

# Copolymerization of Elemental Sulfur with Styrene

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## Synopsis

Copolymerization of elemental sulfur with styrene in the presence and absence of metallic sodium was studied at 120°C and 138°C. Propagation of the reaction was followed by gel permeation chromatography (GPC). Glass transition temperatures of all samples were obtained by differential scanning calorimetry (DSC). Reaction products were fractionated with a preparative-type GPC, and each fraction was characterized by DSC, vapor pressure osmometry, infrared spectrophotometry, and both proton and carbon-13 nuclear magnetic resonance spectrometry. Results indicate that the product is a true copolymer of styrene and sulfur. Kinetics of the copolymerization were studied using GPC to monitor styrene and sulfur concentrations. The initial rate of copolymerization (as followed by the consumption of styrene and sulfur) decreases with increasing initial styrene to sulfur ratio. From kinetic analyses, ratios of the rate constants of homo- and copolymerization were determined. Copolymerization of the reactants is more spontaneous than homopolymerization. The reactivity ratios obtained are 0.2 for styrene and 0.6 for sulfur.

## INTRODUCTION

Styrene and its derivatives have been the subject of more scientific research and publications than any other monomer type! And indeed it is well known that styrene can be polymerized by all known polymerization processes.<sup>1</sup>

Elemental sulfur in the eight-membered unstrained ring-form has long been known to polymerize on heating. The polysulfur which is formed, however, is thermodynamically unstable at room temperature and easily reverts to the octal form.<sup>2</sup>

Efforts to copolymerize sulfur and styrene have been sporadic, so far. Baumann and Fromm<sup>3</sup> did heat styrene with sulfur under a vertical coolant and found that all of the sulfur dissolved when the boiling point of styrene (145°C) was reached. On further heating to 190°C, hydrogen sulfide (H<sub>2</sub>S) was driven off, and above 200°C ethylbenzene was formed and refluxed. When no further H<sub>2</sub>S was driven off, the residue in the reaction was found to contain a considerable amount of 2,4-diphenylthiophene and a smaller amount of 2,5-diphenylthiophene.

Later, Michael<sup>4</sup> heated a mixture of styrene and sulfur to a temperature of about 155°C and believed he isolated impure styrene sulfide. Meyer and Hohenemser<sup>5</sup> heated styrene several hours at its boiling point in the presence of sulfur. On cooling 2,4-diphenylthiophene crystallized out. Moureu, Dufraisse, and Badoche<sup>6</sup> stated sulfur to be substantially inactive as an antioxidant for styrene. Currell et al.<sup>7</sup> reported that styrene and sulfur react to form polymeric polysulfide but a large percentage of the free sulfur reverts to the elemental form. Presumably, the controlling factor that holds this sulfur in the product is its

TABLE I  
Reaction Data on the Consumption of Styrene with Elapsed Time

Expt no.	Initial charge			Temp (°C ±2)	Unreacted styrene (mole fraction)									Initial styrene consumption (%/h)		
	Styrene (mol)	Sulfur (mol)	Sodium (g)		0	0.5	1	1.5	2	3	4	5	6		7	8
9	1.5	0.225	0.46	138	1.0	0.98	0.93	—	0.86	—	0.71	0.59	0.51	0.39	0.22	7
11	1.5	0.015	0.46	138	1.0	—	0.55	0.20	—	—	—	—	—	—	—	45
12	1.0	0.25	—	138	1.0	—	0.81	—	—	0.56	0.49	0.40	—	—	—	18
14	1.0	0.25	0.31	138	1.0	—	0.86	—	0.74	0.51	0.16	—	—	—	—	15
15	1.0	0.10	—	138	1.0	—	0.92	—	0.86	0.80	0.73	0.64	0.53	0.41	—	7
16	1.0	0.25	—	120	1.0	—	—	—	0.79	—	0.56	—	0.34	—	0.18	11
17	1.0	0.25	0.31	120	1.0	—	—	—	0.75	—	0.60	0.42	—	0.34	—	11
18	1.0	1.00	—	138	1.0	—	—	—	0.51	0.31	0.14	—	—	—	—	24

