

Volatile Combustion Products of Polycarbonate and Polysulfone

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Synopsis

Thermal analysis of polycarbonate and polysulfone has shown each plastic to undergo a two-step decomposition, the first step involving production of high-boiling chain scission and volatile products, the second resulting, in addition, in production of large amounts of carbon dioxide and carbon monoxide. Ten to fifteen volatile products of each plastic have been quantitatively analyzed under several combustion conditions and also in several temperature ranges chosen on the basis of TGA curves. Polycarbonate products include a moderate amount of methane, small amounts of other aliphatic hydrocarbons through C₅, methanol, acetaldehyde, and several aromatics. Volatile products account for 40-60% of polycarbonate, with phenol and substituted phenols predominating in the large amount of liquid residue formed during chain scission. Polysulfone produces very similar hydrocarbon products as well as sulfur dioxide, which accounts for 85-96% of the sulfur of the plastic, and carbonyl sulfide, which was only detectable during the temperature range 490°-550°C. Volatile products account for 50-60% of polysulfone.

INTRODUCTION

Polycarbonate and polysulfone are specialty thermoplastics developed primarily for their good thermal stability and other properties such as high strength and clarity. Their diverse applications include electronic components, aircraft parts, and food containers.¹ Formulas of the polymers are shown in Figure 1. Although not high-volume plastics such as poly(vinyl chloride) or polyethylene, their combustion products are of interest because they contribute to the overall solid waste disposal problem and also to the toxicity of combustion products of accidental fires in buildings or aircraft.

EXPERIMENTAL

Three polycarbonate and two polysulfone samples were obtained, all in commercial pellet form. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) in helium and air were used to determine the types of reactions occurring on breakdown and the temperature ranges over which these reactions take place. The experimental procedure² for collection and analysis of combustion products and its application to poly(vinyl

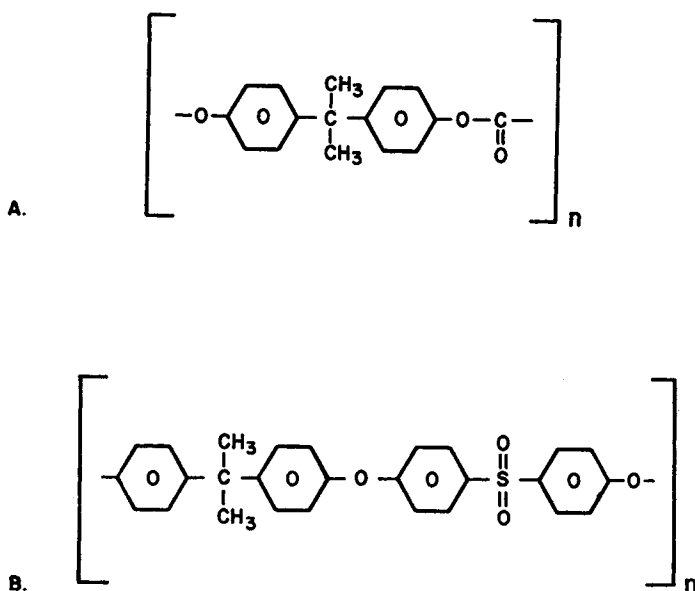


Fig. 1. (A) Bisphenol A-polycarbonate; (B) bisphenol A-polysulfone.

chloride)³ and poly(phenylene oxide)⁴ have been described previously. A 1-g plastic sample is placed in the 1-in.-diameter Vycor gas-tight core of a small combustion furnace. A measured flow of air or air plus oxygen is passed through the combustion tube which is heated rapidly to a temperature 50–100°C below the decomposition temperature of the plastic under study, and then heated to 1000°C at a programmed rate from 5°–50°C per minute.

In choosing air supplies for the study, a compromise had to be made between efficiency of combustion and excessive dilution of minor products. Products of complete combustion would be mainly carbon dioxide, water, and sulfur compounds from polysulfone. Less efficient conditions would surely yield a more realistic picture of the products from an accidental fire and also from municipal incinerators, since these are often poorly designed or operated leading to temperature zones and varying degrees of combustion. A rough calculation for polycarbonate, 76% carbon, assuming the carbon is available to react with oxygen between 500° and 1000°C when heated at 5°C/min, shows that a 100 cc/min air supply would just be sufficient to convert all the carbon to carbon dioxide. This, of course, is deficient because not all the oxygen is in the immediate vicinity of the plastic and thus available for reaction as it flows through the tube. The lowest air supply chosen was 100 cc/min. A mixture of air and oxygen equivalent to about three times this supply was also used.

