

Copolymerization of Sulfur Dioxide with Some Alkenoic Acids

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Synopsis

The copolymerization of sulfur dioxide with some alkenoic acids such as acrylic, 3-butenic, 4-pentenoic, and 10-undecenoic acid was carried out using organic and aqueous media in the presence of $(\text{CH}_3)_3\text{COOH}/\text{SO}_2$ redox system. Elemental analyses, IR, and ^{13}C -NMR revealed that the copolymers synthesized from the acrylic acid/ SO_2 system were of variable composition in organic media, but only polyacrylic acid homopolymer was formed in the presence of water. The other three alkenoic acid/ SO_2 systems gave always polysulfone copolymers of alternating structure regardless of the experimental conditions employed. Thermal analyses (TGA and DTA) of selected samples gave T_g in the 73–101°C range, T_m between 160 and 228°C, and the total weight loss in air from 31 to 97%. Flammability decreased as the S : C mole ratio increased. NMR shows that the complexation of SO_2 with the C=C part of all alkenoic acids is low.

INTRODUCTION

There exists tremendous interest in thermoplastics mainly because of certain attractive properties of these materials such as lightness in weight, chemical corrosion resistance, toughness, and ease of handling. Present economic conditions (inexpensive natural gas and petroleum feedstocks) allow thermoplastics to be highly competitive with materials made from natural sources such as paper, wool, cotton, wood, and leather. From all types of plastics consumed in the developed countries, thermoplastics share roughly 80% of the market. Polysulfones prepared from sulfur dioxide and organic monomers are classified as thermoplastics and polyphenylene sulfone has found commercial application in the plastic industry.

In a number of investigations on the synthesis of sulfur dioxide based copolymers, we have prepared¹⁻⁵ several polysulfones from the copolymerization of liquid SO_2 with terminal aliphatic acetylenes,² phenylacetylene,³ styrene,⁵ and acrylic acid,^{1,4} in the presence of *tert*-butyl hydroperoxide free radical generator. For the terminal aliphatic alkynes and phenylacetylene the resulting polysulfones are alternating regardless of the nature of alkyne, solvent, temperature, and feed ratio. The styrene- SO_2 copolymers showed a 2 : 1 overall molar ratio under homogeneous and heterogeneous reaction conditions.

Vinyl monomers with electron-withdrawing groups directly attached to the vinyl carbon usually give polymers with low SO_2 incorporation.⁶⁻⁸ Preliminary studies¹ on the acrylic acid- SO_2 system have demonstrated that the copolymer composition varies widely from 7 to 43 acrylic acid units per SO_2 molecule.

In the present article, we examined the electron-withdrawing power of the carboxylic acid on the vinyl functional group by analyzing the copolymer composition of some alkenoic acids with sulfur dioxide. The acids employed are acrylic, 3-butenic, 4-pentenoic, and 10-undecenoic acid. Both homogeneous and heterogeneous conditions were used in the presence of *tert*-butyl hydroperoxide/SO₂ redox system, which behaves as a free radical generator. It was also of great interest to examine the thermal stability and flammability of these polysulfones.

EXPERIMENTAL

Materials

Tert-butyl hydroperoxide (Fluka A.G.), 3-butenic acid (Fluka A.G.), 4-pentenoic acid (Alfa Products), and 10-undecenoic acid (Alfa Products), anhydrous sulfur dioxide (Union Carbide), and sodium lauryl sulfate (Fluka) were used as received. Acrylic acid (Fluka A.G.) was distilled under reduced pressure prior to use. All solvents employed in the copolymerization were of HPLC grade.

Instrumentation

Polymer samples were purified by dialysis using spectrapor membrane tubing (Fischer Scientific Co.) which had a cutoff of 12,000 molecular weight. Freeze drying was carried out by an Alpha Freeze Dryer unit manufactured by Martin Christ GmbH and Co. KG (West Germany).

Elemental analysis was performed on an elemental analyzer of Carlo Erba Strumentazione Model 1106 using a para Park QS column 2 m in length for hydrogen and carbon analysis and 0.8 m in length for sulfur analysis.

Infrared spectra were obtained on a Nicolet model 5XD FT-IR spectrophotometer using polymer films prepared on KBr surface discs.