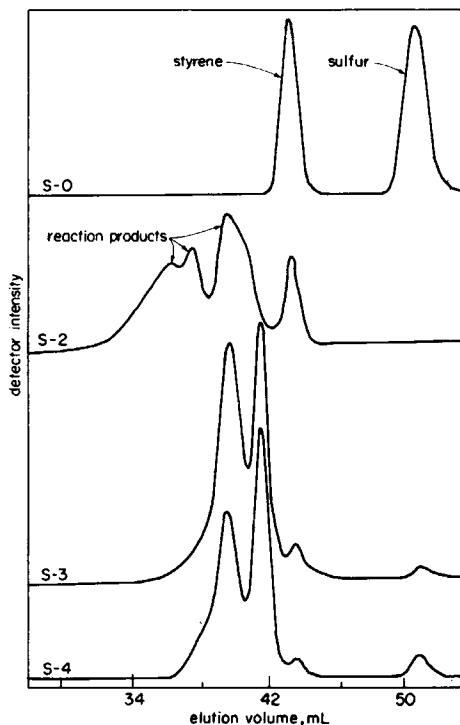


Fig. 1. GPC spectra of reactor contents 0, 2, 3, and 4 h after the start of experiment no. 18 (see Table I for reaction parameters).

solubility in the polysulfide. This, in turn, depends in part on the molecular weight of the latter. The present work has as its objective the development of new outlets for sulfur through its use in the making of new copolymers.

It has been observed in this laboratory that elemental sulfur copolymerizes with styrene well below the floor temperature ( $159^{\circ}\text{C}$ ) related to the homopolymerization of sulfur by thermal initiation. The methods used to prepare and characterize the copolymers obtained are described in the following paragraphs.

### EXPERIMENTAL

Sulfur flower (from Anachemia Chemicals Ltd.) was used as received; styrene, however, (from Aldrich Chemical Co.) was purified by distillation under vacuum and filtration over a molecular sieve to remove residual traces of moisture.

Metallic sodium immersed in liquid paraffin (from British Drug Houses Ltd.—BDH) was cleaned by removing with a sharp knife in petroleum ether the outer surface of the metal. Bright metallic sodium under a dry nitrogen atmosphere was cut into small pieces and placed in the reactor.

The copolymerization reactions were carried out in a 500-mL borosilicate glass wide-mouth reactor immersed in a constant temperature bath ( $120^{\circ}\text{C}$  or  $138^{\circ}\text{C}$ ). The mouth of the reactor was closed with a similar glass cover which allowed access to the reactor through four openings: (1) the passage of a mechanical

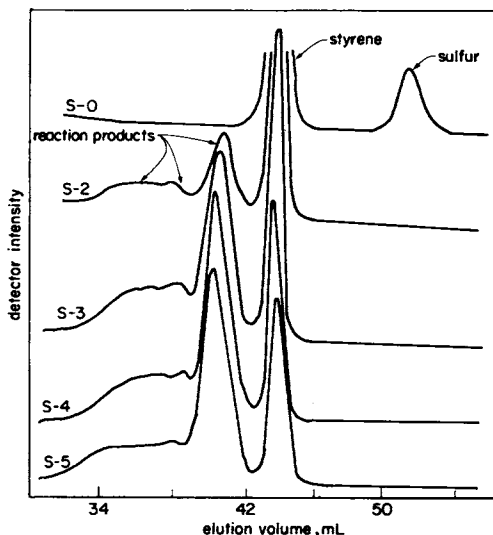


Fig. 2. GPC spectra of reactor contents 1, 2, 3, 4, and 5 h after the start of experiment no. 15 (see Table I for reaction parameters).

stirrer; (2) the inlet for a nitrogen gas purge; (3) the introduction of a thermometer; and (4) the attachment of a reflux condenser equipped with a molecular sieve tube.

The nitrogen purge gas was cleansed before introduction into the reactor by passing it through Fieser's solution to remove traces of oxygen, then through concentrated sulfuric acid to remove traces of humidity, and finally through glass wool to remove possible acid mist.

The quantities of reactants required were measured by weight before introduction into the reactor where the sulfur was found to be totally miscible in styrene under the reaction conditions used. The sodium on the other hand, though small in quantity, was found to be only partially soluble most of the time in the milieu. It was used as an accelerating agent for the copolymerization reaction.

The copolymerization reactions were followed by the analysis of aliquot samples of the reactants dissolved in tetrahydrofuran (THF) (3–5 wt %) by GPC at room temperature with a Water's Associates Model ALC/GPC-201 liquid chromatograph. This apparatus was equipped with microstyragel-packed columns having pore dimensions of  $10^5$ ,  $10^4$ ,  $10^3$ , 500 and  $10^2$  Å, a model M6000A solvent delivery system which served to pump the THF at a rate of 2 mL/min, a differential refractometer as detector and a data module system for the treatment of the raw GPC data.

