

Homogeneous and Heterogeneous Copolymerization of Styrene and Sulfur Dioxide Using the $(\text{CH}_3)_3\text{COOH}/\text{SO}_2$ Redox System

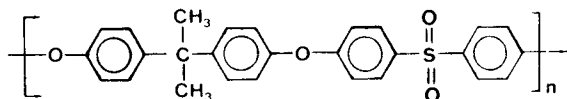
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Synopsis

Styrene was copolymerized with sulfur dioxide in the presence of *tert*-butyl hydroperoxide under homogeneous and heterogeneous conditions. The rate of copolymer formation decreases in the order emulsion, suspension, organic-aqueous, and organic solution. The rate also depends on reaction time, temperature, solvent, and initiator concentration. Several physical methods used to characterize these copolymers, including IR, ^{13}C -NMR, elemental analysis, viscosity, softening point, and isothermal aging. Analysis of the composition of the resulting copolymers revealed that there are on the average about two molecules of styrene per SO_2 present on the copolymer chain. ^{13}C -NMR suggests that these copolymers are made up mostly of the MSM, SMM, and MMS triad monomer sequences whereas the SMS and MMM are present in small amounts. Characterization of polystyrene homopolymers shows that there is lack of stereoregularity in both homogeneous and heterogeneous polymerization systems.

INTRODUCTION

There has been considerable interest in the synthesis of polysulfones probably because of the relatively low cost of sulfur dioxide. Furthermore, the incorporation of the inflexible sulfur dioxide group into a linear polymer chain backbone controls the rotation of the chemical bonds along the chain, which increases stiffness, crystallinity, and hence the thermal stability of the copolymer. An elegant example is the poly(phenylene sulfone), a well-known commercial engineering thermoplastic with high tensile strength and heat durability.



Structure 1.

The synthesis of polysulfones via the copolymerization of sulfur dioxide and various unsaturated hydrocarbons has been the subject of numerous publications. Some good reviews on the subject can be found in the chemical literature.¹⁻⁵

The copolymerization of sulfur dioxide, a gas at room temperature, is usually run in solution or in the solid state by a free radical process. The amount of SO₂ incorporated into the copolymer backbone is affected by the nature of the comonomer. For example, terminal olefins react more readily than those with an internal double bond, but both give an alternating copolymer regardless of the reaction conditions.³ Terminal acetylenic hydrocarbons copolymerize rapidly with sulfur dioxide producing stereoselective alternating copolymers^{6,7} while internal ones are inert under the same conditions.⁶ The presence of various substituents attached directly on the vinyl carbons have a tremendous influence on the degree of the SO₂ units incorporated on the copolymer. Thus, acrylic acid,^{8,9} acrylamide,^{10,11} and vinyl chloride¹²⁻¹⁵ produce polysulfones where SO₂ incorporation depends on polymerization conditions. On the other hand, the monomers α' -methylstyrene, acrylonitrile, and 4-vinylpyridine are not known to copolymerize with sulfur dioxide.

Previous investigators¹⁶⁻²² on the copolymerization of styrene and sulfur dioxide have prepared copolymers with variable compositions. Thus, thermal treatment of the two comonomers with aged paraldehyde free radical initiator or with gamma-radiation at -78°C gave alternating copolymers. However, at higher temperatures the radiation induced copolymerization yielded polysulfones with a higher styrene/SO₂ mole ratio. The thermal copolymerization of styrene and sulfur dioxide in the presence of 2,2-azobisisobutyronitrile (AIBN) gives copolymers with variable composition.

The objective of the present work was to study the effect of homogeneous and heterogeneous (widely used industrial polymerization technique) conditions on the styrene-SO₂ copolymer composition using the *tert*-butyl hydroperoxide/sulfur dioxide redox system as a free radical generator.

EXPERIMENTAL

Materials and Supplies

Styrene, obtained from Fluka Chemical Co., was successively washed with 5% sodium hydroxide aqueous solution, followed by distilled water to remove the radical stabilizer. It was subsequently dried over anhydrous magnesium sulfate, filtered, and distilled under nitrogen. Anhydrous sulfur dioxide (Union Carbide) and *tert*-butyl hydroperoxide (Fluka) were used as received. Sodium lauryl sulfate (99% purity) and poly(vinyl alcohol) were obtained from Fluka. All solvents used were h.p.l.c. grade.