¹³C-NMR spectra were recorded on a Varian XL-200 spectrometer operating in the FT mode with a carbon frequency of 50.3 MHz. Polymer samples were observed in DMSO of solution (~ 500 mg in 2.5 mL DMSO-d₆) at 75°C with TMS as internal standard. Spectra were also recorded for undecenoic acid-SO₂ copolymer samples in CDCl₃ solution at 50°C.

Thermal analyses were done on a thermal analyzer (STA429) manufactured by Netzsch in West Germany. Both thermogravimetric (TGA) and differential thermal analysis (DTA) were carried out simultaneously. The polymer sample (~ 150 mg) was placed in one alumina crucible and the same weight of aluminum oxide (reference sample) on the other alumina crucible. The sample temperature was measured by thermocouples of platinum and of platinum plus 10% rhodium. The temperature was usually raised at a uniform rate of 10°C/min. The analyses were made over a range of temperatures in a dynamic atmosphere of air flowing normally at a rate of 150 mL/min. In the thermograms, sample temperature, its weight loss, and the difference in temperature between sample and reference are plotted simultaneously. The exothermic transition (peaks) appear upward and endotherms downwards with respect to the base line.

Copolymerization Method

Method A. Copolymerization in Organic Medium

A generalized procedure for the copolymerization of sulfur dioxide with alkenoic acids may be described as follows: In a dry flask, fitted with a rubber septum, the required amount of sulfur dioxide was condensed at -50°C using an ethanol/liquid nitrogen bath. The solvent with alkenoic acid was then injected and the reaction mixture was brought to the desired reaction temperature. The system was allowed to equilibrate for a few minutes and then *tert*-butyl hydroperoxide (0.1 mL) was injected into the flask. The reaction mixture was stirred for 30 min at -50°C and then water was added. The resulting polymer produced was dissolved in acetone or methanol and dialyzed against several changes of distilled water. The solution from the dialysis bag, which had a cutoff of 12,000 molecular weight, was freeze-dried.

Method B. Aqueous Copolymerization

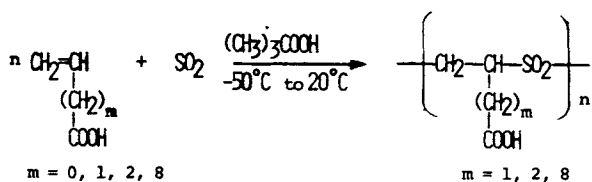
The copolymerization was carried out as described in Method A with the following exception. To the flask, immersed in an ethanol/liquid nitrogen bath (-30°C), containing water and the emulsifier (NLS) was added liquid sulfur dioxide (-30°C) followed by alkenoic acid and *tert*-butyl hydroperoxide. The reaction mixture was then magnetically stirred at room temperature for a specified time in a closed system. The copolymer was then purified by dialysis and freeze-dried.

RESULTS AND DISCUSSION

Copolymerization

A number of alkenoic acids, namely acrylic acid, 3-butenic acid, 4-pentenoic acid, and 10-undecenoic acid were copolymerized with liquid sulfur dioxide in the presence of small amounts of *tert*-butyl hydroperoxide at low temperature using organic and aqueous solvents (Scheme 1):

All polymer samples synthesized in this investigation were purified by dialysis and freeze-dried techniques. The solubility of these sulfones varied. They were generally soluble in dimethylsulfoxide and methanol. In other solvents such as acetone, water, and chloroform, the solubility was moderate to low. Their molecular weight was 12,000 or greater since the membrane of the dialysis tube had a cutoff of 12,000 molecular weight. The freeze-dried samples, which were white flaky solid materials, were subjected to elemental analysis, infrared, nuclear magnetic resonance, thermogravimetric, and differ-



Scheme 1

TABLE I
Copolymerization of Acrylic Acid with Sulfur Dioxide
in Organic Solvents^a

Entry no.	Solvent	Copolymer yield (%) ^b	Copolymer composition ^c			SO ₂ in copolymer (mol %)
			%C	%H	%S	
AA1	C ₂ H ₅ OC ₂ H ₅	62	43.60	5.71	5.59	12.6
AA2	CH ₃ CN	96	39.22	5.22	3.85	9.9
AA3	CH ₃ COCH ₃	73	41.53	5.33	1.09	2.9
AA4	C ₂ H ₅ OCOCH ₃	31	44.20	5.84	0.38	1.0

^a Polymerization conditions: 8 mL liquid SO₂; 1 mL CH₂CHCOOH; 8 mL solvent; 0.1 mL (CH₃)₃COOH; -50°C; 30 min.