At the end of each reaction, the residual mixture was diluted in toluene from which the copolymerization products were precipitated with methanol. The precipitate was recovered and dried under vacuum at  $60^\circ\text{C}$ . Some of the reaction products were separated into six fractions on a modified preparative type GPC (Water's Associates Model Prep LC/500) equipped with three styragel packed preparative-type columns 6.35 cm O.D. by 1.22 m long having pore dimensions of 200 Å. Both the global samples and the isolated fractions were then subjected to standard characterization techniques.

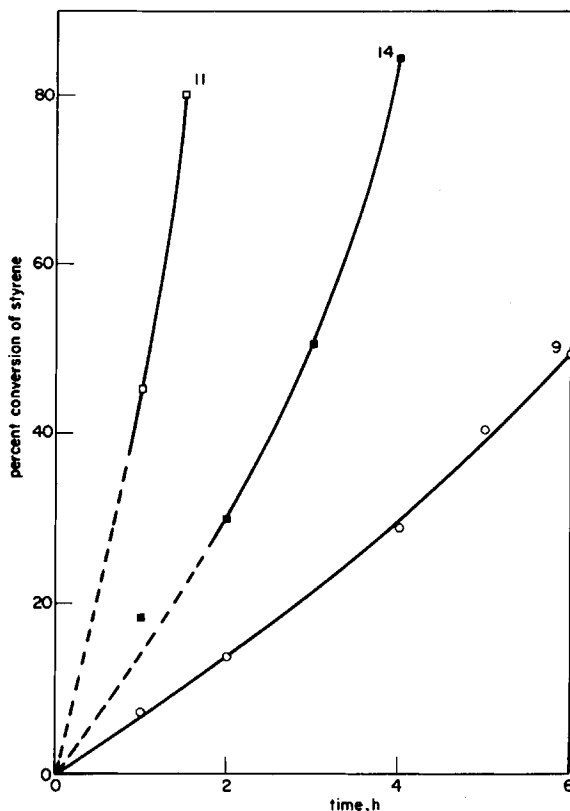


Fig. 3. Styrene conversion vs. time curves for experiments nos. 9, 11, and 14 (see Table I for reaction parameters): Effect of styrene to sulfur molar ratio with sodium.

The glass transition temperature  $T_g$  of each fraction was determined by differential scanning calorimetry (DSC). A Perkin-Elmer Model-2 Differential Scanning Calorimeter (DSC), equipped with a liquid-nitrogen "subambient" accessory system, was operated with helium as the internal carrier gas and dried nitrogen as an environment in the glove box area.

Number-average molecular weights  $\bar{M}_n$  were determined by vapor-pressure osmometry (VPO) using a Mechrolab Inc. Model 301A Osmometer. Toluene was the solvent used and the sample concentrations were 20, 40, 60, and 80 g/L. Benzil was used to calibrate the instrument.

Infrared spectra of the polymer products were obtained with a grating-type infrared spectrophotometer (Perkin-Elmer Model 521). The sample cells were equipped with potassium bromide (KBr) windows.

Proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) spectra of the products were obtained at ambient temperature with a Bruker 90 MHz spectrometer. Samples were dissolved in  $\text{CDCl}_3$  and tetramethylsilane (TMS) was used as the internal standard.

Carbon-13 nuclear magnetic resonance ( $^{13}\text{C-NMR}$ ) spectra were also obtained, at a temperature of  $35^\circ\text{C}$ , with a Bruker 20 MHz spectrometer. Samples were dissolved in  $\text{CDCl}_3$  at a concentration of 10–15%, and TMS was again used as the internal standard.

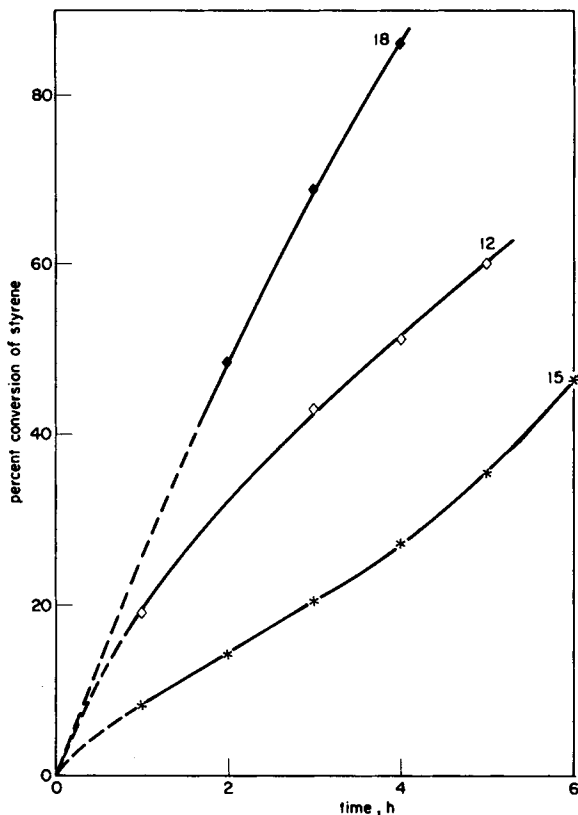


Fig. 4. Styrene conversion vs. time curves for experiments nos. 12, 15, and 18 (see Table I for reaction parameters): Effect of styrene to sulfur molar ratio without sodium.