Volatile products were collected in a Saran bag attached to the end of the combustion tube while higher-boiling products condensed in the cool end of the tube or bag on leaving the heating zone. Attempts to account for the

considerable amount of liquid residue produced by combustion of either polycarbonate or polysulfone by weighing combustion tube and bag or by washing out the residue with solvent proved exceedingly inaccurate, so the amount of residue was determined by difference from volatile products.

Products were separated for qualitative analysis by gas chromatography, collected individually, and identified by mass spectrometry. A 6-ft column of Porapak Q at 100°C was used to separate low-boiling compounds, and a 3-ft Carbowax 20M column, for higher-boiling compounds. Most products were also quantitated by gas chromatography. Carbon dioxide, carbon monoxide, and carbonyl sulfide were quantitated by infrared spectrophotometry, and sulfur dioxide, by both infrared and ultraviolet spectrophotometry.⁵ Water was observed in both the volatile products and liquid residue of each plastic, but was not quantitated. Lack of a heated inlet system and sufficient resolution on our small mass spectrometer limited analyses to compounds boiling below about 130°C.

RESULTS AND DISCUSSION

Thermal Analysis

DTA records in helium and air of one polycarbonate sample are shown in Figure 2. Although this plastic is observed to melt in a combustion furnace at about 370°C, no melting endotherms are evident. Small endotherms at 475°C are the first significant features of the DTA records, followed by much stronger endotherms at 520°C. Many volatile and high-boiling products can be collected at temperatures corresponding to these two endotherms. Above 520°C, the reactions are strongly exothermic in air due in part to formation of carbon monoxide and carbon dioxide, and less strongly exothermic in helium. DTA records of the other two poly-

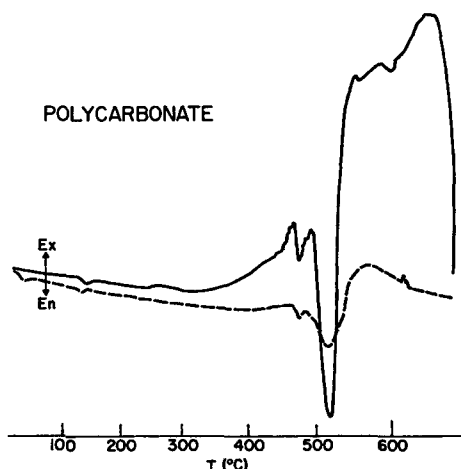


Fig. 2. DTA records of polycarbonate heated at 10°C/min in helium (broken curve) and air (smooth curve).

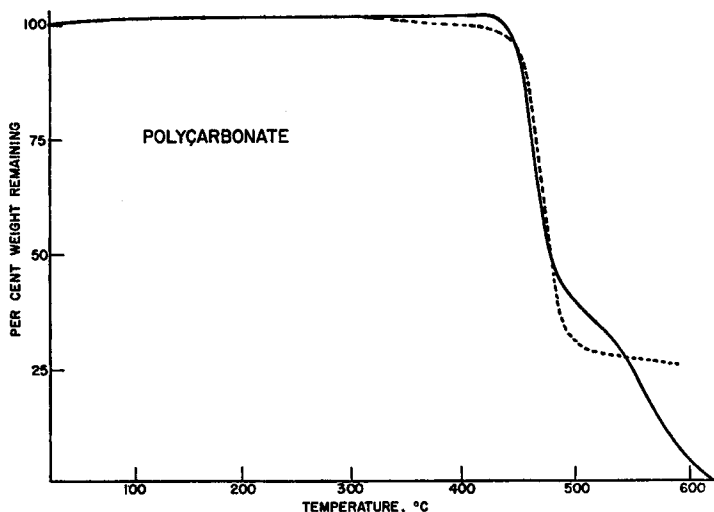


Fig. 3. TGA records of polycarbonate heated at 5°C/min in helium (broken curve) and air (smooth curve).