^b Copolymer yield is based on acrylic acid monomer and on the dialyzed product.

^c Homopolymer: C, 48.6; H, 8.2%; and 1 : 1 copolymer: C, 26.1%; H, 4.4%; S, 23.2%.

ential thermal analysis. The results of these investigations are summarized in Tables I-IX.

As can be seen in Table I the copolymerization of acrylic acid with sulfur dioxide in the presence of *tert*-butyl hydroperoxide at -50°C in various organic solvents allowed to incorporate variable amounts of SO₂ into the resulting copolymers. Thus the diethyl ether solvent allows the copolymerization to produce a polysulfone containing about 13 times more SO₂ than the one prepared in ethylacetate solvent. Acetonitrile and acetone gave polysulfones possessing moderate amounts of SO₂. This behavior could be due to the influence of the medium on the polarity of the propagating acrylic acid radical and hence the propagation reaction rates. In other words, as the overall reaction medium becomes more polar, the growing acrylic acid radical attains more electropositive character and prefers to add to its own kind rather than to the positive sulfur of the SO₂ monomer. Of course, other factors such as hydrogen bonding may play an important role as well. Several reports⁹⁻¹⁵ have demonstrated the importance of solvent polarity⁹⁻¹² and hydrogen bonding¹³⁻¹⁵ on the reactivity ratios in a number of free radical copolymerizations.

The polysulfone copolymer composition for the other three alkenoic acids appears to be insensitive to the copolymerization medium. This observation would be expected to occur since the presence of methylene groups between the vinyl carbon and carboxylic acid carbon reduces the polarity of the growing alkenoic acid radical markedly.

The copolymer yield also was affected by the solvent used in the copolymerization. For example, acetonitrile gave the highest and ethylacetate the lowest yields (Table I). For the other three alkenoic acids employed in the copolymerization with SO₂, the resulting polysulfones (Tables II-IV) have an elemental analysis for C, H, and S that supports an alternating copolymer structure. The copolymer yields for all three alkenoic acids were higher when the copolymerization was run in the presence of large amounts of SO₂ without any organic solvent present in solution. Overall, the 4-pentenoic acid-SO₂ copolymers were obtained in much higher yields than in the other three alkenoic acids.

TABLE II
Copolymerization of 3-Butenoic Acid with Sulfur Dioxide
in Organic Solvents^a

Entry no.	Solvent	Copolymer yield (%) ^b	Copolymer composition ^e			SO ₂ in copolymer (mol %)
			%C	%H	%S	
BA1	SO ₂	71	30.48	4.40	17.60	46.4
BA2	CH ₃ OH	47	33.42	4.59	19.37	46.5
BA3	C ₂ H ₅ OC ₂ H ₅	31	31.24	3.96	19.14	47.9
BA4 ^c	C ₂ H ₅ OC ₂ H ₅	24	30.70	4.25	19.06	48.2
BA5	(CH ₃) ₂ NCOH	11	30.95	3.85	20.12	49.3
BA6	CH ₃ SOCH ₃	17	29.97	4.09	18.88	48.5
BA7 ^d	C ₂ H ₅ OC ₂ H ₅	Trace	30.07	3.78	18.97	48.6

^aPolymerization conditions: 1 mL CH₂ = CHCH₂COOH; 10 mL liquid SO₂; 10 mL solvent; 0.1 mL (CH₃)₃COOH; -50°C; 30 min.

^bCopolymer yield is based on 3-butenic acid and dialyzed copolymer product.

^cReaction temperature used was -35°C.

^dTwo drops of liquid SO₂ were used.

^eTheoretical values for CH₂ = CHCH₂CH:SO₂ copolymer: C, 32.00%; H, 4.03%; S, 21.35%.