Physical Methods

Elemental analysis was carried out on an elemental analyzer of Carlo Erba Strumentazione Model 1106 using a Para Park QS column 2 m in length for C, H analysis and 0.8 m in length for S analysis.

Infrared spectra were recorded on a Nicolet Model 5DX FTIR spectrophotometer using KBr pellets and calibrated against polystyrene.

The proton-decoupled ¹³C-NMR spectra were recorded on a Bruker AC 80 NMR spectrometer, operating at carbon frequency of 20.15 MHz in the FT mode. Samples were made in CDCl₃ solvent and spectra obtained at the

ambient probe temperature of 35°C. The samples prepared in runs 5, 12, 24, and 25 were measured at 50.1 MHz and at 55°C in a Varian XL-200 NMR spectrometer as reported previously.⁶

Viscosity measurements were obtained from an Ostwald type viscometer at 25°C in dimethyl formamide (DMF) (0.25 g polymer in 25 mL DMF).

The softening points of the copolymers were obtained on a Thomas-Hoover melting point apparatus.

Isothermal aging of the copolymers was studied by using an air-circulated oven at 150°C for 48 h.

Copolymerizations

The copolymerizations of styrene and sulfur dioxide were carried out in the presence of small amounts of *tert*-butyl hydroperoxide using homogeneous and heterogeneous techniques. A few homogeneous reactions were run with the 2,2-azobisisobutyronitrile (AIBN) free radical initiator for comparison.

Homogeneous Copolymerization

Using *Tert*-Butyl Hydroperoxide. Into a 50-mL pear-shaped flask were added 10 mL solvent, 1 mL styrene, and 0.1 mL *tert*-butyl hydroperoxide. The reaction system was cooled to -15°C before 5 mL of liquid SO₂ was introduced into the homogeneous solution. It was then allowed to warm up to 0°C or any other desired temperature for a certain period of time. Afterwards, the reaction mixture was poured into a beaker containing methanol, followed by water. Any precipitate that resulted was filtered, dissolved in methylene chloride, and reprecipitated from cyclohexane. More details of experimental conditions are given in Table I. The effect of reaction time on the copolymer yield is depicted in Figure 1.

Using 2,2-Azobisisobutyronitrile. To a solution of styrene (5.3 mL) in 4 mL solvent, 123 mg of AIBN was added. The homogeneous solution was cooled to -30°C using a liquid nitrogen/methanol bath and then 0.7 mL liquid SO₂ was introduced. The resulting solution was heated up to 50°C for 2 h. At the end of this time, it was cooled slowly down to -30°C and diluted with methanol. The polymeric precipitate formed was isolated from the solution, dissolved in chloroform, reprecipitated from methanol, and dried in vacuum. The results are summarized in Table I (runs 13, 14).

Heterogeneous Copolymerization

Organic-Aqueous Polymerization. The contents of a 50-mL pear-shaped flask, namely, 10 mL solvent, 0.1 mL (CH₃)₃COOH, 1 mL styrene, and 5 mL liquid SO₂ were allowed to mix at -15°C for 2 h. No apparent polymerization was observed; hence 12 mL of distilled water were added to the homogeneous solution, and the flask was kept at 20°C for 3 days. Indeed, copolymerization took place slowly in this heterogeneous solution and the resulting copolymer was forming a precipitate while it was synthesized. After 3 days the product was collected, dissolved in dichloromethane, and reprecipitated in cyclohexane. The copolymers prepared in different solvents in water were insoluble in cyclohexane as indicated by the presence of a trace of polymer in mother

TABLE I
Homogeneous Copolymerization of Styrene and Sulfur Dioxide in Organic Solvent Using $(\text{CH}_3)_3\text{COOH}^a$

