

# Thermal Decomposition of Acrylic-SO<sub>2</sub> Copolymers

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## SYNOPSIS

The oxidative thermal degradation of acrylic-SO<sub>2</sub> copolymers was investigated by TG, DTG, and DTA. Their thermograms show that the copolymers decompose in several reaction stages with different weight loss, accompanied by several exo- and endothermic effects. Acrylonitrile-SO<sub>2</sub> and methacrylate-SO<sub>2</sub> copolymers exhibit a two-stage thermal decomposition, whereas the polysulfones of the acrolein-SO<sub>2</sub> and acrylamide-SO<sub>2</sub> systems decompose in four stages. Both the number of SO<sub>2</sub> units present in the copolymer and the polarity of the pendant group on the organic monomer have some effect on the thermal stability and the glass transition temperature of the polymers. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Studies of sulfur dioxide-based copolymers have been of great interest to scientists around the world with respect to both the synthesis and thermal stability of these materials. The driving force behind these investigations is the potential applications of these polymers in radiation resists,<sup>1,2</sup> biomaterials,<sup>3</sup> membranes,<sup>4</sup> fire resists,<sup>5</sup> and polysoaps.<sup>6</sup>

Numerous papers<sup>7-10</sup> on the copolymerization of olefinic hydrocarbons with sulfur dioxide have been documented and have established the alternating nature of these copolymers. Thermal decomposition studies of these materials usually show<sup>11-13</sup> a two-step degradation process. The initial degradation occurs about 100–200°C and most of the thermal decomposition takes place at higher temperatures. The decomposition products are sulfur dioxide, olefinic monomer, and several other organic compounds.

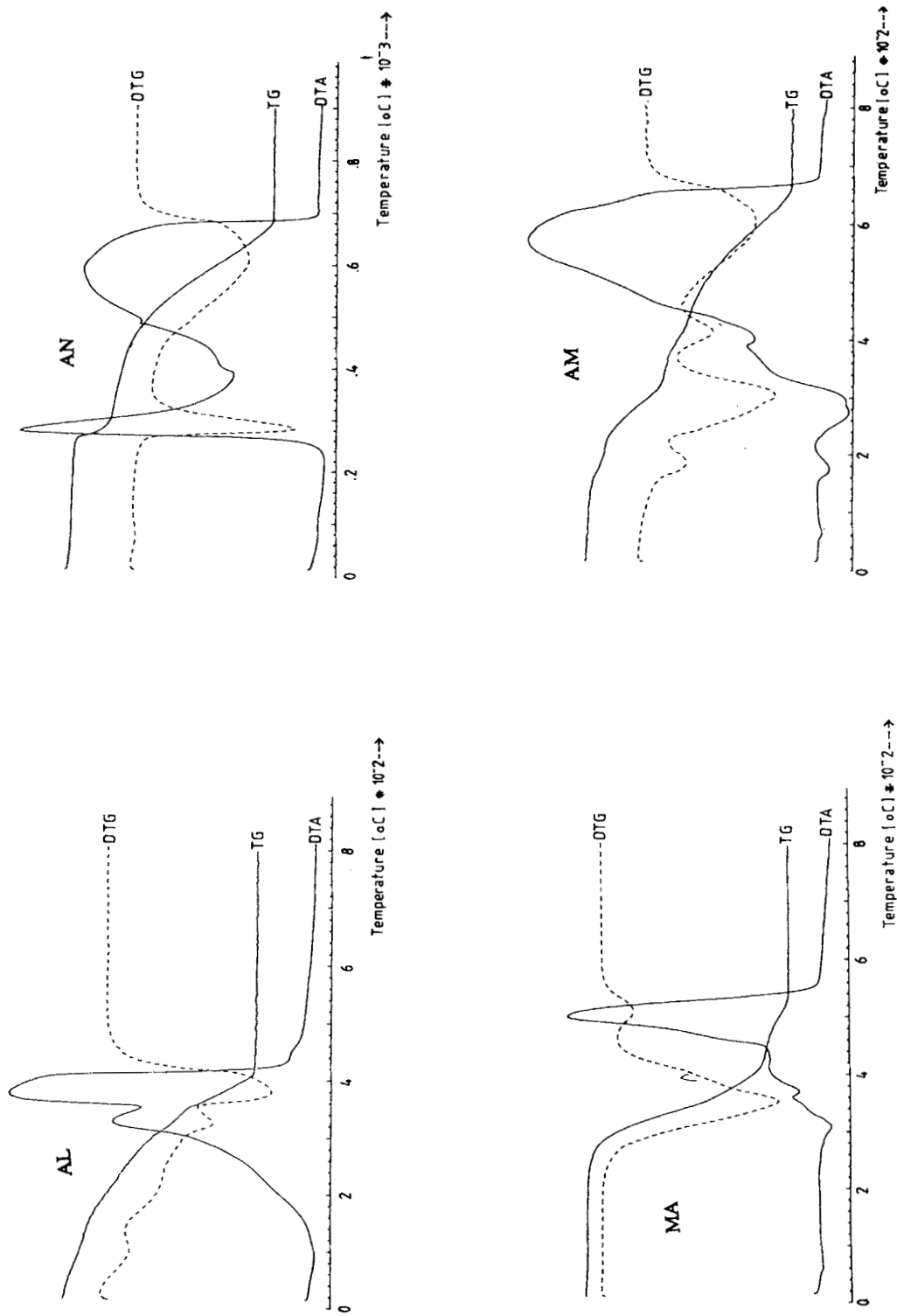
In contrast, copolymers derived from the polymerization of sulfur dioxide with vinyl monomers having electron-withdrawing groups on the vinyl carbon may give homopolymers<sup>14</sup> or random copolymers.<sup>15</sup> Recently, in the present laboratory, a number of investigations have been carried out on the