The effect of feed ratio on the copolymer composition of 3-butenic acid and sulfur dioxide run in dimethylformamide (DMF) at -30°C for 5 h in the presence of *tert*-butyl hydroperoxide was examined and the results appear in Table V. Starting with equal volumes of 3-butenic acid and liquid SO₂ and gradually increasing the amount of 3-butenic acid 3, 5, and 8 times relatively to SO₂ present in the feed, one would hope to force the copolymerization to incorporate more acid than SO₂ on the forming copolymer. However, the polymeric products, analyzed by elemental analyses and NMR, revealed that their copolymer composition is always alternating regardless of the feed ratio. We selected to study the 3-butenic acid because its structure differs from the

TABLE III
Copolymerization of 4-Pentenoic Acid with Sulfur Dioxide
in Organic Solvents^a

Entry no.	Solvent	Copolymer yield (%) ^b	Copolymer composition ^d			SO ₂ in copolymer (mol %)
			%C	%H	%S	
PA1	SO ₂	89	37.77	5.16	17.97	47.1
PA2	CH ₃ OH	62	33.02	5.41	17.61	50.0
PA3	C ₂ H ₅ OC ₂ H ₅	38	35.81	4.30	18.88	49.7
PA4	(CH ₃) ₃ NCOH	45	35.74	4.52	18.67	49.5
PA5	CH ₃ SOCH ₃	76	36.11	4.43	18.43	48.9
PA6 ^c	C ₂ H ₅ OC ₂ H ₅	Trace	36.04	4.79	18.98	49.7

^aPolymerization conditions: 1 mL CH₂ = CH(CH₂)₂COOH; 10 mL solvent; 0.1 mL (CH₃)₃COOH; -50°C; 30 min.

^bCopolymer yield is based on 4-pentenoic acid and dialyzed copolymer product.

^cThree drops of liquid SO₂ were added.

^dTheoretical values for CH₂ = CH(CH₂)₂COOH:SO₂ = 1:1 copolymer: C, 36.58%; H, 4.91%; S, 19.53%.

TABLE IV
Copolymerization of 10-Undecenoic Acid with Sulfur Dioxide
in Organic Solvents^a

Entry no.	Solvent	Copolymer yield (%) ^b	Copolymer composition ^c			SO ₂ in copolymer (mol %)
			%C	%H	%S	
UA1	SO ₂	41	52.36	8.16	12.07	48.8
UA2	(CH ₃) ₃ NCOH	81	51.91	8.20	11.51	47.7
UA3	CH ₃ SOCH ₃	49	51.65	8.12	12.10	49.1
UA4	CH ₃ OH	57	52.06	8.18	12.35	49.4

^aPolymerization conditions: 1 mL CH₂ = CH(CH₂)₈COOH; 10 mL SO₂; 10 mL solvent; 0.1 mL (CH₃)₃COOH; -15°C; 1 h.

^bCopolymer yield is based on 10-undecenoic acid and dialyzed copolymer product.

^cTheoretical values for CH₂ = CH(CH₂)₈COOH:SO₂ = 1 : 1 copolymer: C, 53.20%; H, 8.11%; S, 12.91%.

acrylic acid by one methylene group, and we were interested to see whether this group was able to reduce or eliminate the electron withdrawing power of the carboxylic acid on the vinyl group. The results suggest that the methylene group of the 3-butenic acid completely eliminates the electron withdrawing effect of the carboxylic acid probably by removing the resonance electron withdrawing effects. It also reveals that the vinyl group of the acid does not feel the inductive electron withdrawing power of the carboxylic acid.

The effect of water and sodium lauryl sulfate emulsifier on the copolymerization of alkenoic acids with sulfur dioxide was also examined. Table VI shows that the presence of water and/or emulsifier has a detrimental effect on the incorporation of SO₂ into the polymer product. Thus, samples AA5, AA6, and AA7 prepared under the above aqueous condition gave only polyacrylic acid homopolymers. In contrast, the polymers prepared from the polymerization of the other three alkenoic acids with SO₂ were all polysulfone copolymers of alternating structure and appear to be unaffected by the presence of water and/or emulsifier.

TABLE V
Feed Ratio Effect on the Copolymer Composition of 3-Butenoic Acid
and Sulfur Dioxide^a

Entry no.	Feed (mL) ratio (acid/SO ₂)	Copolymer yield (%) ^b	Copolymer composition ^c			SO ₂ in copolymer (mol %)
			%C	%H	%S	
BA8	1	Trace	29.80	3.82	20.96	51.3
BA9	3	15	30.81	3.97	20.70	50.0
BA10	5	19	30.70	4.25	21.03	50.7
BA11	8	25	31.09	4.17	20.90	50.2

^aPolymerization conditions: 10 mL (CH₃)₂NCOH; 1 mL SO₂; 0.1 mL (CH₃)₃COOH; -30°C; 5 h.

^bCopolymer yield based on limiting reactant and dialyzed copolymer product.