## RESULTS AND DISCUSSION

The data obtained from the various experiments are summarized in Table I. This table includes information on the initial conditions for each experiment as well as changes in the styrene concentration with time; also included is information on the initial rate of consumption of styrene.

The disappearance of styrene in two typical reactions, as followed by GPC, is shown in Figures 1 and 2. From GPC peak area data of both the products and the styrene monomer, kinetic curves were drawn and are shown, respectively, in Figures 3 and 4 for the cases where metallic sodium is present and absent from the reaction mixture. To determine the relative reactivities of the monomers, copolymerization reactions were carried out with various initial monomer concentrations. Likewise, copolymerizations of styrene with sulfur were carried out at several temperatures both in the absence of and in the presence of metallic sodium (Fig. 5: curves 12 and 16 and 14 and 17, respectively).

From Figures 1 and 2, it can be observed that sulfur disappears very rapidly compared to the time required for the disappearance of styrene, and this even when the styrene to sulfur molar ratio has a value of 1.

If heating of the reaction mixture is prolonged, especially when the sty-

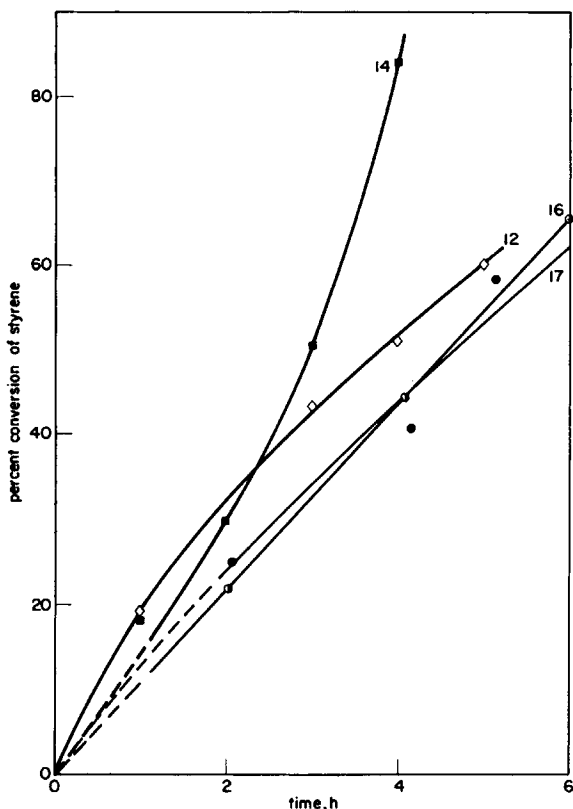


Fig. 5. Styrene conversion vs. time curves for experiments nos. 12, 14, 16, and 17 (see Table I for reaction parameters).

rene-to-sulfur ratio is relatively high, the sulfur reappears in the ultimate products (Fig. 2) due, it would seem, to the degradation of reaction products.

From a plot of the percent conversion of styrene vs. reaction time (Fig. 3), where the metallic sodium content was held constant at 0.31 g/mol of styrene present and where only the proportions of sulfur to styrene were varied, it is observed that, at the lower concentrations of sulfur, the reaction is very rapid. It would seem that this is due to a reduction in the retarding effects of sulfur. As the sulfur content is increased, the rate of consumption of styrene decreases as expected, but, afterwards, the rate increases with further additions of sulfur. In the plot percent conversion of styrene vs. time (Fig. 4) for the case where metallic sodium is absent, the same phenomenon as that shown in Figure 3 is observed.

From the plot of percent conversion of styrene vs. time for conditions where only the reaction temperature is changed (Fig. 5: curves 12 and 16), again in the absence of metallic sodium, it is observed that the rate of consumption of styrene increases slightly with an increase of temperature.