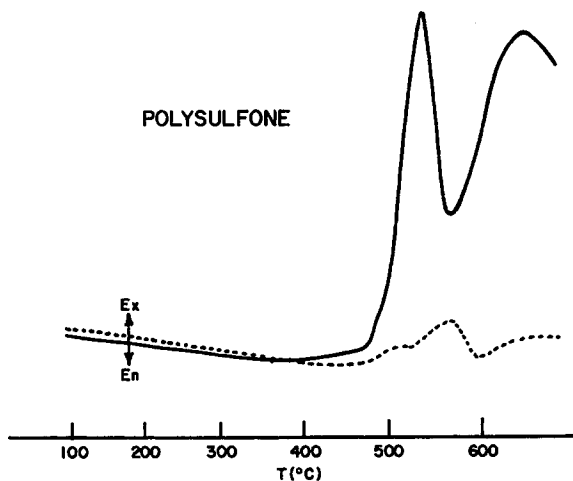


Fig. 4. DTA records of polysulfone heated at 10°C/min in helium (broken curve) and air (smooth curve).

carbonate samples were very similar, except for weaker 520°C endotherms in air.

TGA records of another polycarbonate sample are shown in Figure 3. In helium, a one-step degradation is observed with a 75% weight loss between 420° and 520°C. The plastic also begins to break down at 420°C in air, losing approximately 55% of its weight by 480°C. Another 17% of the weight is lost more gradually between 480° and 545°C, with the remaining 28% lost by 600°C. Thus, the 75% weight loss occurring in one step in

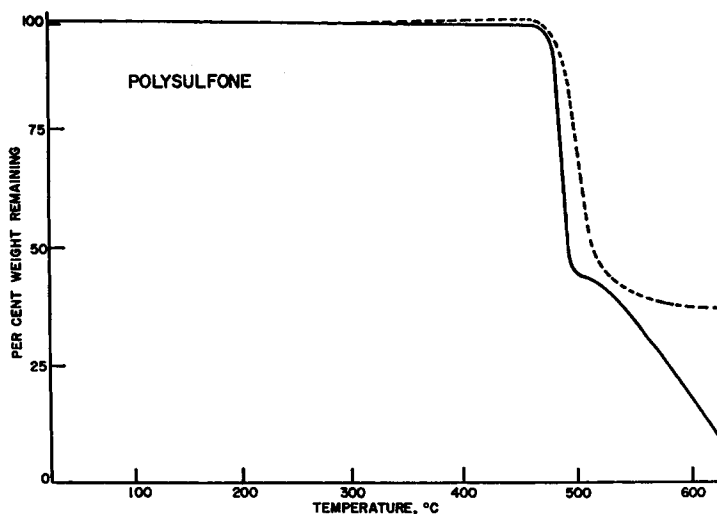


Fig. 5. TGA records of polysulfone heated at 5°C/min in helium (broken curve) and air (smooth curve).

helium occurs in two steps in air, indicating somewhat different reaction mechanisms.

Several studies of the mechanism of degradation of polycarbonate have been published. Davis and Golden have shown that thermal degradation in vacuo occurs by random chain scission,⁶ and if volatile products are continuously removed, the polymer is rapidly crosslinked to form a gel.⁷ Lee⁸ has proposed schemes for the decomposition based on products identified at 475°C under vacuum and in air, but pointed out that above 450°C a complicated mixture of reactions is rapidly taking place.

DTA records of a polysulfone sample are shown in Figure 4. This plastic is liquid by 350°C, but no melting endotherms are evident. The only significant features of either curve are two exothermic peaks at 535° and 645°C in air, both corresponding to temperatures where production of volatile and nonvolatile products is rapidly occurring. Polysulfone TGA records are shown in Figure 5. In helium, there is a 62% weight loss between 460° and 520°C, while in air, a 55% weight loss occurs more rapidly between 460° and 500°C. The remaining 45% of the weight in air is lost much more gradually above 510°C. Davis⁹ has shown that crosslinking is an important factor in polysulfone degradation, although chain scission is also involved.

Qualitative and Quantitative Analysis

Table I lists quantities of combustion products (in milligrams per gram of plastic) of polycarbonate under several combustion conditions. Quantities of products were so similar for the three polycarbonates tested that results were averaged. Standard deviations were calculated which include