^cTheoretical values for CH₂ = CHCH₂COOH:SO₂ = 1 : 1 copolymer: C, 32.00%; H, 4.03%; S, 21.35%.

TABLE VI
 Aqueous Copolymerization of Alkenoic Acids with Sulfur Dioxide^a.

Entry no.	Acid	H ₂ O (mL)	SO ₂ (mL)	NLS ^b (mg)	Copolymer yield (%) ^c	Copolymer composition			% SO ₂ in copolymer
						%C	%H	%S	
AA5	Acrylic	5	2.5	0	35	42.56	5.44	0	0
AA6	Acrylic	5	2.5	20	30	40.80	4.89	0	0
AA7	Acrylic	5	2.5	40	40	41.62	4.90	0	0
BA12	Butenoic	5	2.5	0	18	28.08	3.67	17.10	47.8
BA13	Butenoic	5	2.5	20	37	28.31	4.12	18.50	49.5
PA7	Pentenoic	5	2.5	0	44	32.21	4.32	18.26	51.5
PA8	Pentenoic	5	2.5	20	20	34.74	4.51	18.02	49.3
PA9	Pentenoic	5	2.5	40	26	35.05	4.60	18.31	49.4
UA5	Undecenoic	5	2.5	0	20	54.94	9.05	10.71	44.5
UA6	Undecenoic	10	2.5	20	29	52.84	9.08	10.30	44.6

^a Polymerization conditions: 1 mL alkenoic acid; 0.1 mL (CH₃)₃COOH; 20 h.

^b NLS = sodium lauryl sulfate.

^c Copolymer yield is based on the limiting reactant and dialyzed copolymer product.

Copolymer Characterization

Elemental Analysis

Elemental analyses of C, H, and S show that all polysulfones prepared from 3-butenic, 4-pentenoic, and 10-undecenoic acids with sulfur dioxide in the presence of *tert*-butyl hydroperoxide in various experimental conditions always have on the average one mole of SO₂ per mole of acid (Tables II–V). However, the acrylic acid–SO₂ copolymers synthesized under similar conditions produced polysulfones whose overall molar composition varies from 1 to 13 mol of SO₂/100 mol sample. The elemental analysis of carbon is more consistent and therefore more reliable than that measured for the hydrogen and sulfur elements.

Infrared

The infrared spectra of some alkenoic acid–SO₂ copolymers in the BA, PA, and UA series were examined and revealed a few important bands. Two strong bands in the 1120–1310 cm⁻¹ region are due to symmetric and asymmetric stretching modes of the sulfone. A strong band around 1710 cm⁻¹ was assigned to carbonyl group absorption.

NMR Analysis

The ¹³C-NMR spectra of 3-butenic acid–SO₂, 4-pentenoic acid–SO₂, and 10-undecenoic acid–SO₂ copolymers recorded at elevated temperatures show only two signals resulting from the two carbons of the main chain. The chemical shifts of these signals clearly show that these carbons are bonded to sulfone group (~C–SO₂–C~). This observation confirms the results of the elemental analysis that all the polysulfones of these three alkenoic acids

are alternating in nature irrespective of the polymerization conditions employed in this work.

The ^{13}C -NMR chemical shifts for some of the copolymers examined are given in Table VII. The chemical shifts of the main-chain carbons depend on the different conformation and their relative populations. Theoretically, there are 27 possible conformations for the polysulfone main-chain containing three repeat units with three possible conformations around each bond. If one calculates the Coulombic interactions in the 27 conformational sequences in the $-\text{SO}_2-\text{CH}_2-\text{RCHSO}_2-$ copolymer segment, it will show that the trans carbon-carbon bonds are significantly populated, leaving only a few accessible sequences that will have a gauche carbon-carbon bond. Studies for the system $-\text{CH}_2-\text{CH}(\text{CH}_3)\text{SO}_2-$, have shown¹⁶ that only the conformational states of the two main-chain bonds adjacent to the chiral centers are important, and this reduces the possible conformations to five.

In the present study, the ^{13}C -NMR spectra for the 10-undecenoic acid- SO_2 copolymers were carried out in DMSO-d_6 solvent. Figure 1 shows that the CH and CH_2 signals of the main-chains are partially resolved revealing the triad sequence. The same sample in CDCl_3 solvent gave a spectrum where fine structure was less resolved. The triad structure for the α -carbon could be interpreted in terms of the tacticity difference owing to mm, mr, and rr triads. The fact that the triad structure has a near 1:2:1 intensity ratio suggests that the copolymer may be essentially atactic.