synthesis and structural characterization of several polysulfones derived from sulfur dioxide and olefinic,<sup>16</sup> acetylenic,<sup>17,18</sup> and acrylic<sup>19-21</sup> monomers. The objective of the present study was to investigate the thermal behavior of some acrylic-SO<sub>2</sub> copolymers by TG, DTG, and DTA. The chief aims were, first, to establish the temperature ranges in which thermal transformations of these copolymers occur and, second, to compare the thermal stability of these polysulfones by examining the effect of SO<sub>2</sub> and the type of acrylic monomer present in the copolymers.

## EXPERIMENTAL

The copolymer samples used in the present investigation were prepared by free-radical solution polymerization methods at low temperature. The samples, for the present thermal analysis study, were selected randomly. Details on the synthesis and structural characterization of these polysulfones were reported previously.<sup>20,21</sup>

Thermal analyses were carried out on a simultaneous thermal analyzer (STA429) manufactured by Netzsch (Germany). It performs thermogravimetry and differential thermal analysis simultaneously. Powder copolymer samples of 0.05 g were



**Figure 1** Thermoanalytical (TG, DTG, and DTA) thermograms of some representative acrolein-SO<sub>2</sub> (AL), methacrylate-SO<sub>2</sub> (MA), acrylonitrile-SO<sub>2</sub> (AN), and acrylamide-SO<sub>2</sub> (AM) copolymers.

subjected to a dynamic atmosphere of air with a flow rate of 150 mL/min and a heating rate of 10°C/min. In the thermograms, the weight loss, the differential temperature, and the temperature of the sample are plotted simultaneously. The endothermic peaks are shown downward and the exothermic peaks are shown upward with respect to the base line.

## RESULTS AND DISCUSSION

A simultaneous working thermogravimetry derivative and differential thermal analysis (TG, DTG, DTA) have been employed to examine the oxidative thermal degradation process of some acrylic-SO<sub>2</sub> copolymers prepared under various experimental conditions. Some typical thermograms are shown in Figure 1.

