

Thermal Decomposition of Polysulfones*

ERIC WELLISCH, EDWARD GIPSTEIN, and ORVILLE J. SWEETING, *Packaging Division, Film Operations, Olin Mathieson Chemical Corporation, New Haven, Connecticut*

Synopsis

The thermal decomposition of the C₄, C₆, and C₈ polymethylene sulfones has been investigated at 275°C. under reduced pressure. The gaseous decomposition products, collected and identified by infrared and mass-spectrometer analysis, were found to consist primarily of sulfur dioxide, olefins, alkanes, water, and hydrogen. A mechanism is proposed in which the rate-determining step consists of a concerted attack of the sulfone group on the β -hydrogen atom with elimination resulting in α -olefins and a sulfinic acid. The sulfinic acid rapidly decomposes to give sulfur dioxide, hydrogen, and alkyl free radicals. The final products are formed by transfer and termination reactions of the free radicals and isomerization of the olefins in the presence of sulfur dioxide. Experimental evidence confirming this mechanism consists of rate studies of polymer decomposition whose initiation was found to be independent of polymer purity and of added free-radical initiators. A further proof of the rate-determining step was obtained by comparison of the decomposition products of bis-1,4-(butanesulfonyl)butane with those of structurally comparable sulfinic acids: 1,4-butanedisulfinic acid and 1-butanedisulfinic acid.

INTRODUCTION

Polysulfones prepared by the addition of sulfur dioxide to ethylene and other olefins, diolefins, and acetylenes decompose at or below their melting points to give olefins and sulfur dioxide; when heated at temperatures higher than room temperature, but still well below the melting point, a random degradation takes place which results in a large decrease in molecular weight.¹ The fact that random degradation of the polymer chain occurs at rather low temperatures is clearly shown for poly-1-butene sulfone. When this polymer was heated alone or in solution at 70°C., no appreciable loss in weight was noted, but the specific viscosity decreased. Illumination increased the decomposition as noted by a fall in viscosity, loss in weight, and the formation of sulfur compounds of low molecular weight. At 130°C. complete breakdown of the polymer to monomers occurred.

Naylor and Anderson have determined the apparent first-order rate constants for the thermal decomposition of various olefin polysulfones.² In

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these pyrolytic reactions, random cleavage of the polysulfones seemed to accompany the formation of monomer.

Polysulfones obtained from condensation reactions between dihalides and dimercaptans followed by oxidation³⁻⁵ or by free-radical-catalyzed addition of dimercaptans to diolefins^{6,7} have been described with four or more carbon atoms between the sulfone groups. Not much information is available concerning their thermal properties. Noether states⁵ that polytetramethylene sulfone decomposes near the melting point of 271°C., and that polyhexamethylene sulfone, m.p. 220°C., appears to be stable. Correlation of the thermal stabilities with the number of methylene groups in the polymer unit has not been thoroughly investigated.

EXPERIMENTAL

In the present investigation, we have studied the thermal behavior of polymethylene sulfones by identifying the decomposition products of tetramethylene, hexamethylene, and octamethylene sulfone polymers heated at 275°C. under vacuum in the absence of solvent.

Preparation of Polysulfones

The polymethylene sulfones were prepared by condensation of the corresponding dimercaptides and dihalides as carried out by Carothers³ and modified by Noether.^{4,5} All three polysulfones were purified by recrystallization from concentrated sulfuric acid. The polymers were dissolved at 40–70°C. and recovered by dilution with ice water. The polymers were then extracted with hot water in a Soxhlet extractor for 24 hr., washed with ether, and dried for 24 hr. at 100°C. under reduced pressure.

(a) Polytetramethylene sulfone, m.p. 265–269°C.; yield 73%.

ANAL. Calcd. for $(-C_4H_8SO_2-)_n$: C, 40.11%; H, 6.72%; S, 26.66%. Found: C, 39.63%; H, 6.63%; S, 25.58%.

(b) Polyhexamethylene sulfone, m.p. 212–215°C.; yield 84.5%.