TABLE I
Combustion Products of Polycarbonate at Several Combustion Conditions

Air flow, cc/min	100		100		100	
Oxygen flow, cc/min	0		40		0	
Heating rate, °C/min	5		5		50	
Carbon dioxide	1146	± 157	747	± 36	991	± 34
Carbon monoxide	395	± 36	425	± 34	76	± 12
Methane	27.2	± 1.0	9.5	± 1.6	25.9	± 0.20
Ethylene	1.57	± 0.27	1.31	± 0.16	2.94	± 1.67
Ethane	0.92	± 0.08	0.80	± 0.02	0.99	± 0.11
Propylene	0.82	± 0.33	0.56	± 0.12	1.24	± 0.81
Propane	0.23	± 0.11	0.14	± 0.04	0.25	± 0.14
Methanol	1.48	± 0.18	1.89	± 0.32	1.07	± 0.11
Acetaldehyde	0.72	± 0.38	0.90	± 0.41	0.58	± 0.34
1-Butene	0.26	± 0.12	0.20	± 0.07	0.56	± 0.38
Butane	0.08	± 0.07	0.05	± 0.05	0.09	± 0.08
Benzene	1.97	± 0.08	2.48	± 0.69	3.75	± 0.22
Toluene	1.10	± 0.12	1.31	± 0.22	3.33	± 0.25
Ethylbenzene	0.67	± 0.18	0.69	± 0.03	1.90	± 0.15
Styrene	0.10	± 0.03	0.10	± 0.01	0.31	± 0.02
% Plastic accounted for	60		49		43	
% Residue (by difference)	40		51		57	

in this case differences between the three plastics as well as experimental error and the randomness of the combustion process. One sample contained some filler material which contributed excess hydrocarbons, so the averages for some minor products are weighted toward that sample. Where deviations are larger than 25%, such as for propylene and butane, that sample is responsible. Carbon monoxide, carbon dioxide, and methane are the major volatile products. The latter two show significant decreases in the presence of excess oxygen, perhaps because the run with added oxygen had a 40% higher flow rate resulting in gases being swept out of the heating zone faster with less opportunity for secondary reactions to occur. The faster heating rate allows most of the reaction with oxygen to occur at higher temperatures and thus favors production of carbon dioxide over carbon monoxide. Aliphatic hydrocarbons are present in amounts which decrease with chain length. The unsaturated aliphatic is consistently present in greater amount than the corresponding saturate. Relatively small amounts of volatile aromatic hydrocarbons were detected. This may be due to the fact that the large amount of liquid residue consists of phenol and substituted phenols into which the lower-boiling aromatics are quite soluble. Per cent plastic accounted for was calculated as the sum of volatile products, assuming half of the 16% oxygen in polycarbonate formed carbon dioxide and carbon monoxide, the remainder of these compounds being formed by reaction of the carbon skeleton of the plastic with oxygen in the air. Volatile products identified in less than 2 mg/g quanti-

ties but not otherwise quantitated include methyl acetylene, acetone, isobutane, *cis*-2-butene, pentane, cyclopentene, and xylene.

Table II shows quantities of combustion products of one polycarbonate sample during temperature ranges selected on the basis of the TGA curve. Totals for this sample are quite representative of the two unfilled polycarbonates. As expected, carbon dioxide and carbon monoxide form primarily in the last stage, but also are significantly present in the first stage. This is the first plastic tested to form these compounds at such low temperatures, indicating decomposition of the carbonate linkages. If all the oxygen of carbon dioxide and carbon monoxide in the first temperature range came from carbonate linkages, about half the oxygen of the plastic

TABLE II
Polycarbonate Combustion Products* During Several Temperature Ranges

Compound	<475°C	475- ^o 500°C	500 ^o - 550°C	>550°C	Total
Carbon dioxide	90	60	133	997	1280
Carbon monoxide	10.3	14.6	60	248	333
Methane	2.25	2.48	5.69	3.75	14.2
Ethylene	0.09	0.31	0.39	0.33	1.12
Ethane	0.057	0.19	0.36	0.12	0.73
Propylene	0.095	0.17	0.085	0.026	0.37
Propane	0.022	0.067	0.03	—	0.12
Methanol	0.093	0.43	0.36	0.14	1.02
Acetaldehyde	0.092	0.10	0.06	0.085	0.34
1-Butene	0.062	0.038	0.008	0.042	0.15
Butane	0.001	0.004	0.001	0.004	0.01
Benzene	0.045	0.077	0.72	1.06	1.90
Toluene	0.066	0.19	0.46	0.18	0.90
Ethylbenzene	0.013	0.088	0.21	0.17	0.48
Styrene	0.006	0.008	0.014	0.036	0.06
% Plastic accounted for					59
% Residue (by difference)					41

* Air flow, 100 cc/min; heating rate, 5°C/min.

would be accounted for. Methane is the only compound whose amounts for the stages did not add up to a total reasonable with that expected from Table I, the per cent plastic accounted for being about the same. The first stage is quite deficient in aliphatic hydrocarbons, but otherwise no trends are evident. Aromatic hydrocarbons are formed primarily in the last two stages, i.e., after the 520°C endotherm.