Examination of the curves of these thermograms reveal that the thermal decomposition of these copolymers occurs in several reaction stages of weight loss of different natures, accompanied by a number of exo- and endothermic effects. The thermal analyses of some representative acrylic-SO<sub>2</sub> copolymers are summarized in Tables I-III.

### Thermogravimetric Analysis

The thermal stability of the acrylic-SO<sub>2</sub> copolymers was evaluated by TG and DTG. The data reveal

that the polymer samples exhibit different oxidative thermal stability. Thus, acrolein-SO<sub>2</sub> copolymers and acrylamide-SO<sub>2</sub> copolymers undergo a four-step degradation process with different rates as shown in the DTG curves, whereas methacrylate-SO<sub>2</sub> and acrylonitrile-SO<sub>2</sub> copolymers exhibit a two-step decomposition.

Table I shows the temperature range for each stage of thermal degradation for the samples that were investigated. It should be pointed out that the degradation temperatures indicated at the first stage (40-75°C) are too low for any polymer to degrade. The initial weight loss could be due to removal of low molecular weight components. The absence of moisture or any solvent in the samples was ascertained by freeze-drying techniques for several days.

The thermal analytical results obtained from thermogravimetric studies in some representative acrylic-SO<sub>2</sub> copolymers are summarized in Table II. It shows the temperature ( $T_i$ ) at which the weight loss began during thermolysis, the temperature ( $T_f$ ) at which the thermal decomposition ended, and the maximum pyrolysis temperature ( $T_m$ ) with the weight loss for each stage. The mol % of SO<sub>2</sub> incorporated into each copolymer samples is also shown in Table II.

The samples of acrolein-SO<sub>2</sub> copolymers show that approximately 22% of the decomposition of the polymer occurs in the first stage: temperature range ca. 40-155°C. During the second stage, temperature range ca. 155-290°C, the weight loss was twice as

**Table I** Temperature Ranges of the Stages of Thermolysis of Some Acrylic-SO<sub>2</sub> Copolymers

Sample No.	First Stage Temp Range (°C)	Second Stage Temp Range (°C)	Third Stage Temp Range (°C)	Fourth Stage Temp Range (°C)
AL1	40-145	145-240	240-330	330-540
AL3	40-140	140-290	290-350	350-500
AL4	45-150	150-270	270-340	340-530
AL5	45-160	160-300	300-350	350-510
AM3	70-210	210-375	375-485	485-715
AM7	75-230	230-380	380-450	450-720
AM9	65-210	210-370	370-510	510-730
AM10	65-210	210-360	360-500	500-715
MA1	265-490	490-600	—	—
MA2	260-485	485-605	—	—
MA3	250-460	460-580	—	—
MA9	305-495	495-565	—	—
AN1	250-350	350-660	—	—
AN4	260-370	370-690	—	—
AN5	240-330	330-640	—	—
AN7	255-370	370-695	—	—

**Table II Thermogravimetric Data of Some Acrylic-SO<sub>2</sub> Copolymers**

Sample No.	% Mol SO <sub>2</sub> in Copolymer	Temp Range (°C)		First Stage		Second Stage		Third Stage		Fourth Stage	
		T <sub>i</sub>	T <sub>f</sub>	T <sub>m</sub>	Weight Loss (%)	T <sub>m</sub>	Weight Loss (%)	T <sub>m</sub>	Weight Loss (%)	T <sub>m</sub>	Weight Loss (%)
AL1	25	40	540	115	22	270	47	290	18	370	9
AL3	28	40	500	110	23	200	46	255	21	370	10
AL4	27	45	530	110	23	175	40	247	23	365	8
AL5	24	45	510	110	22	260	47	300	17	375	8
AM3	23	65	715	95	11	290	50	400	10	600	40
AM7	20	75	720	190	14	305	27	405	8	610	47
AM9	17	60	725	130	10	310	20	410	17	625	51
AM10	19	60	720	110	12	270	23	390	19	620	44
MA1	29	265	600	330	90	530	9	—	—	—	—
MA2	21	260	605	325	86	530	12	—	—	—	—
MA3	27	265	610	360	91	525	8	—	—	—	—
MA9	05	305	565	410	93	520	6	—	—	—	—
AN1	07	250	740	285	24	620	74	—	—	—	—
AN4	05	290	750	320	26	660	73	—	—	—	—
AN5	11	240	640	260	25	570	70	—	—	—	—
AN7	03	270	700	300	30	630	67	—	—	—	—