ANAL. Calcd. for $(-C_6H_{12}SO_2-)_n$: C, 48.64%; H, 8.10%; S, 21.62%. Found: C, 48.05%; H, 8.30%; S, 22.03%.

(c) Polyoctamethylene sulfone, m.p. 199–204°C.; yield 76.7%.

ANAL. Calcd. for $(-C_8H_{16}SO_2-)_n$: C, 54.54%; H, 9.09%; S, 18.18%. Found: C, 54.77%; H, 9.44%; S, 18.17%.

Decomposition of Polysulfones

For decomposition, the polysulfones were weighed into tared Pyrex glass tubes (a glass-wool plug inserted to prevent mechanical loss during heating) and the sample tubes were attached to the vacuum system already described.⁸ The entire apparatus was evacuated to 0.05 mm. and the temperature of the sample was slowly raised to 275°C. and held for 1 hr. (Preliminary experiments at 30°C. above the melting point of each polymer had

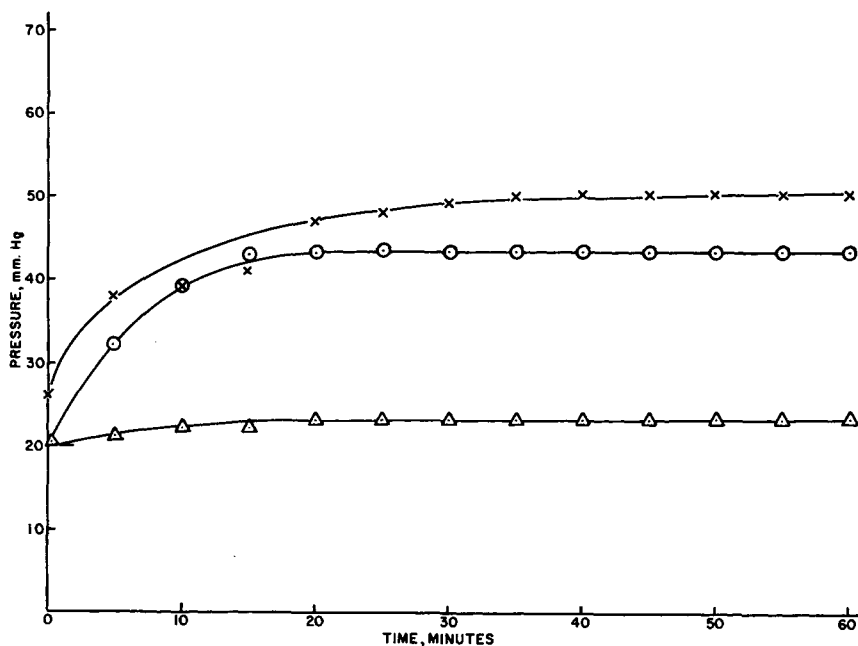


Fig. 1. Vapor pressure curves at 275°C. as a function of time for: (X) polytetramethylene sulfone; (O) polyhexamethylene sulfone; (Δ) polyoctamethylene sulfone.

TABLE I
Decomposition Products of Polymethylene Sulfones at 275°C. for 1 Hr.

Sulfone polymer	Decomposition, mole-% ^a	Sulfur dioxide, mole-% ^b	Other major products	Minor products
Tetramethylene	7.6	34	1,3-Butadiene, ethylene, <i>cis</i> -2-butene	Butane, H ₂ O, H ₂ , CO, CO ₂ , COS
Hexamethylene	4.8	72	Benzene, 1-hexene, 1,5-hexadiene, 1-octene	1-Butene, 1,3-butadiene, <i>cis</i> -2-butene, ethylene, H ₂ O, H ₂ , CO, CO ₂ , COS
Octamethylene	3.7	32	Benzene, ethylene, 1,3-butadiene, saturated and unsaturated C ₈ hydrocarbons	H ₂ O, H ₂ , CO, CO ₂ , COS

^a The decomposition in mole per cent is based on the weight loss of the sulfone during decomposition.