In the presence of metallic sodium (Fig. 5: curves 14 and 17), an increase in temperature causes the rate of consumption of styrene to go up. Furthermore, in the case of identical styrene and sulfur concentrations and at any given tem-

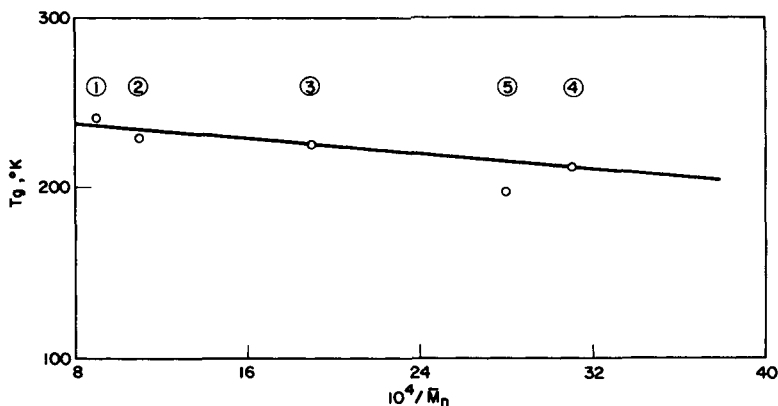


Fig. 6. Glass transition temperature vs. molecular weight as prepared with fractions 1-6 obtained from the products of experiment no. 18 (see Tables I and II for reaction parameters and other data).

perature, the presence of metallic sodium has no significant effect on the initial stage of the reaction but ultimately enhances the reaction rate as shown in Figure 5 (curves 12 and 14).

The precipitated reaction products of experiment 18 were separated into six fractions by prep-GPC described earlier.  $T_g$  and  $\bar{M}_n$  were also determined for each of the fractions. The results are given in Table II.

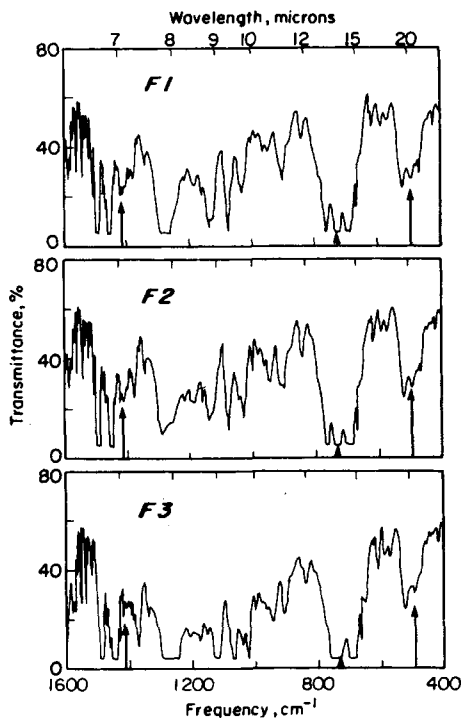


Fig. 7. Infrared spectra of fractions 1-6 obtained from the products of experiment no. 18 (see Tables I and II for reaction parameters and other data).



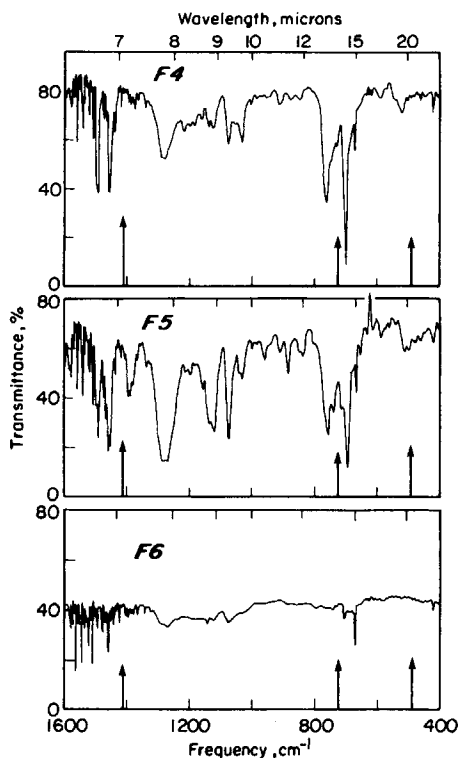


Fig. 7 (Continued from the previous page.)

From the plot of  $T_g$  vs.  $\bar{M}_n^{-1}$  shown in Figure 6, it is observed that, as the molecular weight decreases, so does the glass transition temperature. One should note that  $\bar{M}_n$  of the fifth fraction is slightly higher than that of the fourth, whereas the  $T_g$  of the fifth is less than that of the fourth. This may be explained by invoking that the fifth fraction is a mixture of oligomers and sulfur. As for the sixth and final fraction for which no  $T_g$  value could be found, only a melting temperature was obtained, which is assumed to be that of sulfur.

