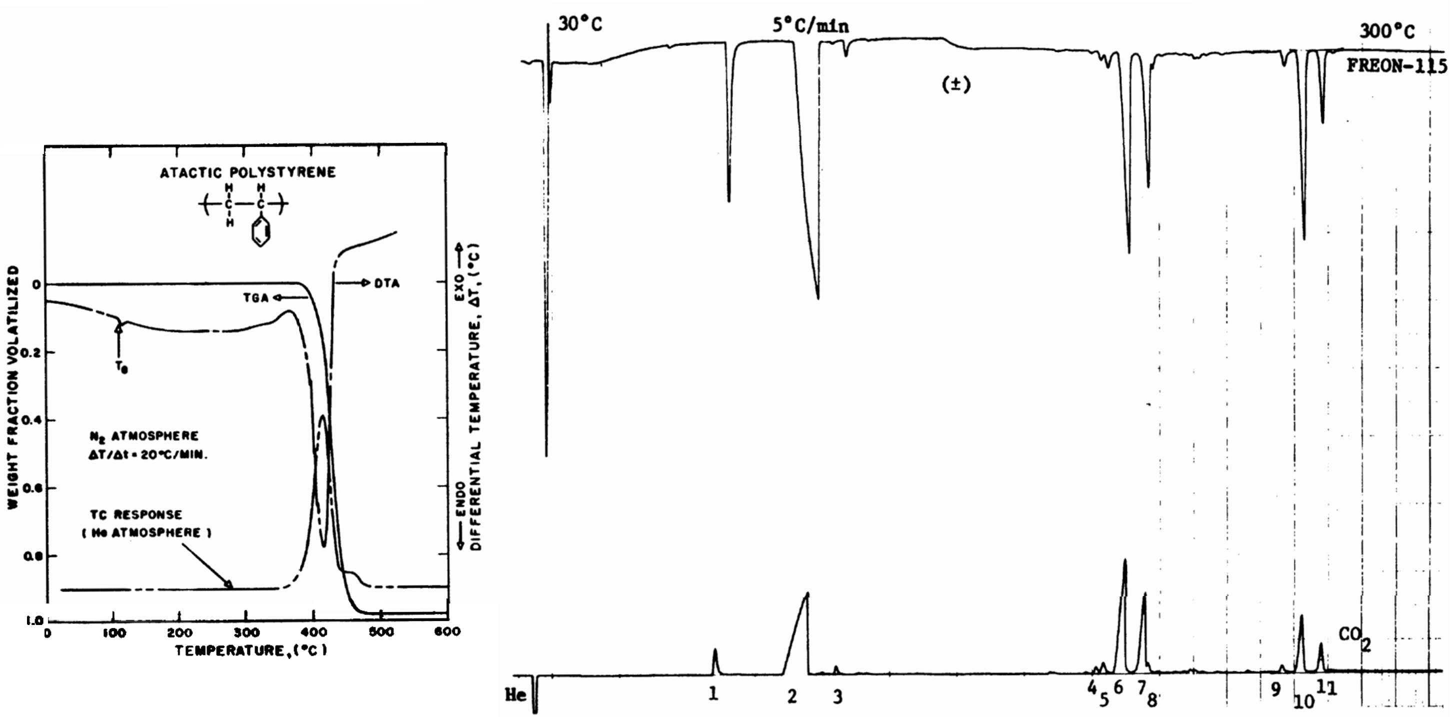


Fig. 8. Left: Thermal history before and during pyrolysis of atactic polystyrene. Right: Mass chromatogram of pyrolysis products of polystyrene. The columns (SE-30) were program heated (at 5°C/min) from 30° to 300°C. In both channels, peak attenuations were ×16 (peak 1), ×128 (peak 2), ×16 (peak 3), and ×32 thereafter. The symbol ± indicates the location at which the polarity of the Freon-115 detector was reversed. Molecular weights (calculated from peak height ratios) are tabulated in Table VII. (Detector response for peak 2, the major product, was beyond the dynamic range of the detector.)

TABLE VII
Decomposition Products of Polystyrene

Peak no.	A_1/A_2[a]	Calculated MW	Compound with comparable MW Structure (MW)
1	−5.95	92.3	toluene (92)
2			styrene (104)
3	−2.21	119.0	α-methylstyrene (118)
4	1.5	198.1	1,3-diphenylpropane (196)
5	1.68	205.8	
6	1.75	209.0	2,4-diphenyl-1-butene (208)
7	1.68	205.8	
8	1.67	205.4	
9	2.07	225.4	2,4-diphenyl-1-pentene (222)
10	3.24	328.9	2,4,6-triphenyl-1-heptene (326)
11	2.43	248.2	

[a] Response ratio, Freon-115/CO_2.

spectrometer, constituents with mass number 204 were observed and were attributed to phenylnaphthalene, which is presumably formed by cyclization and dehydrogenation of the dimer.

That oligomers higher than the trimers of styrene are not observed in Figure 8 suggests that in the course of decomposition radical migration along the main chain in polystyrene is probably not as easy as in polyolefins.[3] This appears reasonable since the backbone chain in polystyrene is not as flexible (the bulky phenyl rings hinder local coiling for intramolecular radical transfer) and since the phenyl ring can provide resonance stabilization for the free radical and thereby further decrease the probability of transfer reactions. However, the absence of higher oligomers can also be simply due to boiling point limitations; they may have been retained in traps that cannot be heated above 250°C in the present system.

It is interesting to compare the chromatograms of polystyrene and poly(styrene sulfone). Figure 9 shows that for poly(styrene sulfone), many additional compounds in the molecular weight range of dimeric styrene (see Table VI) are formed. In contrast, no products with molecular weights comparable to that

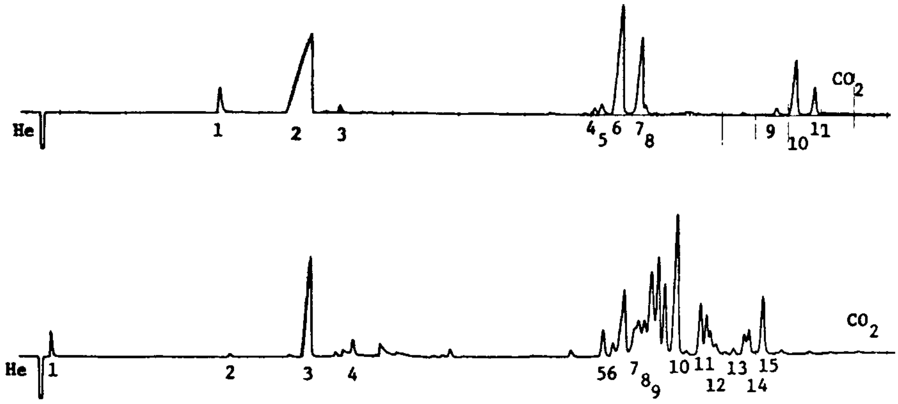


Fig. 9. Comparison of the CO_2 channel of the mass chromatogram of pyrolysis products of polystyrene (top) and poly(styrene sulfone) (bottom). (See Figs. 8 and 4 for details.)

of trimers of styrene are observed. These observations can be explained by proposing that in poly(styrene sulfone) with a 2/1 styrene/SO_2 ratio, the cleavage of C—S bonds results in styrene segments which are already in dimeric form. The dimer can then undergo rearrangement reactions of the type described in the literature[16] to form additional compounds with molecular weights similar to that of the dimer. It is not known at present if the dimeric segments formed upon cleavage of the C—S bonds in poly(styrene sulfone) combine and form tetramers of styrene; tetramers of styrene were not analyzable in the experimental system.

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