^b The mole per cent of sulfur dioxide was found from a calibration curve prepared from pure sulfur dioxide; it is based on the total amounts of decomposition products.

pointed to the choice of 275°C. for comparable studies of the three polymers.) Changes in pressure owing to decomposition as a function of time and temperature are shown in Figures 1 and 2. [Figure 2 includes the decomposition curve for a nonpolymeric model compound, bis(1,4-butane-sulfonyl)-butane, which will be discussed later.] At the completion of each run, the gaseous products were condensed into the cold finger of an infrared gas cell cooled with liquid nitrogen. The decomposition products were immediately investigated by infrared and mass spectrometry. The non-condensable gases were identified by mass spectrometer alone. The

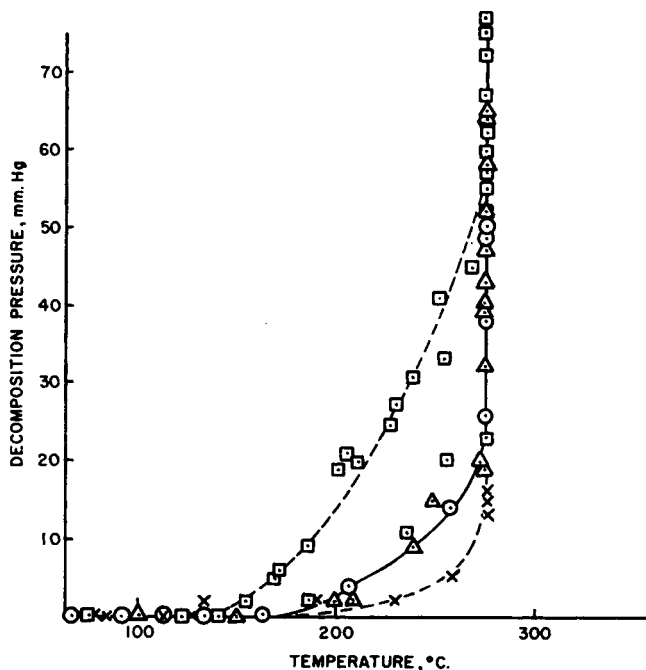


Fig. 2. Thermal decomposition of sulfones heated gradually from room temperature to 275°C. and held at that temperature for 1 hr.; (X) model compound; (O) tetramethylene sulfone; (Δ) hexamethylene sulfone; (□) octamethylene sulfone.

residues were weighed after decomposition and the percentage loss in weight was determined.

The decomposition results are shown in Table I. These data show that all of the polymers decomposed at 275°C. The tetramethylene sulfone polymer shows a maximum rate of decomposition, followed by the hexamethylene and octamethylene sulfone polymers in that order. Sulfur dioxide and olefins are the major decomposition products. Minor products are alkanes, water, hydrogen, carbon dioxide, carbon monoxide, and carbonyl sulfide. The methylene chains show a further breakdown and rearrangement indicative of a free-radical decomposition.

DISCUSSION OF RESULTS

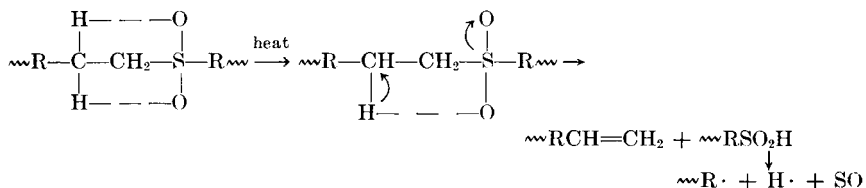
The major decomposition products of the C_4 , C_6 , and C_8 polymethylene sulfones under the defined experimental conditions are sulfur dioxide and C_n olefins. Minor products are other saturated and unsaturated hydrocarbons, hydrogen, water, carbon dioxide, carbon monoxide, and carbonyl sulfide. Benzene is formed in substantial quantity when the C_6 and C_8 polysulfones are further degraded.