Run	Solvent	Temp (°C)	Time	Copolymer ^b Yield (%)	Copolymer composition ^c						
					% C	% H	% S	Mol % SO ₂	Mol % styrene	Mole ratio (styrene/SO ₂)	
1	$(\text{C}_2\text{H}_5)_2\text{O}$	0	3 h	Trace	—	—	—	—	—	—	—
2	CH_3COCH_3	0	3 h	Trace	—	—	—	—	—	—	—
3	$\text{C}_2\text{H}_5\text{OCOCH}_3$	0	3 h	Trace	—	—	—	—	—	—	—
4	CH_3CN	0	3 h	2	—	—	—	—	—	—	—
5	CH_2Cl_2	0	3 h	74	91.96	7.88	0	0	100	—	—
6	CH_3OH	20	3 days	21	67.98	5.79	12.38	35	65	1.9	1.9
7	$(\text{CH}_3)_2\text{SO}$	20	3 days	62	68.44	5.78	12.41	35	65	1.9	1.9
8	$(\text{CH}_3)_2\text{NCHO}$	20	3 days	48	70.00	6.18	11.44	33	67	2.1	2.1
9	CH_3COCH_3	20	3 days	10	68.54	6.03	12.04	34	66	1.9	1.9
10	CH_3CN	20	3 days	6	68.65	6.15	11.35	33	67	2.0	2.0
11	$\text{C}_2\text{H}_5\text{OCOCH}_3$	20	3 days	12	68.34	6.16	11.39	33	67	2.0	2.0
12	SO_2	-15	2 h	73	91.46	7.89	0	0	100	—	—
13	$(\text{CH}_3)_2\text{NCHO}^d$	50	2 h	20	73.32	6.34	8.35	25	75	3.0	3.0
14	CH_2Cl_2	50	2 h	8	70.02	5.90	10.02	27	73	2.3	2.3

^a Polymerization conditions: 10 mL solvent; 1 mL styrene; 0.1 mL $(\text{CH}_3)_3\text{COOH}$; 5 mL liquid SO_2 .

^b Copolymer yield is based on styrene.

^c Theoretical values for $\text{PhCH} = \text{CH}_2/\text{SO}_2 = 2:1$ copolymer: C, 70.56%; H, 5.92%; S, 11.77%.

^d AIBN was used in the homogeneous solution instead of *tert*-butyl hydroperoxide.

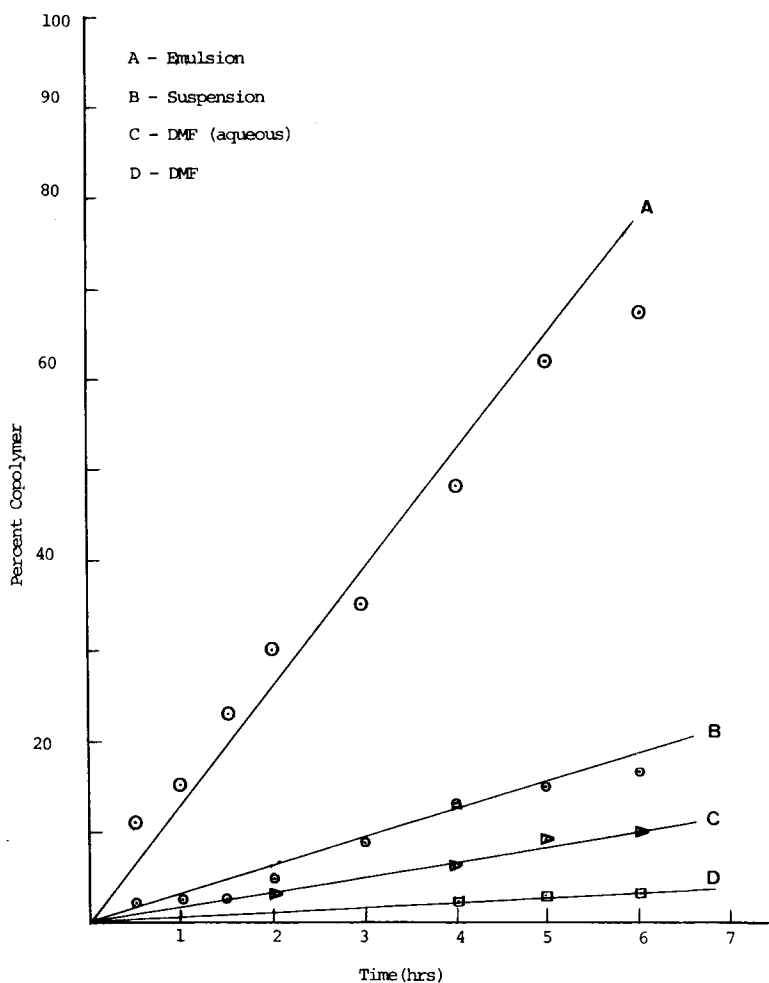


Fig. 1. Plot of percent polymer yield vs. polymerization time at 20°C, under conditions (A) (emulsion) as in Table III, (B) (suspension) 1.0 mL styrene, 2.5 mL SO₂, 5.0 mL H₂O, 0.10 mL (CH₃)₃COOH, 10 mg poly(vinyl alcohol), (C) (DMF, aqueous) as in Table II, and (D) (DMF) as in Table I.