The triad signal for the β -carbon should show either dyad or tetrad sensitivity. A similar problem has been encountered¹⁶ in the propene- SO_2 copolymer system, where the methyl carbons showed dyad rather than triad sensitivity. This phenomenon makes rather impossible to say which of the two chiral centers determines its chemical shifts. The chiral centers in polysulfones are linked through the SO_2 groups and hence their effect may be diminished compared to that in vinyl polymers. On the other hand, it is possible¹⁷ to get a

TABLE VII
 ^{13}C -NMR Chemical Shifts^a of Alkenoic Acid- SO_2 Copolymers

x	C_α	C_β	C_α	COOH	Solvent	Temp	
0	55.0 (t)	49.7 (t)	33.3 (t)	170.7 (s)	DMSO-d_6	75°C	
1	56.2 (t)	48.0 (t)	23.3 (d)	175.5 (s)	DMSO-d_6	75°C	
7	57.0 (t)	48.8 (t)	26.3 (s)	173.9 (s)	DMSO-d_6	75°C	
7	57.6 (br)	52.4 (br)	26.1 (s)	174.0 (s)	CDCl_3	50°C	
			24.9	28.7	29.0	29.4	34.0

^aIn ppm relative to internal TMS. s = singlet; d = doublet; t = partially resolved triad; br = broad singlet.

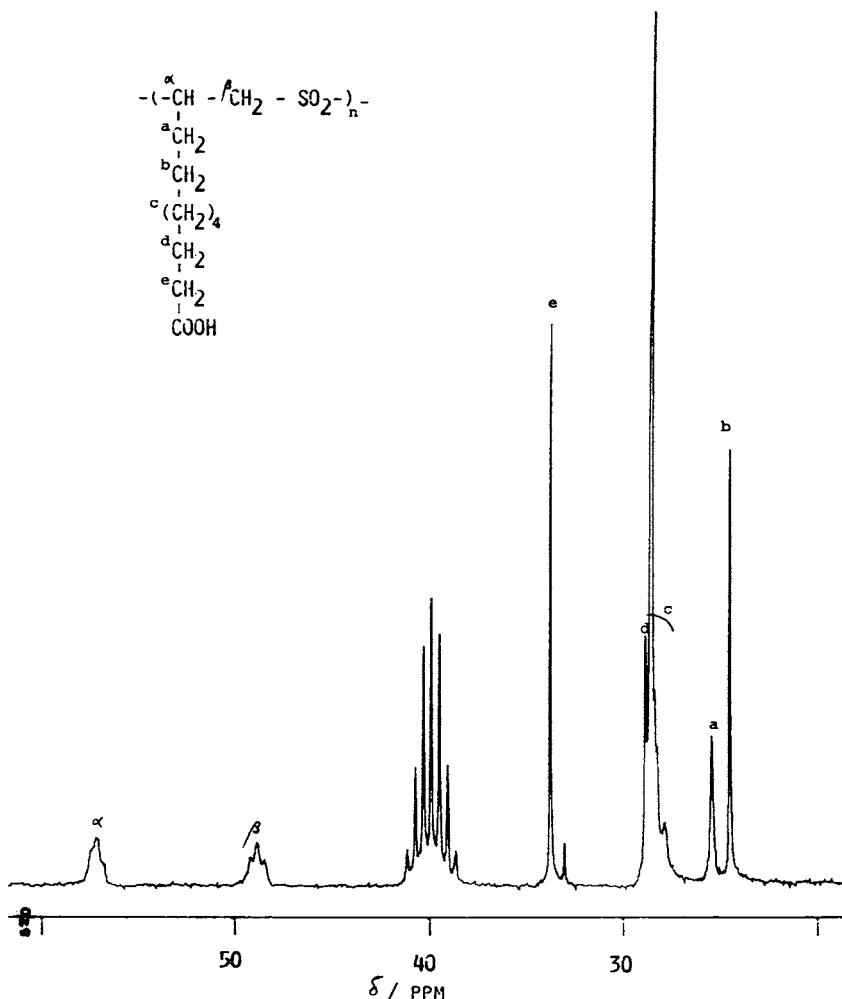


Fig. 1. Proton-decoupled ^{13}C -NMR spectrum of 10-undecenoic acid- SO_2 copolymer in $\text{DMSO}-d_6$ at 75°C .

triplet signal from a tetrad sequence where some peaks may overlap to produce the triplet.