In proposing a mechanism of polymer decomposition a number of facts and findings of other investigators must be considered. Carbon-sulfur scission alone cannot be considered the rate-determining step because the decomposition energy of the C—S bond of 65 kcal./mole gives a specific first-order rate constant much too small to account for the observed rapid rate of decomposition.⁹ Our experimental results indicate neither random degradation nor exclusive breaking of terminal C—S bonds, but rather some intermediate path. This is suggested by the fact that the decomposition pressure reaches a constant value rather than increasing with time (Fig. 2). A termination step or equilibrium condition is indicated.

Naylor and Anderson's degradation studies² of polymers of olefins and sulfur dioxide show decomposition rates which parallel the total number of hydrogen atoms on the β -carbon atoms, suggesting β -elimination as the rate-determining step. β -Elimination has been suggested as the rate-determining step in the decomposition of *tert*-butyl sulfoxide.¹⁰ The reaction involves a cyclic transition state in which the β -hydrogen forms a bond to the sulfonyl oxygen while at the same time the α -carbon-sulfur bond is broken.

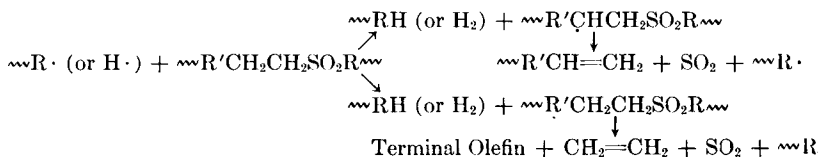
From these considerations and the decomposition products obtained, we suggest a mechanism of sulfone degradation initiated by a concerted attack of the sulfone group on the β -hydrogen atoms with elimination resulting in α -olefins and a sulfinic acid. The sulfinic acid then rapidly decomposes to sulfur dioxide and alkyl free radicals.⁸ Intermolecular or intramolecular hydrogen transfer then occurs to produce saturated or unsaturated hydrocarbons and hydrogen,¹¹ and more free radicals. Termination occurs by free-radical dimerization, or disproportionation, or reaction with sulfur dioxide. *cis*-2-Butene is formed by the isomerization of 1-butene in the presence of sulfur dioxide.¹² The minor carbonyl products and water are formed by oxidation-reduction side reactions which occur in the presence of free radicals and sulfur dioxide.^{1,13}

Initiation:

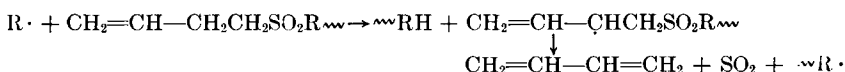


where R is an alkyl radical of an even number of carbon atoms.

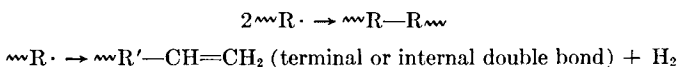
Propagation:



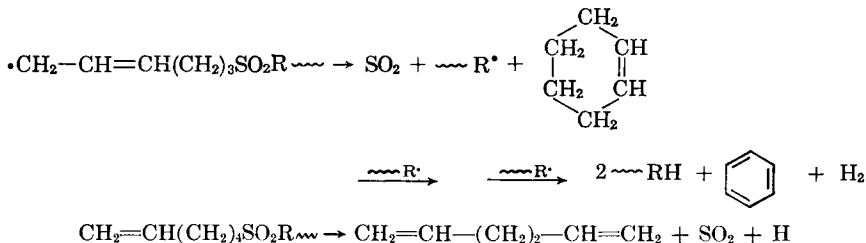
Transfer:



Termination:



The formation of all of the observed decomposition products can be explained by this mechanism. The production of benzene in the decompositions of hexamethylene and octamethylene polysulfones may be explained by hydrogen-transfer reactions which would also account for formation of 1,5-hexadiene.



Further Evidence Favoring the Proposed Mechanism

To confirm the free-radical participation in the propagation step of our mechanism the decomposition of hexamethylene sulfone polymer was carried out with a free-radical initiator, calcium peroxide, which decomposes at elevated temperatures to calcium oxide and oxygen atoms. The products were compared with the results of a decomposition experiment without initiator.