liquor after evaporation. The data of this investigation are summarized in Table II. The effect of copolymerization time on the amount of copolymer yield under the same conditions is shown in Figure 1.

Suspension Polymerization. The reactions were run under the same condition as in organic-aqueous polymerization except 10 mg of poly(vinyl alcohol) (suspension agent) was added to the polymerization solution before the reaction began. The results are shown in Figure 1.

Emulsion Polymerization. Several experiments were carried out for the copolymerization of styrene and sulfur dioxide in emulsion systems. A typical run was as follows. A heterogeneous solution consisting of 5 mL distilled water, 24 mg of sodium lauryl sulfate emulsifier, and 1 mL styrene were allowed to cool before 2.5 mL liquid SO₂ was added followed by 0.1 mL (CH₃)₃COOH initiator. They were then allowed to reach 20°C and were

TABLE II
 Copolymerization of Styrene and Sulfur Dioxide in Organic-Aqueous Mixture Using $(\text{CH}_3)_3\text{COOH}^a$

Run	Solvent	Copolymer ^b yield (%)	Copolymer composition ^f						Mole ratio (styrene/ SO_2)
			% C	% H	% S	Mol % SO_2	Mol % styrene		
15	$(\text{CH}_3)_2\text{SO}$	80	69.36	5.72	12.00	34	66	1.9	
16	CH_3OH	75	70.06	6.05	10.50	31	69	2.2	
17	$(\text{C}_2\text{H}_5)_2\text{O}$	47	71.03	5.61	11.37	32	68	2.1	
18	$\text{C}_3\text{H}_5\text{OCOCH}_3$	46	71.73	5.84	11.24	32	68	2.1	
19	$(\text{CH}_3)_2\text{NCHO}$	30	69.05	6.02	10.81	32	68	2.1	
20	CH_3COCH_3	17	68.48	5.79	11.52	34	66	1.9	
21	SO_2^d	75	70.78	5.92	11.24	32	68	2.1	
22	SO_2^e	18	71.87	6.03	10.85	31	69	2.2	
23	SO_2^e	5	70.15	6.31	10.64	31	69	2.2	
24	CH_2Cl_2	72	90.70	8.04	0	0	100		
25	C_6H_{12}	64	89.83	7.51	0	0	100		

^aPolymerization conditions: 10 mL solvent; 1 mL styrene; 0.1 mL $(\text{CH}_3)_3\text{COOH}$; 5 mL liquid SO_2 ; 12 mL H_2O ; 3 days; 20°C.

^bCopolymer yield is based on styrene.

^cTheoretical values for $\text{PhCH} = \text{CH}_2/\text{SO}_2 = 2:1$ copolymer; C, 70.56%; H 5.92%; S, 11.77%.

^dReaction time 8 h.

^eReaction time 4 h.

TABLE III
Emulsion Copolymerization of Styrene and Sulfur Dioxide using (CH₃)₃COOH^a

Run	Time (h)	Copolymer ^b yield (%)	Copolymer composition ^c					Mol % styrene	Mole ratio (styrene/SO ₂)
			% C	% H	% S	Mol % SO ₂	Mol % styrene		
26	0.5	11	71.76	5.91	10.64	31	69	2.2	
27	1 ^d	15	70.93	5.98	10.62	31	69	2.2	
28	1 ^e	17	68.90	6.08	10.97	32	68	2.1	
29	2	30	67.61	5.49	12.38	35	65	1.9	
30	3	35	68.10	6.02	11.47	34	67	2.0	
31	5	62	68.79	5.90	11.64	34	66	1.9	
32	6	67	67.71	5.35	12.53	36	64	1.8	
33	8	72	67.89	5.52	12.69	36	64	1.8	
34	10	100	68.95	6.04	11.32	33	67	2.0	

^a Polymerization conditions: 2.5 mL liquid SO₂; 1 mL styrene; 5 mL H₂O; 24 mg sodium lauryl sulfate; 0.1 mL (CH₃)₃COOH; 20°C.