The side-chain carbon attached to the chiral centers in 3-butenoic acid- SO_2 copolymers showed a triad signal, whereas the corresponding carbons in the 4-pentenoic acid- SO_2 copolymers showed a dyad signal and in the 10-undecenoic acid- SO_2 copolymer system it was insensitive to tacticity. The carbonyl carbon resonances in the three alkenoic- SO_2 copolymers were sharp singles, probably indicating no tacticity effects and rapid motion of the side chain.

The main-chain carbon resonances in the three alkenoic acid- SO_2 copolymers are similar when recorded in the $\text{DMSO}-d_6$ solvent, suggesting that the repeating unit has similar structural environment in all the three copolymer

systems. This is to be anticipated as the side chains are linear, without any α -branching, showing identical interactions in corresponding conformations.

The acrylic acid-SO₂ copolymers had similar ¹³C-NMR spectra as those reported earlier.⁴ Those acrylic acid-SO₂ reactions that were performed in aqueous media did not incorporate any SO₂ into the polymer. Their ¹³C-NMR spectra were characteristic of polyacrylic acid, the α -carbon showing a broad peak at 44.8 ppm and the β -carbon a triad structure with peaks at 36.8, 37.0, and 37.4 ppm with relative intensities of 0.28, 0.43, and 0.29, respectively. The triplet pattern may arise from the overlap of peaks due to the tetrad structures. A similar phenomenon has been observed for the β -carbon resonance in the ¹³C-NMR spectrum of polyacrylonitrile.¹⁷

Thermal Analysis

The thermal stability of some representative alkenoic-SO₂ copolymers was evaluated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Data from the thermal stability of some alkenoic-SO₂ copolymers using nonisothermal TGA in air are tabulated in Table VIII. The glass transition temperature (T_g), crystalline melting point (T_m), and weight losses in various scanning temperature ranges are summarized in Table IX. In all thermograms, the values of T_m of DTA for the same copolymer sample correspond to the onset of decomposition in the TGA thermograms, and may reflect true crystalline melting. Of course, to confirm or reject the presence of crystallinity one would have to carry out X-ray analysis for these copolymers. Small weight losses before rapid weight loss were observed which may be due to the presence of moisture in the samples.

TABLE VIII
Thermal Stability of Some Alkenoic-SO₂ Copolymers Using Nonisothermal Thermogravimetric Analysis (TGA) in Air^a

Copolymer	Step	Min. temp (°C)	Max. temp (°C)	Weight loss (%)
UA6	1	14.9	174.3	3.31
	2	176.5	300.4	35.23
	3	302.5	540.0	3.18
	4	17.9	534.1	41.45
	Total	14.9	540.0	41.94
PA3	1	20.0	155.5	8.85
	2	155.0	230.4	35.69
	3	279.9	320.2	3.79
	4	399.9	460.4	7.68
	5	479.9	560.2	2.38
Total	20.0	560.2	67.18	
BA9	1	39.7	110.3	2.33
	2	130.2	210.2	21.04
	3	270.1	340.2	1.85
	4	19.9	550.1	35.58
	Total	19.9	550.1	35.58

^aAir flow was 150 mL/min at a heating rate of 10°C/min.

TABLE IX
Thermal Analysis of some Alkenoic Acid-SO₂ Copolymers in Air^a

Copolymer	From DTA		From TGA	Scanning temp range (°C)
	T_g (°C)	T_m (°C)	Total weight loss (%)	
BA1	90	178	97	40-550
UA6	—	228	42	15-540
BA9	73	162	35	20-550
PA3	101	185	67	20-560
BA8	75	161	77	40-550
BA11	80	160	40	20-550
UA2	—	180	41	21-540
PA5	100	180	31	20-550
PA1	78	208	97	25-550

^aAir flow was 150 mL/min at a heating rate of 10°C/min.

As can be seen in Table IX, the copolymers reveal T_g in the 73–101°C range and T_m between 160 and 228°C. The total weight loss was lowest (31%) for sample PA5 and highest (97%) for samples PA1 and BA1 for similar scanning temperatures and times. These wide differences in thermal stability may reflect the overall nature of each copolymer such as its molecular weight, heat of fusion, cohesive energy, symmetry, rigidity, specific heat, and the motion in the amorphous region of the copolymer.