The addition of 5% calcium peroxide to the polymer somewhat increased the decomposition as measured by weight loss from 7.2% (for a control experiment) to 8.5% and resulted in large amounts of ethylene as the major decomposition product in addition to sulfur dioxide; benzene was now only a minor product.

These results support the proposed mechanism which predicts an increased amount of ethylene at the expense of benzene and hexamethylene fragments. The relatively small increase in weight loss indicates only a minor contribution, if any, to the primary rate of decomposition by the peroxide in addition to the major effects on the decomposition products by secondary reactions.

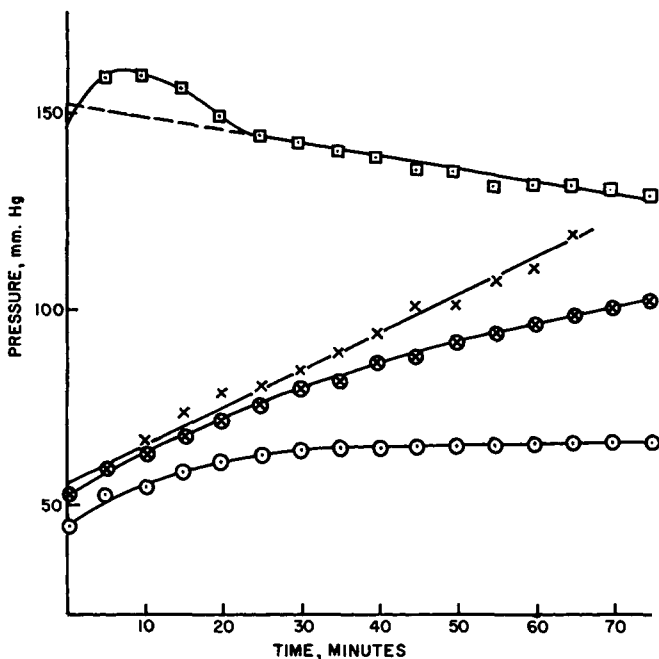


Fig. 3. Variation in decomposition rate of polyhexamethylene sulfone with different treatments prior to heating at 275°C.: (○) standard; (⊗) purified with sulfuric acid; (×) treated with sodium *m*-cresoxide; (□) with calcium peroxide added.

In these decompositions, polymer impurities, or bromine atoms at the end of a chain may contribute to the decomposition in the rate-determining step, or they may participate only in secondary reactions. To answer this question, polyhexamethylene sulfone was treated with sodium *m*-cresoxide in *m*-cresol solvent at 100°C. for 4 hr. to react with the bromine ends. The decomposition of the cresol-treated polymer is compared in Figure 3 with that of a polymer purified by treatment with sulfuric acid, an unpurified polymer, and a polymer treated with calcium peroxide.

Decomposition pressures decrease with time with calcium peroxide addition, increase with purification by *m*-cresoxide or sulfuric acid and level off for a standard decomposition. These results may be ascribed to recombinations of sulfur dioxide with the olefinic products. Thus a steady state results as the rate of recombination becomes equal to the rate of decomposition. A pressure decrease is caused by the large amount of ethylene formed by secondary decomposition and its recombination with sulfur dioxide. On the other hand, increased pressure results when pretreatment of the polymer reduces the amount of olefinic products without affecting the first-order decomposition. Impurities present in small amounts seem, therefore, not to influence the rate of decomposition. They cause only a further breakdown of the primary decomposition products to give more olefin by secondary reactions.

To evaluate the mechanism further, a prototype dimeric sulfone, bis-1,4-(butanesulfonyl)butane of the same skeletal structure as the repeat unit of tetramethylene sulfone polymer, was prepared by condensation of 1-bromobutane with dipotassium 1,4-butanedisulfinate¹⁴ in dimethylformamide and pyrolyzed. The identity of this new compound was confirmed by infrared and elementary analysis.

ANAL. Calcd. for $C_{12}H_{26}O_4S_2$: C, 48.32%; H, 8.71%; S, 21.40%. Found: C, 48.21%; H, 8.66%; S, 21.00%.