Infrared spectra of the six fractions are shown in Figure 7. After careful observation, it is evident that the spectra of fractions 1 and 2 are similar to one another, though quite different to that of the standard, polystyrene. These spectra show additional peaks at the following wave numbers: 490, 725, and 1410  $\text{cm}^{-1}$ . According to the literature,<sup>9</sup> these peaks are identified as arising from S—S (490  $\text{cm}^{-1}$ ), C—S (725  $\text{cm}^{-1}$ ), and  $\text{CH}_2$ —S bonds (1410  $\text{cm}^{-1}$ ). This information indicates that fractions 1 and 2 contain styrene-sulfur copolymers.

The IR spectra of fractions 3, 4, and 5 are likewise dissimilar to that of polystyrene but there are no characteristic peaks in the region of 725 and 1410  $\text{cm}^{-1}$  while the spectrum of fraction 6, which, from the DSC-2 study, is believed to be mainly sulfur, shows no characteristic peaks.

The  $\text{H}^1$ -NMR spectra of a standard polystyrene (MW 600) and of fractions 1 and 4 are shown in Figure 8. The spectra of fractions 1 and 4 are dissimilar to that of polystyrene.

TABLE II  
Molecular Weight and Glass Transition Temperature Data on Fractions Obtained from  
Experiment No. 18

Fraction number	$\bar{M}_n$	$T_g$ Heating rate (K/min)				1 <sup>a</sup>
		80	40	20	10	
1	1044	261	258	255	252	242
2	897	247	244	241	238	229
3	528	243	239	236	234	226
4	320	231	228	225	222	213
5	355	208	206	204	202	196
6 <sup>b</sup>	—					

<sup>a</sup> As calculated from the expression<sup>8</sup>  $\log q = a - b/T_g$  ( $^{\circ}\text{K}$ ).

<sup>b</sup> Fraction 6 is nonstyrenic in nature and shows no  $T_g$  transition.

Similarly, the  $\text{C}^{13}$ -NMR spectra of polystyrene (MW 600) and of fractions 1 and 4 which are shown in Figure 9 are seen to be dissimilar to one another. From these studies one is also led to believe that the reaction products are indeed constituted of real copolymers.

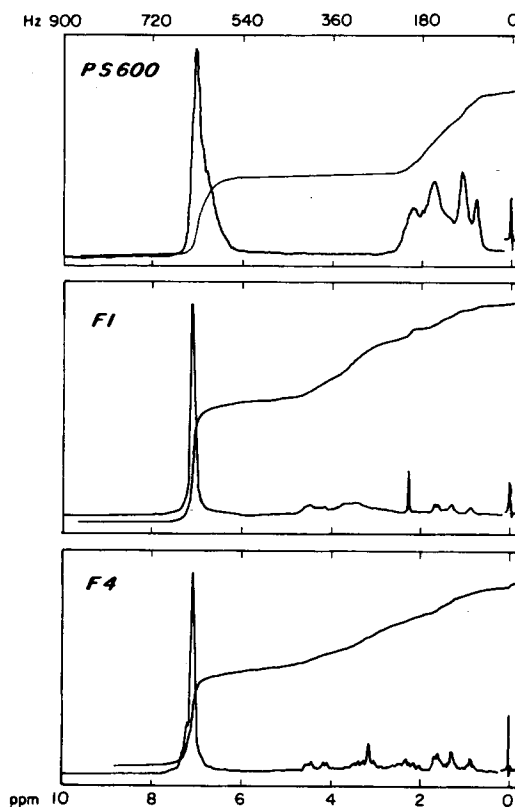


Fig. 8. Proton nuclear magnetic resonance spectra of fractions 1 and 4 (products of experiment no. 18) and a standard polystyrene (mol wt 600).

TABLE III  
Kinetic Reaction Data Taken at 138°C without Sodium

Expt no.	Styrene: sulfur ratio	Monomer	Unreacted monomer (mol)									
			Elapsed time of reaction (min)									
			0	10	20	40	60	65	80	110	120	
K-1	1:1	Styrene	1.00	1.00	0.96	0.68	0.57	—	—	—	—	
		Sulfur	1.00	1.00	0.96	0.43	0.08	—	—	—	—	
K-2	2:1	Styrene	1.00	1.00	0.97	0.93	0.89	—	0.81	—	—	
		Sulfur	0.5	0.5	0.45	0.35	0.23	—	0.08	—	—	
K-4	4:1	Styrene	1.00	1.00	1.00	0.96	—	0.89	0.83	—	—	
		Sulfur	0.25	0.25	0.25	0.24	—	0.19	0.11	—	—	
K-8	8:1	Styrene	1.00	1.00	1.00	0.93	0.87	—	0.84	—	0.76	
		Sulfur	0.125	0.125	0.125	0.09	0.07	—	0.05	—	—	