The complex collection of exotherms and endotherms that appear between 250 and 550°C is characteristic of polymer degradation. Direct connection of TGA to GC/MS for analysis and characterization of the volatile degradation products should provide some information on the structural changes of the copolymer for every transition on the TGA thermograph.

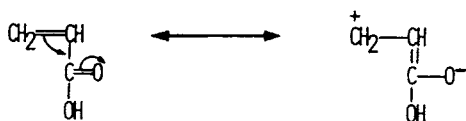
Flame Resistance

A number of polysulfone samples were examined for flammability using open flame in the presence of air. Samples with low SO₂ content relative to hydrocarbon (e.g., acrylic acid-SO₂ and 10-undecenoic acid-SO₂ copolymers) were not self-extinguished when the external flame was removed. However, those samples with high SO₂ content (e.g., 3-butenic acid-SO₂ and 4-pentenoic acid-SO₂ copolymers) turned black (carbonized) and were not flammable. These observations are very interesting since there has been considerable research effort^{18,19} to develop nonburning plastics useful for the construction and textile industry.

MECHANISTIC ASPECTS

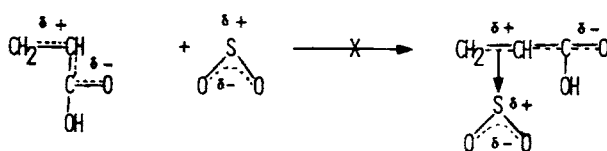
The copolymers produced from the copolymerization of acrylic acid with SO₂ were of variable composition, whereas the other three alkenoic acids gave always alternating polysulfone copolymers under the same reaction conditions. These observations suggest that the carboxylic acid functional group exerts its electronwithdrawing power only when it is attached directly on the

vinyl group thereby depleting the effective electron density of the carbon-carbon double bond (Scheme 2):



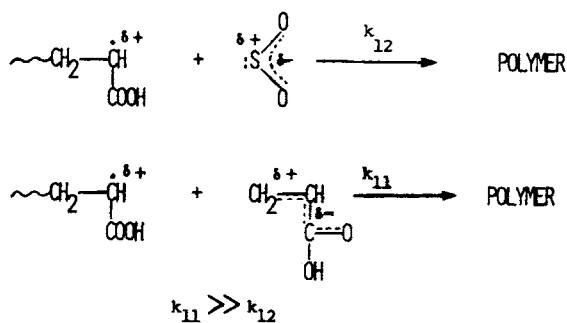
Scheme 2

Thus, the positive nature of the vinyl group should not allow the SO_2 with its electropositive sulfur to interact, form a complex (Scheme 3) and copolymerize in alternating fashion:



Scheme 3

There exists also the possibility that in the two propagating reactions (Scheme 4) $k_{11} \gg k_{12}$:



Scheme 4

For the other three alkenoic acids, the fact that they form alternating copolymers when they react with SO_2 in the presence of $(\text{CH}_3)_3\text{COOH}$ may be attributed to their inability to homopolymerize. This hypothesis was substantiated by allowing large excess of each acid to react with traces of SO_2 (Tables II and III). The results show clearly that only traces of alternating copolymers were formed based on the SO_2 limiting reactant, and the free radicals that were generated in solution were unable to homopolymerize these alkenoic acids.

One could argue that the alternating alkenoic- SO_2 copolymer formation could be due to the generation and participation of a charge transfer complex, which may come about from the interaction of the SO_2 with the vinyl system of the alkenoic acid. The formation of such a complex was monitored by NMR using acrylic, butenoic, and pentenoic acid. Each acid was taken in NMR

tubes and added SO₂ to give an equimolar mixture. A drop of TMS was added into the tubes and were sealed. The proton NMR spectra were recorded at 200 MHz and compared with the spectra of neat sample of each acid. The proton of the carboxylic acid showed shifts of about 0.5–0.7 ppm upfield in the SO₂ media. The olefinic proton cis to the side chain exhibited a much smaller downfield shift (0.08–0.09 ppm). The other two olefinic protons, which are cis to each other, and the side chain methylene protons did not reveal any measurable shift. These observations probably suggest that there may be a weak complexation of SO₂ with the carbon—carbon pi bonds for all these alkenoic acids examined here.

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