^b Copolymer yield is based on the limiting reactant.

^c Theoretical values for PhCH = CH₂/SO₂ = 2 : 1 copolymer: C, 70.56%; H, 5.92%; S, 11.77%.

^d Reaction was run at 10°C.

^e Reaction was run at 40°C.

TABLE IV
The Effect of Initiator Concentration on the Copolymerization of Styrene and Sulfur Dioxide under Emulsion Reaction conditions^a

Run	(CH ₃) ₃ COOH (mL)	Copolymer ^b yield (%)	Copolymer composition ^c					
			% C	% H	% S	Mol % SO ₂	Mol % styrene	Mole ratio (styrene/SO ₂)
35	0.05	18	68.72	5.72	11.95	34	66	1.9
36	0.10	72	66.89	5.52	12.69	36	64	1.8
37	0.15	84	70.78	5.96	11.50	33	67	2.0
38	0.20	100	69.97	5.66	11.10	32	68	2.1

^a Conditions: 2.5 mL liquid SO₂; 1 mL styrene; 5 mL H₂O; 24 mg sodium lauryl sulfate; 20°C; 8 h.

^b Copolymer yield is based on limiting reactant.

^c Theoretical values for PhCH = CH₂/SO₂ = 2 : 1 copolymer: C, 70.56%, H, 5.92%, S, 11.77%.

magnetically stirred for a specific period of time. After the desired time had elapsed the mixture was cooled and poured into a 100 mL aqueous solution containing sodium chloride. The polymer was filtered and repeatedly washed with water, dried, dissolved in methylene chloride, and reprecipitated from cyclohexane. The results obtained are tabulated in Tables III and IV and depicted in Figure 1.

RESULTS AND DISCUSSION

Homogeneous Copolymerization

The copolymerization of styrene and sulfur dioxide in the presence of *tert*-butyl hydroperoxide was first attempted in homogeneous phase using several organic solvents at -15°C. To our surprise, it was observed that practically no copolymerization took place within 2 h. This contrasts the copolymerization of phenylacetylene/sulfur dioxide,⁷ aliphatic acetylene/sulfur dioxide,⁶ or acrylic acid/sulfur dioxide,^{8,9} systems which copolymerize rapidly under the same reaction conditions. The data in Table I show that, even at 0°C for 3 h in the presence of ether, acetone, ethylacetate, and acetonitrile, the copolymer was obtained in trace amounts only with the exception of methylene chloride that gave 74% product. However, the polymer was plain polystyrene without any SO₂ incorporation. A homopolymer was also obtained when the same reaction was run at -15°C in the presence of SO₂ solvent (neat). This probably suggests that the reactivity of the styryl radicals might be very low relatively to the styryl carbonium ion in CH₂Cl₂ and SO₂ solvents producing homopolymers by a (pseudo-)cationic mechanism in which SO₂ as a monomer does not enter. Low viscosity numbers obtained for these homopolymers are typical for a cationic process. As can be seen in Table I, the copolymerization of styrene with sulfur dioxide in various solvents at 20°C required 3 days to yield reasonable copolymer yields.

For comparison a few copolymers of styrene/SO₂ were prepared in various organic solvents under homogeneous conditions using AIBN at 50°C. The data (runs 13 and 14) (Table I) show that good copolymer yields were

obtained on a relative short time (2 h). Their elemental analysis suggests that their copolymer composition is richer in styrene relative to those prepared with *tert*-butyl hydroperoxide initiator (Table I). This was not investigated further because this system has been studied previously.²¹

It should be emphasized at this point that the AIBN free radical initiator requires thermal activation ($\sim 50^\circ\text{C}$) to generate organic radicals in solution, whereas the $(\text{CH}_3)_3\text{COOH}$ decomposes into free radicals⁷ even at -96°C on coming into contact with SO₂.

Heterogeneous Copolymerization

Since the copolymerization of styrene and SO₂ in the presence of $(\text{CH}_3)_3\text{COOH}$ in the homogeneous phase using several solvents was not very successful, we decided to examine the same reaction system in heterogeneous phase.