This sulfone was found to decompose only 0.77% at 275°C. to give sulfur dioxide, 1-butene, and *cis*-2-butene as primary products and 1,3-butadiene, ethylene, butane, water, and hydrogen as secondary products. These are the products predicted by the mechanism already outlined. Thus, bis-1,4-(butanesulfonyl)butane decomposes initially via 1,4-butanedisulfinic acid or 1-butanedisulfinic acid to yield products similar to the decomposition products reported previously for these sulfinic acids.*

All of these results are consistent with a view that the mechanism of sulfone decomposition is by β -elimination resulting in terminal olefins and a sulfinic acid. The sulfinic acid rapidly decomposes to give sulfur dioxide, hydrogen atoms, and alkyl free radicals. The final decomposition products are then formed by transfer and termination reactions of the free radicals and by isomerization of the olefinic products in the presence of sulfur dioxide. The minor carbonyl products and water are formed by oxidation-reduction side reactions in the presence of free radicals and sulfur dioxide.

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Résumé

La décomposition thermique des polyméthylènes sulfones en C_4 , C_6 et C_8 a été étudiée à 275°C sous pression réduite. Les produits de décomposition gazeux, recueillis et identifiés par analyse infrarouge et par spectrométrie de masse sont constitués principalement de SO_2 , d'oléfine, d'alcane, d'eau et d'hydrogène. On propose un mécanisme dans lequel l'étape déterminante de vitesse consiste en une attaque concertée du groupe

sulfone sur l'atome d'hydrogène en bêta, suivie d'élimination avec formation d'oléfines- α et d'acide sulfinique. Cet acide sulfinique se décompose rapidement en anhydride sulfureux, hydrogène et radicaux libres alkyles. Les produits finaux sont issus des réactions de transfert et de terminaison des radicaux libres ainsi que de l'isomérisation des oléfines en présence l'anhydride sulfureux. Une confirmation expérimentale de ce mécanisme est fournie par des études sur la vitesse de décomposition des polymères, réaction dont l'initiation est indépendante de la pureté du polymère et de l'addition d'initiateurs de réaction radicalaire. On a obtenu une preuve supplémentaire concernant l'étape déterminante de vitesse par comparaison des produits de décomposition du bis-1,4-(butanesulfonyl) butane avec ceux d'acides sulfiniques de structure comparable: l'acide 1,4-butanedisulfinique et l'acide 1-butanedisulfinique.

Zusammenfassung

Die thermische Zersetzung von C_4 -, C_6 - und C_8 -Polymethylensulfonen unter vermindertem Druck bei 275° wurde untersucht. Die gasförmigen Zersetzungsprodukte wurden gesammelt und durch infrarotund massenspektrometrische Analyse identifiziert. Sie bestehen hauptsächlich aus Schwefeldioxyd, Olefinen, Alkanen, Wasser und Wasserstoff. Es wird ein Mechanismus vorgeschlagen, in welchem als geschwindigkeitsbestimmender Schritt ein Angriff der Sulfongruppe auf das β -Wasserstoffatom gleichzeitig mit einer Eliminierung unter Bildung von α -Olefinen und einer Sulfinsäure auftritt. Die Sulfinsäure zerfällt rasch in Schwefeldioxyd, Wasserstoff und Alkylradikale. Die Endprodukte entstehen durch Übertragungs- und Abbruchsreaktionen der Radikale und Isomerisierung der Olefine in Gegenwart von Schwefeldioxyd. Dieser Mechanismus wird experimentell durch Untersuchungen über die Geschwindigkeit der Polymerzerstörung gestützt, deren Start von der Reinheit des Polymeren und von zugesetzten radikalischen Startern unabhängig ist. Als weiterer Beweis für den geschwindigkeitsbestimmenden Schritt wird der Vergleich der Zersetzungsprodukte von Bis-1,4-(butansulfonyl)-butan mit denjenigen der strukturell vergleichbaren Sulfinsäuren 1,4-Butandisulfinsäure und 1-Butansulfinsäure angesehen.

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