### KINETIC ASPECTS OF THE COPOLYMERIZATION OF STYRENE AND SULFUR

Styrene and sulfur were mixed in the following molar ratios: 1:1, 2:1, 4:1, and 8:1. Reactions were carried out under a nitrogen atmosphere at 138°C and at atmospheric pressure. Samples were taken from the reaction vessel at regular intervals and the progress of the reaction was followed by liquid chromatography, as is shown in Table III. The moles of unreacted monomers with time are shown in Figures 10(A) and (B) for styrene and sulfur, respectively.

For the copolymerization of styrene (St) and sulfur (S), the following propagation steps can be assumed to be taking place:



Establishing mass balance equations for St and S and assuming steady-state conditions, one can derive<sup>10</sup> the well-known equation

$$\frac{d[\text{St}]}{d[\text{S}]} = \frac{[\text{St}]}{[\text{S}]} \cdot \frac{r_1[\text{St}] + [\text{S}]}{r_2[\text{S}] + [\text{St}]} \quad (2)$$

where  $r_1 = k_{11}/k_{12}$  and  $r_2 = k_{22}/k_{21}$  are the reactivity ratios of styrene and sulfur, respectively.

TABLE IV  
Reactivity Ratio Data

Reactivity ratio	Styrene conversion			For average conversion
	5%	10%	20%	
$r_1$	0.4	0.2	0.1	0.2
$r_2$	0.6	0.4	0.9	0.6

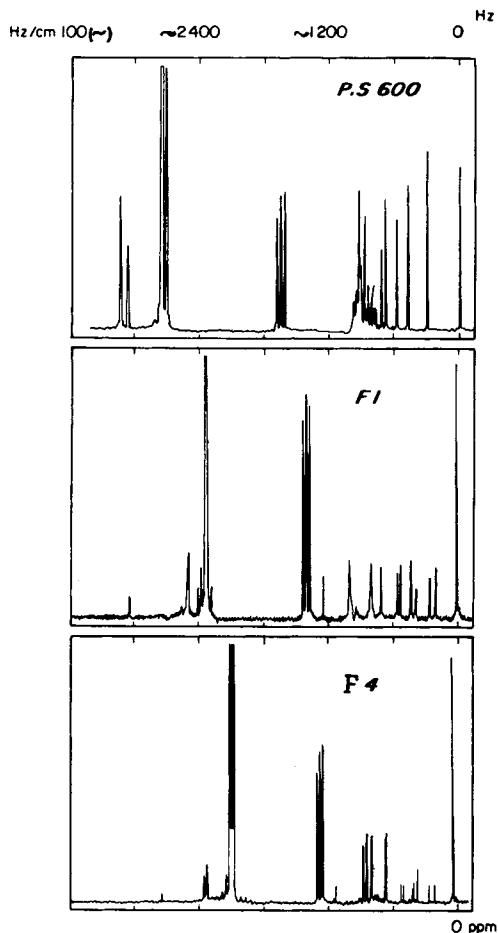


Fig. 9.  $^{13}\text{C}$  nuclear magnetic resonance spectra of fractions 1 and 4 (products of experiment no. 18) and a standard polystyrene (mol wt 600).

Differential equation (2) can be applied directly to experiments where the relative concentrations of the unreacted monomers remain essentially constant. In most monomer systems, unless the conversions are very low, use of the integrated form of eq. (2) is necessary for accuracy<sup>11</sup>:

$$\log \frac{[S]}{[S_0]} = \frac{r_2}{1-r_2} \log \frac{[S_0][St]}{[St_0][S]} - \frac{1-r_2r_1}{(1-r_2)(1-r_1)} \times \log \frac{(r_1-1)[St]/[S] - r_2 + 1}{(r_1-1)[St_0]/[S_0] - r_2 + 1} \quad (3)$$

$$r_2 = \log \frac{[S_0]}{[S]} - \frac{1}{P} \log \frac{1-P[St]/[S]}{1-P[St_0]/[S_0]} \bigg/ \log \frac{[St_0]}{[St]} + \log \frac{1-P[St]/[S]}{1-P[St_0]/[S_0]} \quad (4)$$