Table II summarizes the results obtained from copolymerization of styrene and sulfur dioxide using *tert*-butyl hydroperoxide and various solvents mixed with water. The copolymer yields improve markedly when water was used as a cosolvent. All highly polar solvents gave good copolymer yields whereas the two less polar solvents methylene chloride and cyclohexane gave polystyrene homopolymer. The formation of polystyrene homopolymers in these two solvents could be explained by the fact that the two relatively non-polar solvents do not mix with water; hence the polymerization occurs in these solvents which are good solvents for styrene, which, due to its similar polarity, is accumulated in that phase. Most of SO₂ is probably in the aqueous phase so that it may have very little contact with styrene for copolymerization to occur.

When the same heterogeneous reactions were carried out in the presence of poly(vinyl alcohol) suspension agent, the copolymer yields did not improve considerably (Fig. 1).

Numerous copolymerizations were also run under emulsion reaction conditions. Table III shows the effect of reaction time on the copolymer yield, which appears to increase with increasing polymerization time.

The effect of *tert*-butyl hydroperoxide concentration on the copolymerization of styrene with sulfur dioxide under emulsion polymerization conditions has a dramatic effect on the copolymer yield (Table IV). Thus, the presence of 0.05 mL $(\text{CH}_3)_3\text{COOH}$ produces an 18% copolymer yield whereas 0.20 mL $(\text{CH}_3)_3\text{COOH}$ gives a 100% copolymer yield. Previous work^{23,24} has demonstrated that when $(\text{CH}_3)_3\text{COOH}$ reacts with SO₂, free radicals are formed via a redox process. In fact, SO₂ is acting in catalytic capacity and efficiently decomposing the *tert*-butyl hydroperoxide into free radicals, which may initiate the polymerization. However, the concentration of these radicals is reduced with time by a side reaction forming sulfuric acid, *tert*-butyl peroxide, and in some cases acetone.²⁵

The elemental analyses of several copolymers prepared in this work are summarized in Tables I–IV. The mole percent of SO₂ incorporated into the copolymers varies from 25 to 35%. Although the reaction time differs substantially from run to run, depending on the copolymerization method, the overall average mole ratio in all copolymers is approximately 2 mol of styrene per

TABLE V
Triad Monomer Sequence Distribution of Some Styrene-SO₂ Copolymers
Determined by ¹³C-NMR

Run	Triad monomer sequence ^a					Mole % SO ₂ in copolymer ^b
	SMS	MSM	SMM	MMS	MMM	
6	0.00	0.33	0.33	0.33	0.00	33
7	0.00	0.33	0.33	0.33	0.00	33
8	0.00	0.33	0.33	0.33	0.00	33
15	0.04	0.33	0.29	0.29	0.05	33
17	0.08	0.32	0.24	0.24	0.11	32
20	0.06	0.32	0.26	0.26	0.11	32
21	0.10	0.37	0.26	0.26	0.00	37
23	0.11	0.37	0.26	0.26	0.00	37
27	0.00	0.24	0.24	0.24	0.28	24
28	0.04	0.32	0.28	0.28	0.07	32
29	0.15	0.38	0.23	0.23	0.00	38
34	0.15	0.37	0.22	0.22	0.04	37
36	0.07	0.32	0.25	0.25	0.12	32

^aThe term S represents SO₂ units; and M styrene units in the copolymer.

^bDetermined by ¹³C-NMR.

mole of SO₂. The exceptions were runs 5, 12, 24, and 25, which produce polystyrene homopolymers exclusively.

Some typical ¹³C-NMR spectra recorded for the styrene-SO₂ copolymers prepared by homogeneous and heterogeneous conditions using the (CH₃)₃COOH/SO₂ are shown in Table V and Figure 2. The assignment of the peaks was based on the methods discussed previously.^{26,27} The triad monomer sequence probabilities, derived from the intensity of NMR peaks, are summarized in Table V. It can be seen that the copolymers are made up mostly of MSM, SMM, and MMS sequences. The SMS and MMM probabilities are relatively small.

In a recent paper²⁷ some styrene-SO₂ copolymers, prepared from the copolymerization of styrene and sulfur dioxide in *o*-dichlorobenzene using AIBN as the initiator in the temperature range of 30–60°C were analyzed by ¹³C-NMR and were assigned tetrad monomer sequences, α(MMMS), and α(MMMM) based on their chemical shifts. The ¹³C-NMR spectra (Fig. 2) in our investigation show only one peak corresponding to α(MMMS). This observation confirms that copolymers prepared in this work do not contain styrene sequences greater than triad level.