The codes AL, AM, MA, and AN represent crolein, acrylamide, methacrylose, and acrylonitrile sulfur dioxide copolymers, respectively. T<sub>i</sub> is the temperature where polymer weight loss begins; T<sub>f</sub>, the temperature where polymer weight loss ends; and T<sub>m</sub>, the maximum thermal decomposition temperature.

much as in the first stage. At the third stage, temperature range of ca. 290–340°C, there was, on average, a similar weight loss as in the first stage. In

the last stage, temperature range ca. 340–520°C, the weight loss was less than 10% of the total sample weight.

**Table III DTA Data of the Thermal Effects (TE) with Their Maximum Temperature (T<sub>m</sub>, °C) of Some Representative Acrylic-SO<sub>2</sub> Copolymers**

Sample	TE <sub>1</sub>	T <sub>m1</sub> (T <sub>g</sub> )	TE <sub>2</sub>	T <sub>m2</sub>	TE <sub>3</sub>	T <sub>m3</sub>	TE <sub>4</sub>	T <sub>m4</sub>	TE <sub>5</sub>	T <sub>m5</sub>
AL1	—	—	Endo	105	EXO	350	—	—	—	—
AL3	—	—	Endo	100	EXO	325	EXO	375	—	—
AL4	—	—	Endo	105	EXO	310	EXO	360	—	—
AL5	—	—	Endo	100	EXO	260	EXO	305	—	—
AM3	Endo	60	Endo	140	Endo	280	Endo	410	EXO	550
AM7	Endo	65	Endo	180	Endo	280	EXO	400	EXO	560
AM9	Endo	55	Endo	110	Endo	310	EXO	410	EXO	620
AM10	Endo	55	Endo	100	Endo	275	EXO	350	EXO	600
MA1	Endo	70	Endo	290	EXO	350	EXO	460	EXO	520
MA2	Endo	65	Endo	285	EXO	350	EXO	480	EXO	510
MA3	Endo	70	Endo	310	EXO	360	EXO	420	EXO	510
MA9	Endo	105	Endo	360	Endo	410	EXO	500	—	—
AN1	Endo	90	EXO	290	EXO	560	—	—	—	—
AN4	Endo	95	EXO	295	EXO	570	—	—	—	—
AN5	Endo	90	EXO	280	EXO	555	—	—	—	—
AN7	Endo	95	EXO	285	EXO	560	—	—	—	—

The notation T<sub>g</sub> stands for glass transition temperature. Endo represents endothermic thermal transitions and EXO represents exothermic thermal transitions.

The thermal decomposition of acrylamide-SO<sub>2</sub> copolymers takes place in four stages as well, but at higher-temperature ranges in comparison to acrolein-SO<sub>2</sub> copolymers. On average, the  $T_i$  and  $T_f$  for the acrylamide-SO<sub>2</sub> copolymers is 30 and 200°C higher than the  $T_i$  and  $T_f$  of acrolein-SO<sub>2</sub> copolymers, respectively. Most of the weight loss in acrylamide-SO<sub>2</sub> copolymers occurs during the fourth stage with a  $T_m$ , on average, of 610°C, whereas the acrolein-SO<sub>2</sub> copolymers lose a similar amount of weight in the third stage with a  $T_m$  of roughly 250°C. These observations clearly demonstrate that acrylamide-SO<sub>2</sub> copolymers have much higher thermal stability than that of the acrolein-SO<sub>2</sub> copolymers.