Only three major compounds were identified in polycarbonate residue: phenol, *p*-cresol, and *p*-ethylphenol. These compounds comprise about 15% of the residue. Gas chromatography indicates 30-40 compounds are present. Lee⁸ has identified some other higher-boiling compounds, including isopropenylphenol, isopropylphenol, diphenyl carbonate, and bisphenol A.

Combustion products of polysulfone are shown in Table III. Results for the two samples were often nearly identical, as indicated by the calculated deviations. Again, adding oxygen leads to less carbon dioxide and methane, while fast heating suppresses carbon monoxide production. The two polysulfone samples tested had 7.62% and 7.56% sulfur, meaning about 76 mg sulfur must be accounted for in each gram of plastic. In all cases, over 85% of the sulfur of polysulfone is accounted for as sulfur dioxide. Carbonyl sulfide is the only other sulfur compound identified, although hydro-

TABLE III
Combustion Products of Polysulfone at Several Combustion Conditions

Air flow, cc/min	100	100	100
Oxygen flow, cc/min	0	40	0
Heating rate, °C/min	5	5	50
Carbon dioxide	1072 ± 125	861 ± 47	1414 ± 82
Carbon monoxide	250 ± 4	261 ± 9	87 ± 6
Sulfur dioxide	145 ± 1	139 ± 8	131 ± 4
Methane	28.4 ± 0.4	9.68 ± 0.20	23.5 ± 0.10
Ethylene	0.76 ± 0.02	0.63 ± 0.16	1.17 ± 0.06
Ethane	0.72 ± 0.03	0.60 ± 0.18	0.60 ± 0.03
Benzene	5.39 ± 0.03	4.76 ± 0.01	8.69 ± 1.57
Toluene	2.59 ± 0.01	2.16 ± 0.25	3.61 ± 1.17
Ethylbenzene	0.60 ± 0.03	0.53 ± 0.06	0.67 ± 0.13
Styrene	0.12 ± 0.01	0.12 ± 0.04	0.20 ± 0.08
% Sulfur accounted for	95.6	91.6	86.0
% Plastic accounted for	58	50	59
% Residue (by difference)	42	50	41

TABLE IV
Polysulfone Combustion Products* During Several Temperature Ranges

Compound	<450°C	450°- 490°C	490°- >550°C	7550°C	Total
Carbon dioxide	—	—	31	1104	1135
Carbon monoxide	—	2.28	35	213	250
Sulfur dioxide	6.75	29.3	93	11.3	140
Carbonyl sulfide	—	—	0.52	—	0.52
Methane	0.38	2.86	10.2	6.59	20.0
Ethylene	0.01	0.10	0.39	0.33	0.83
Ethane	0.01	0.06	0.33	0.14	0.54
Benzene	—	0.10	1.64	3.82	5.56
Toluene	0.01	0.02	0.54	1.18	1.75
Ethylbenzene	0.01	—	0.04	0.37	0.42
Styrene	—	—	—	—	—
% Sulfur accounted for					92.6
% Plastic accounted for					60
% Residue (by difference)					40

* Air flow, 100 cc/min; heating rate, 5°C/min.

gen sulfide has been reported.¹⁰ Hydrogen sulfide would not be observed in such small quantities with the hydrogen flame detector or on the infrared spectrophotometer. A moderate amount of methane and small amounts of ethylene and ethane were found, along with some aromatic compounds. Consistently these compounds account for 50–60% of the plastic.

Table IV shows amounts of compounds in stages again chosen on the basis of the TGA curve. Carbon dioxide and carbon monoxide are absent in the first stage, and only a small amount of the latter is formed in the second stage. Sulfur dioxide is formed primarily in the third stage, where carbonyl sulfide is also found. This compound was probably too dilute to be detectable in the samples of Table III. Aliphatic hydrocarbons peak in the third stage, while aromatics peak in the fourth. Again, over 90% of the sulfur and about 55% of the plastic are accounted for.

Three compounds identified in polysulfone residue are phenol, cresol, and *p*-tolyl phenylether. This residue is also a complex mixture of about 30 compounds.

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