

# Copolymerization of Styrene with Vinyl Monomers Substituted by Nitrile and Sulfonyl Groups

DAFNA KNANI and DAVID H. KOHN\*

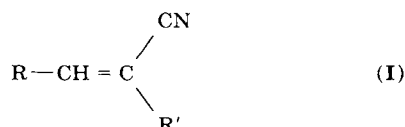
Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel

## SYNOPSIS

Two trisubstituted vinyl monomers, 2-phenylsulfonyl(crotonitrile) and 2-phenylsulfonyl(cinnamitrile) were synthesized and characterized by proton NMR, IR,  $^{13}\text{C}$ -NMR, and mass spectroscopy. Both monomers were copolymerized with styrene by free-radical initiation. The copolymerization parameters of both systems were determined, and the mutual reactivity of the monomers of the two systems is discussed. The new copolymers were characterized by proton NMR and IR spectroscopy, melting range,  $T_g$ , and intrinsic viscosity. The influence of the chemical structures of the two comonomers on these two latter properties of the copolymers is discussed.

## INTRODUCTION

In continuation of our studies on the polymerization and copolymerization of vinyl monomers, substituted by electron-withdrawing groups of the general formula (I), with styrene,<sup>1-4</sup> we wish to report now on the copolymerization of two vinyl monomers, substituted by a sulfonyl group in addition to the nitrile group:



(R:  $-\text{C}_6\text{H}_5$ ,  $-\text{CH}_3$ )

(R':  $-\text{CN}$ ,  $-\text{COOR}''$ ,  $-\text{CONH}_2$ )

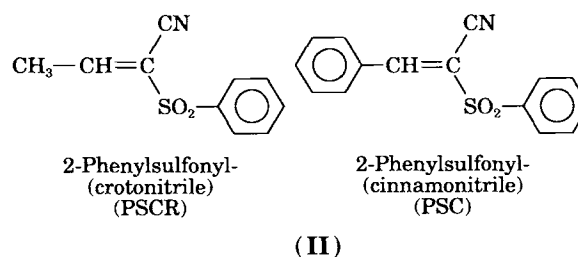
The polymerization and copolymerization of  $\alpha,\beta$ -unsaturated sulfones has been, comparatively, little investigated,<sup>5a</sup> although some of the vinyl sulfone polymers show quite interesting technical properties,<sup>5b</sup> such as thermal stability and solvent resistance.

This paper is taken in part from a dissertation submitted by Dafna Knani to the Department of Chemistry, Technion-Israel Institute of Technology, Haifa, in September 1985, in partial fulfillment of the degree of M.Sc.

\* To whom correspondence should be addressed.

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The two sulfonyl- and nitrile-substituted monomers (II), reported in this paper, are



As far as known to us, 2-phenylsulfonyl(crotonitrile) does not appear yet in the chemical literature.

## EXPERIMENTAL

### Materials and Preparation of Monomers

Styrene was purified by distillation under reduced pressure and benzoyl peroxide was recrystallized from methanol. Tetrahydrofuran (THF) was distilled over calcium hydride and stored over alumina.

The two phenylsulfonyl comonomers were synthesized as follows: 2-Phenylsulfonyl(cinnamitrile) (PSC) was synthesized from benzaldehyde and phenylsulfonyl acetonitrile<sup>6</sup> by two methods:

Table I IR Spectra

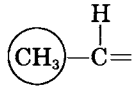
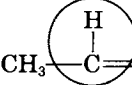
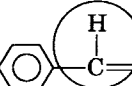
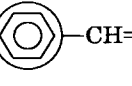
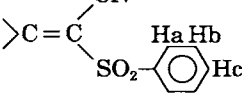
Assignment to group	Monomer Absorption (cm <sup>-1</sup> )	
	PSCR	PSC
	$\text{CH}_3-\text{CH}=\text{C} \begin{array}{l} \diagup \text{CN} \\ \diagdown \text{SO}_2\text{Ph} \end{array}$	$\text{PhCH}=\text{C} \begin{array}{l} \diagup \text{CN} \\ \diagdown \text{SO}_2\text{Ph} \end{array}$
—CN	2230	2220
\SO <sub>2</sub>	1345, 1164	1335, 1158
\C=C\, Ph	1625, 1587, 1450	1600, 1575, 1450
—CH <sub>3</sub>	3060–3020	3060–3000
	1375	—

1. According to Beck and Günther,<sup>6</sup> equivalent quantities of the two reactants were condensed with piperidine as catalyst in a boiling mixture of dimethylformamide and benzene with continuous removal of water in a Dean-Stark trap. The yield of the product was



rather low because of losses during recrystallization from isopropanol.