The samples of methacrylate-SO<sub>2</sub> and acrylonitrile-SO<sub>2</sub> copolymers exhibit two-stage thermal decomposition with different rates as shown by the DTG curves. In the first stage, temperature range ca. 270–480°C, the methylacrylate-SO<sub>2</sub> copolymers lose approximately 90% of their total weight. During the second stage, temperature range ca. 480–590°C, the remaining sample is practically decomposed.

The acrylonitrile-SO<sub>2</sub> copolymer samples show different thermal behavior than that of the methacrylate-SO<sub>2</sub> copolymers. During the first stage of their thermal decomposition, temperature range ca. 250–360°C, they showed an approximately 25% weight loss. In the second step, temperature range ca. 360–670°C, the weight loss was around 70%. This thermal phenomenon reveals that the overall thermal stability of acrylonitrile-SO<sub>2</sub> copolymers is higher than those samples obtained from the methacrylate-SO<sub>2</sub> copolymers.

The amount of SO<sub>2</sub> present in each copolymer sample of the same organic comonomer does not differ considerably to show a significant effect on the initial thermal stability of the copolymers. However, samples with large differences in SO<sub>2</sub> units support the view that the initial thermal stability of the copolymer reduces with increase in the number of SO<sub>2</sub> units (the C—S bond cleaves easier than does the C—C bond). For example, in Table II, samples MA3 with 27% SO<sub>2</sub> and MA9 with 5% SO<sub>2</sub> exhibit initial thermal stability at 265 and 305°C, respectively. A similar argument can be given for samples AN5 and AN7.

### Differential Thermal Analysis

The DTA thermograms of acrylic-SO<sub>2</sub> copolymers show that the oxidative thermal decomposition of these polymers occurs in several reaction stages of

weight loss of different natures followed by exo- and endothermic effects. The DTA experimental data collected from all the samples were tabulated and are shown in Table III.

The glass transition temperature ( $T_g$ ) was determined from the DTA slope of the base line that began to deviate. The  $T_g$  (first thermal effect) for acrylonitrile-SO<sub>2</sub> and methacrylate-SO<sub>2</sub> samples appears at about 65–70°C, whereas the acrylonitrile-SO<sub>2</sub> copolymers exhibit higher  $T_g$  (ca. 90°C). The higher  $T_g$  for acrylonitrile-SO<sub>2</sub> copolymers relative to other systems that were investigated may suggest that the segmental rotation of the polymer chains is restricted more and, hence, may require higher energy. This restriction, lower backbone flexibility, could be due to the low SO<sub>2</sub> incorporation and the presence of the highly polar-CN pendant groups.

The TG, DTG, and DTA data obtained simultaneously were very useful and informative because an endotherm detected by DTA may be caused by glass transition temperature, melting point temperature, or merely a loss of volatile byproduct. If the thermal effect is caused by weight loss, it is readily observable by DTG.

In the first endothermic effect, the glass transition temperature was exhibited by all polysulfones except by the acrolein-SO<sub>2</sub> copolymers, which showed low thermal stability (Table III). The DTA thermogram of acrolein-SO<sub>2</sub> copolymers shows three thermal transitions: the first weak endotherm with its peak maximum at 100°C, followed by two exotherms with their respective peak maximum at approximately 325 and 375°C.

The curves of acrylamide-SO<sub>2</sub> copolymers appear as three endotherms with their peak maximum temperature at different temperatures ranging from 55 to 65°C for TE<sub>1</sub>, 100 to 180°C for TE<sub>2</sub>, and 275 to 310°C for TE<sub>3</sub>. The thermal effect TE<sub>4</sub>, temperature range 350–410°C, appeared as an exotherm for all acrylamide-SO<sub>2</sub> copolymers except for sample AM<sub>3</sub>, which exhibited an endotherm of 410°C. The last thermal effect TE<sub>5</sub>, with  $T_m$  = 550–620°C, was exothermic for all acrylamide-SO<sub>2</sub> copolymer samples.