$St_0$  and  $S_0$  are the initial concentrations of styrene and sulfur, respectively, and

$$P = (1-r_1)/(1-r_2) \quad (5)$$

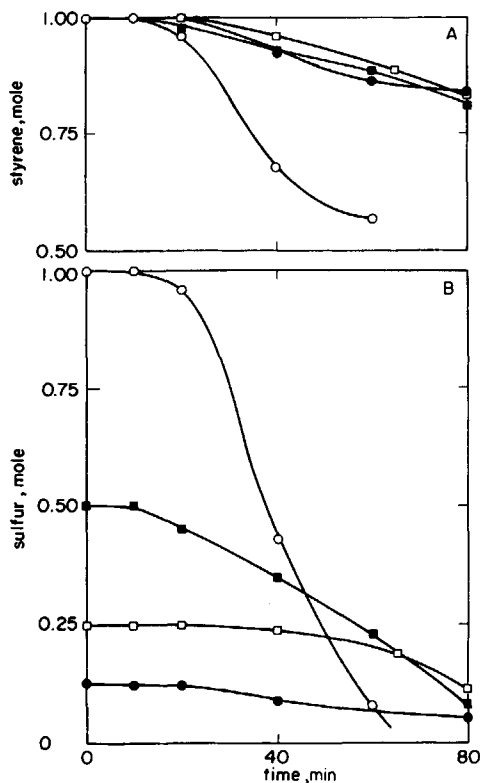


Fig. 10. (A) Unreacted styrene and (B) unreacted sulfur vs. time curves for experiments nos. K-1 (O), -2 (■), -4 (□), and -8 (●) (see Table III for reaction data).

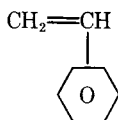
Now  $r_1$  and  $r_2$  can be determined graphically from eq. (4). The reactivity ratios were calculated separately for 5, 10, and 20% conversions of styrene to products. Plotting all of the  $r_1$  vs.  $r_2$  lines together (figure not shown) for the above-mentioned conversion range, average reactivity ratios were determined. The results are shown in Table IV.

From Figures 10(A) and (B), it is evident that, with an increase in sulfur content, the consumption of reactants increases more rapidly. The reactivity ratio data indicate a strong tendency for styrene to react with sulfur as well as itself.

The same phenomenon is observed in Figures 3 and 4, where, with an increase in sulfur content in the reaction mixture (respectively with and without sodium), the rate of disappearance of styrene is rapid. With a lower sulfur content, the rate of disappearance of styrene is slow. In other words, in the presence of more sulfur with or without sodium, greater copolymerization of styrene with sulfur is possible, and styrene disappears more rapidly, while on the contrary, when the sulfur content is low, less sulfur is available for copolymerization. Furthermore, under these conditions, the products of copolymerization are thought to retard the homopolymerization of styrene. The result, of course, will be a decrease in the rate of disappearance of styrene.

## ON THE MECHANISM OF THE COPOLYMERIZATION REACTION

In an attempt to establish the location of the sulfur attack on styrene, isopropyl benzene and benzene were both treated with sulfur at a temperature of 138°C; no reaction, however, could be detected. From these experiments, it was concluded that sulfur, under these conditions, does not attack the benzene ring when brought into contact with styrene. Rather, it reacts in some manner with the vinyl group only.



It is believed that, in view of the relatively rapid disappearance of sulfur in the reaction compared to that of styrene (see Figs. 1 and 2), this reaction cannot be described as proceeding in a simple manner with the two species, styrene and sulfur alone. Rather, sulfur is thought to undergo a ring-opening reaction most likely by a free radical mechanism involving the normally stable eight-member ring form to create active species of varying lengths which react in a random fashion with active styrene oligomers likewise of varying lengths. From kinetic analyses, it is evident that copolymerization is more prevalent than homopolymerization.

The molecular weight of the largest species found in the reaction products surpasses by little 1000; the value of  $n$ , the degree of polymerization, is therefore somewhere between 1 and 10.

The products in their present form might find limited use as tar/asphalt components; however, other more valuable uses are being sought. Higher molecular weights in particular would undoubtedly be beneficial, and it is towards this end that further research is being carried out in this laboratory.

### CONCLUSION

Styrene and sulfur react with each other at elevated temperatures both in the presence of and in the absence of metallic sodium to form copolymers. Sodium has no apparent effect on the reaction during the early stages of the reaction but temperature has a significant effect on the reaction rate. Copolymerization of the reactants is more spontaneous than homopolymerization. Sulfur is thought to be attached to the vinyl backbone of styrene. The copolymer formed is of low molecular weight.

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