2. According to the method of Lamm and Anker,<sup>7</sup> benzaldehyde (5.4 g; 0.05 mol) and phenylsulfonyl acetonitrile (9.0 g; 0.05 mol) were condensed in absolute ethanol (150 mL)

Table II Proton NMR Spectra

Assignment to proton	Monomers $\delta$ (ppm)	
	PSCR	PSC
	$\text{CH}_3-\text{CH}=\text{C} \begin{array}{l} \diagup \text{CN} \\ \diagdown \text{SO}_2\text{Ph} \end{array}$	$\text{PhCH}=\text{C} \begin{array}{l} \diagup \text{CN} \\ \diagdown \text{SO}_2\text{Ph} \end{array}$
	<i>d</i> 2.19, 2.22	—
	<i>d</i> 7.68, 7.7	—
	—	<i>s</i> 8.2
	—	<i>t</i> 7.47, 7.49, 7.51 <i>t</i> 7.55, 7.57, 7.59 <i>d</i> 8.0, 8.02
	<i>t</i> 7.57, 7.59, 7.61 <i>t</i> 7.715, 7.7, 7.73 <i>d</i> 7.93, 7.95	<i>t</i> 7.58, 7.6, 7.62 <i>t</i> 7.68, 7.7, 7.72 <i>d</i> 7.9, 7.92

**Table III** NMR  $^{13}\text{C}$  Spectra

Assignment to carbon	Monomers $\delta$ (ppm)	
	PSCR	PSC
$\text{CH}_3\text{-CH}=\text{C}\begin{matrix} \text{CN} \\ \text{SO}_2\text{Ph} \end{matrix}$		$\text{PhCH}=\text{C}\begin{matrix} \text{CN} \\ \text{SO}_2\text{Ph} \end{matrix}$
$\begin{matrix} \text{H} \\   \\ \text{C}=\end{matrix}$	155.71	151.45
$\text{H}_3\text{C-}$	17.61	—
$\begin{matrix} \text{CN} \\   \\ \text{C} \\   \\ \text{SO}_2\text{Ph} \end{matrix}$	122.34	114.81
$\text{-CN}$	110.00	113.06
$\text{-SO}_2\text{-}$ 	128.59, 129.65, 134.65, 137.65	128.68, 129.47, 134.59, 137.90
 -CH=	—	129.65, 130.17 130.99, 134.08

with ammonium acetate (4 g) as catalyst. After boiling for about 10 min and standing afterward at room temperature for several hours, the product precipitated. Recrystallized from ethanol, the monomer melted at 135–137°C (yield: 52%); Lamm and Ankner reported a mp of 137°C.<sup>7</sup> The products from both methods were identical, as confirmed by proton NMR,  $^{13}\text{C}$ -NMR, IR, and MS (Tables I–IV).

*2-Phenylsulfonyl(crotonitrile) (PSCR)* (cf. Ref. 8): In a three-necked flask, fitted with a dry ice-cooled reflux condenser, dropping funnel, thermometer, and magnetic stirrer, phenylsulfonyl acetonitrile (5.43 g; 0.03 mol) was dissolved in glacial acetic acid (80 mL). The three-necked flask was placed in a cooling bath and acetaldehyde (1.4 g; 0.031 mol) was added. Then, a solution of piperidine (0.35 mL) in glacial acetic acid (3.5 mL) was added at such a rate to keep the temperature of the reaction mixture below