The homopolymers shown in Table VI revealed triplet structure for the phenyl C(1) carbon signal in their NMR spectra. The intensity distribution in the triplet was used to calculate percentages of different microstructures based on published²⁸ signal assignments. It can be seen clearly that the percent of isotactic, syndiotactic, and heterotactic in these polystyrene chains is practically the same for all samples prepared by the (CH₃)₃COOH/SO₂ free radical initiator system in both homogeneous and heterogeneous environments. These observations suggest that there is lack of tacticity control in these polymerization systems.

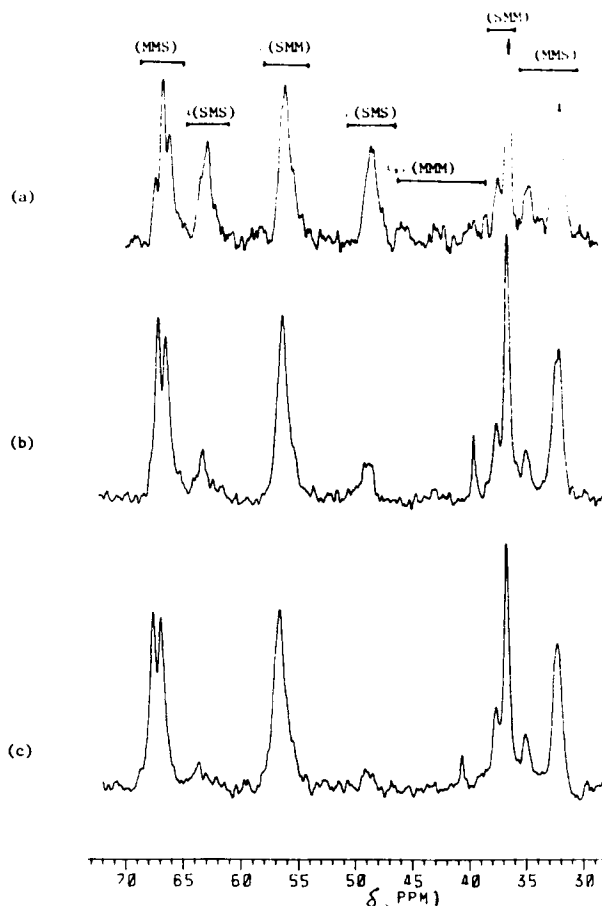


Fig. 2. Proton decoupled ¹³C-NMR spectra of the backbone carbons of styrene-SO₂ copolymers obtained in runs (a) 36, (b), 20, and (c) 15.

The infrared spectra of several of these copolymers were examined and appear to be identical. The two strong bands of the asymmetric and symmetric —SO₂— vibrations absorb at 1330 and 1140 cm⁻¹, respectively.

Measurements of reduced viscosity for a number of these polymers were carried out at 25°C in dimethyl formamide (DMF) solution using 0.250 g

TABLE VI
Configuration of Polystyrene Prepared in Homogeneous
and Heterogeneous Solution^a

Run	% Isotactic	% Syndiotactic	% Heterotactic
5	22	27	51
12	20	28	52
24	23	26	51
25	22	26	52

^a Determined by ¹³C-NMR. Chemical shifts (PPM): Isotactic, 146.0–146.2; Syndiotactic, 145.3; Heterotactic 145.6–145.8.

TABLE VII
Viscosity, Softening point and Weight Loss of some Styrene-SO₂ Copolymers

Run	Reduced ^a viscosity (dL/g)	Softening ^b point (°C)	Weight ^c loss (%)
5	0.09	100-105	2.3
6	3.67	220-231	9.9
7	3.86	190-220	10.2
9	0.72	209-224	4.6
15	2.86	190-220	8.8
16	2.54	210-215	9.5
21	1.70	180-190	5.9
25	0.14	115-130	2.7
29	1.46	215-225	10.6
30	1.44	224-242	10.2
34	1.66	224-232	3.1
36	1.96	210-218	4.9
38	1.21	220-232	9.5

^a Determined by Ostwald viscometer, 0.25 g polymer in 25 mL DMF at 25°C.