The copolymers, derived from the methacrylate-SO<sub>2</sub> system, gave two endotherms at 70 and 310°C and three exotherms with peak maximum temperatures of 360, 420, and 510°C. Of great interest was sample MA9 whose DTA thermogram was completely different from the other three (MA1, MA2, and MA3). In fact, this MA9 sample showed a glass transition temperature of 105°C and two endothermic transitions with maximum temperatures of 360 and 410°C. The only exotherm that appeared

had a maximum temperature of 500°C. The MA9 sample had a different thermogram with higher  $T_g$  and higher  $T_m$  than those of the other MA samples. These differences may be explained by the fact that the MA9 sample had extremely low SO<sub>2</sub> content relative to the other samples.

The samples examined for the acrylonitrile-SO<sub>2</sub> copolymers showed DTA traces completely different from the other three acrylic-SO<sub>2</sub> copolymers. There was an endotherm ( $T_g$ ) at ca. 90°C and two exotherms with peak maximum temperature of about 295 and 570°C.

Although the DTA shape of all thermograms obtained from each set of samples, based on the same acrylic monomer, was practically the same, the peak maximum temperature was different from one sample to another (Table III). This could be attributed to the fact that the monomer sequence distributions of these copolymers differ markedly. Detailed analysis<sup>21</sup> of the composition of these polysulfones, by elemental analysis and <sup>13</sup>C-NMR, shows that they are made mostly of the MMA, SMM, MMS, and MSM triad monomer sequences.

### Mechanistic Aspects

The thermal behavior of these acrylic-SO<sub>2</sub> copolymers may be divided into two main parts: The first portion of the thermoanalytical curves usually shows the initial weight loss, which may represent the weak bonds of the polymer. These thermal transformations normally occur at relatively low temperatures. The second part (higher temperature) usually provides information about the indiscriminate chain scission.

The present study reveals that the amount of SO<sub>2</sub> incorporated into the copolymer had some effect on both the glass transition temperature and the initial thermal stability of the copolymer chains. They were reduced as the polymer contained more sulfur dioxide. These observations probably suggest that the initiation mechanism involves a homolytic cleavage of the carbon-sulfur bond, which will allow the chain to undergo a random scission at the C—S weak linkages. There also exists the possibility that the labile methylene  $\beta$ -hydrogens (CH<sub>2</sub>CHSO<sub>2</sub>) will react with molecular oxygen to form  $\beta$ -carbon radicals, which break further with heat to release SO<sub>2</sub> and produce chain fragments with a vinyl end group. Reports<sup>11,12</sup> on the thermal degradation studies of several olefin-SO<sub>2</sub> alternating copolymers show that the major degradation products are sulfur dioxide,

olefin monomer, and other unsaturated hydrocarbons. The formation of these products also supports the involvement of the  $\beta$ -elimination reaction and the random C—S bond cleavage.

The rate of the thermal degradation should depend on the number of radical sites generated on the copolymer chain. Furthermore, the higher the stability of the radical formed at the end of the fragmented copolymer chain, the lower its degradation temperature will be. The readiness with which the four electron-withdrawing pendant groups stabilize free radicals diminishes in the order —CHO, —CONH<sub>2</sub>, —CO<sub>2</sub>CH<sub>3</sub>, —CN. Hence, the lower thermal stability of copolymers derived from acrolein-SO<sub>2</sub>, followed by acrylamide-SO<sub>2</sub> monomer systems, could possibly be due to the destabilizing effect of the electron-withdrawing pendant groups on the chain-end radicals. Of course, other factors such as the monomer sequence distributions and a number of different chemical structural changes may also affect the overall thermal stability of these acrylic-SO<sub>2</sub> copolymers.

The fact that AL and AM copolymers exhibit a four-stage degradation, whereas AN and MA samples show a two-stage degradation, under the same thermal conditions, suggests that the chain fragmentation patterns differ markedly. The information that can be obtained about the chain fragmentation pattern in a four-stage degradation would be more detailed and, hence, more informative.

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