**Table IV** Mass Spectra

Mass ( $m/e$ )	Ion	Monomers	
		PSCR	PSC
		$\text{CH}_3\text{-CH}=\text{C}\begin{matrix} \text{CN} \\ \text{SO}_2\text{Ph} \end{matrix}$	$\text{PhCH}=\text{C}\begin{matrix} \text{CN} \\ \text{SO}_2\text{Ph} \end{matrix}$
269.0521	$\text{C}_{15}\text{H}_{11}\text{NO}_2\text{S}$	—	52.72%
207.0340	$\text{C}_{10}\text{H}_9\text{NO}_2\text{S}$	99.88%	—
140.99	$\text{C}_6\text{H}_5\text{SO}_2$	100%	24.52%
125.00	$\text{C}_6\text{H}_5\text{SO}$	13.96%	7.79%
128.05	$\text{C}_9\text{H}_6\text{N}$ (M— $\text{SO}_2\text{Ph}$ )	—	99.33%
205.09	$\text{C}_{15}\text{H}_{11}\text{N}$ (M— $\text{SO}_2$ )	—	2.60%
143.07	$\text{C}_{10}\text{H}_9\text{N}$ (M— $\text{SO}_2$ )	24.70%	—

**Table V Copolymerization of Styrene ( $M_1$ ) and PSC ( $M_2$ ) in Tetrahydrofuran<sup>a</sup>**

Experiment No.	Monomer Feed Mol Fraction		Time (min)	Conversion (%)	Rate of Conversion (%/h)	Elemental Analysis (N %)	Copolymer				
	$M_1$	$M_2$					Mol Fraction		Melting Range (°C)	$T_g$ (°C)	$\eta$ (dL/g)
NSB (18)	—	1.0	1560	0	0	—	—	—	—	—	—
NSB (13)	0.70	0.30	1315	5.4	0.25	1.42	0.873	0.127	143–155	120	0.067
NSB (17)	0.75	0.25	390	1.92	0.29	1.33	0.883	0.117	130–150	—	—
NSB (12)	0.80	0.20	1315	8.06	0.37	1.23	0.893	0.107	131–153	118.3	0.068
NSB (11)	0.85	0.15	1315	9.76	0.45	0.89	0.926	0.074	132–155	—	0.084
NSB (15)	0.90	0.10	420	6.98	1.00	0.76	0.938	0.062	138–148	114.7	0.156
NSB (14)	0.95	0.05	420	6.24	0.89	0.43	0.966	0.034	118–138	—	0.186
NSB (18)	1.0	—	230	13.4	3.49	—	1.0	—	115–145	103	0.322

The copolymers were precipitated in methanol and were obtained as white powders after reprecipitation by methanol from their solution in THF.

<sup>a</sup> Initiator: Benzoyl peroxide, 0.23%.

20°C. After warming for 1 h at 40°C, the mixture was left overnight at room temperature. Poured onto ice, a white solid precipitated that was filtered off and dried. The product, purified by dissolving in tetrahydrofuran and reprecipitation upon addition of *n*-hexane, melted at 89–93°C. Yield: 75%. The structure of this new monomer was confirmed by spectral data (Tables I–IV).

### Copolymerization

The copolymerization experiments for the kinetic measurements in bulk were carried out in sealed Pyrex tubes with a bulb at the lower end and with a constriction near the upper end. Copolymerizations in solution, applied for reaction systems with low mutual solubility of the monomers, were carried

out in sealed Pyrex tubes with two bulbs: The lower one, having a volume slightly less than 5 mL, which is connected to the upper bulb by a short glass tube, thus enabled calibration of the requested volume (5.0 mL) and ensured constant concentration of the reactants. For the reactions in bulk, the monomers and the initiator (benzoyl peroxide: 0.2% by weight) were introduced into the reaction tubes, whereas for the reactions in solution, the solvent, THF, was also added ( $M_1 + M_2 = 5$  mol/L). A small magnetic stirrer was put into the reaction tubes. The contents were frozen, and then the tubes were degassed under reduced pressure, flushed twice with nitrogen, evacuated to about 0.1 mmHg, and sealed off. The reactions were carried out in a temperature-controlled bath at  $70 \pm 0.5^\circ\text{C}$  with magnetic stirring. The proper time, that is, the time needed for conversions