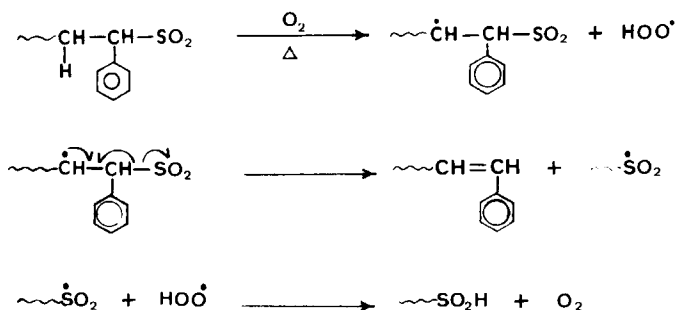
^b Recorded on a Thomas-Hoover melting point apparatus.

^c Estimated by using an air-circulated oven at 150°C for 48 h.

sample in 25.0 mL DMF. The viscometer used was of the Ostwald type. As can be seen in Table VII, the reduced viscosity ranges from 0.09 to 3.86 dL/g, which probably suggests that the polymer molecular weights vary widely. The polysulfones have moderate to high molecular weights ($\eta_{\text{red}} = 0.72\text{--}3.86$ dL/g) whereas the homopolymers (runs 5 and 25) are of low molecular weight ($\eta_{\text{red}} = 0.09\text{--}0.14$ dL/g).

The softening points for all copolymers (Table VII) are roughly 200°C with the exception of the two homopolymers (~ 110°C). The incorporation of the SO₂ inflexible group into polystyrene backbone controls the rotation of the chemical bonds and thus increases the softening point of the polysulfones by about 90°C. Of course, polymer chain size and tacticity control the softening points of these samples as well.

The thermal stability of all styrene-SO₂ copolymers is relatively moderate to low. This is an inherent problem for polysulfones^{29,30} with labile β -hydrogen. Molecular oxygen usually abstracts the labile β -H and the polymer chain breaks down with heat:



Scheme 1.

Isothermal aging experiments were conducted in some representative polymers (Table VII). The weight loss was in the 2.3–10.6% range after a heating period of 2 days at 150°C in an air-circulating oven.

ON THE COPOLYMERIZATION MECHANISM

In the present study several polysulfones have been prepared by the copolymerization of styrene and sulfur dioxide using (CH₃)₃COOH in both homogeneous and heterogeneous conditions.

A comparison of the homogeneous and heterogeneous copolymerization method (Fig. 1) reveals that styrene–SO₂ copolymers are formed readily in heterogeneous solution whereas the copolymer yield in homogeneous environment are practically negligible. The rate of copolymer formation in different methods using the (CH₃)₃COOH/SO₂ redox system decreases in the order: emulsion ≫ suspension > organic–aqueous > organic. This behavior probably suggests that the free radicals produced from the redox breakdown of the (CH₃)₃COOH/SO₂ system enter the micelles in the emulsion heterogeneous solution and initiate the copolymerization of styrene and sulfur dioxide. The formation of micelles has the effect of separating the growing chains from each other, and there is only one or no radical at all at one time in the particle. This phenomenon, at least in part, lowers the importance of bimolecular termination. In the suspension and organic–aqueous environment the copolymerization probably takes place within the organic droplets. The copolymerization kinetics in these media is usually similar to those characteristic of bulk or organic solution.

In conclusion, we can say that, for the copolymerization of styrene and sulfur dioxide in both homogeneous and heterogeneous conditions, the rate of copolymerization depends on reaction time, temperature, solvent, concentration of initiator, and type of copolymerization method.

The overall copolymer composition is about 2 mol of styrene per mole of SO₂ but the monomer sequence distribution on the copolymer varies and does not appear to be controlled by the copolymerization method. These observations suggest that the mechanism of the copolymerization of styrene and sulfur dioxide is still not understood. A number of questions remain unanswered such as to what degree the styrene/SO₂ charge transfer complex, the free (uncomplexed) styrene, and SO₂ monomers participate and control the copolymer composition. Does free styrene compete effectively with styrene/SO₂ complex for addition to its own radicals while copolymerization occurs? Finally the propagation/depropagation equilibrium and penultimate factors that might affect the copolymer composition are worth considering.

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