**Table VI Copolymerization of Styrene ( $M_1$ ) and PSCR ( $M_2$ ) in Tetrahydrofuran<sup>a</sup>**

Experiment No.	Monomer Feed Mol Fraction		Time (min)	Conversion (%)	Rate of Conversion (%/h)	Elemental Analysis (N %)	Copolymer				
	$M_1$	$M_2$					Mol Fraction		Melting Range (°C)	$T_g$ (°C)	$\eta$ (dL/g)
NSM (1)	—	1.0	190	0	0	—	—	—	—	—	—
NSM (7)	0.65	0.35	1020	3.90	0.23	2.83	0.734	0.266	120–160	114	0.058
NSM (2)	0.75	0.25	205	1.25	0.37	2.55	0.766	0.234	120–150	—	—
NSM (6)	0.80	0.20	410	1.97	0.29	2.44	0.779	0.221	130–150	—	—
NSM (5)	0.85	0.15	410	2.83	0.41	2.21	0.804	0.196	—	—	—
NSM (4)	0.90	0.10	180	1.59	0.53	1.70	0.855	0.145	145–160	—	0.063
NSM (3)	0.95	0.05	180	3.99	1.33	1.16	0.905	0.095	135–145	116	0.092
NSB (18)	1.0	—	230	13.4	3.49	—	1.0	—	115–145	103	0.322

The copolymers were precipitated in hexane. White powders were obtained after reprecipitation by hexane from their solution in THF.

<sup>a</sup> Initiator: Benzoyl peroxide, 0.2%.

Table VII Copolymerization of Styrene ( $M_1$ ) and PSCR ( $M_2$ ) in Bulk<sup>a</sup>

Experiment No.	Monomer Feed		Time (min)	Conversion (%)	Rate of Conversion (%/h)	Elemental Analysis (N %)	Copolymer				
	Mol Fraction						Mol Fraction		Melting Range (°C)	$T_g$ (°C)	$\eta$ (dL/g)
	$M_1$	$M_2$					$m_1$	$m_2$			
NSM (1)	—	1.0	190	0	0	—	—	—	—	—	—
NSM (26)	0.75	0.25	460	4.65	0.61	2.5	0.772	0.228	155–175	—	0.074
NSM (25)	0.80	0.20	455	4.80	0.63	2.27	0.797	0.203	155–170	—	0.084
NSM (19)	0.85	0.15	420	4.40	0.63	2.52	0.770	0.230	155–165	—	0.102
NSM (16)	0.90	0.10	435	6.69	0.92	2.26	0.798	0.202	145–165	126.1	0.106
NSM (20)	0.925	0.075	275	4.42	0.96	2.08	0.817	0.183	145–150	117.3	0.107
NSM (18)	0.95	0.05	190	3.83	1.21	1.69	0.856	0.144	135–145	—	—
NSM (21)	0.975	0.025	127	2.92	1.37	1.27	0.896	0.104	130–145	—	—
NSH (16)	1.0	—	135	9.12	4.05	—	—	—	110–125	101.5	0.616

The copolymers were precipitated in methanol and were obtained as white powders after reprecipitation in methanol from their solution in THF.

<sup>a</sup> Initiator: Benzoyl peroxide, 0.2%.

up to 10%, was determined by trial and error for each monomer pair. At the fixed time, the tubes were cooled and opened and the mixtures poured into a suitable precipitant. The product copolymers were purified by reprecipitation and dried at about 50°C under reduced pressure.

The composition of the copolymers was determined by elemental microanalyses of their nitrogen content. Details on the reaction conditions, results, and some basic properties of the product copolymers are summarized in Tables V–VII.

## Physical Test Methods

### Spectroscopic Measurements

Infrared spectra of the copolymers in chloroform solution were carried out on a Perkin-Elmer 298 grating infrared spectrometer. Proton NMR spectra of the copolymers in solution of  $CDCl_3$  with tetramethylsilane as internal standard were performed on a Varian T-60 and on a Bruker AM 400 spectrometer.

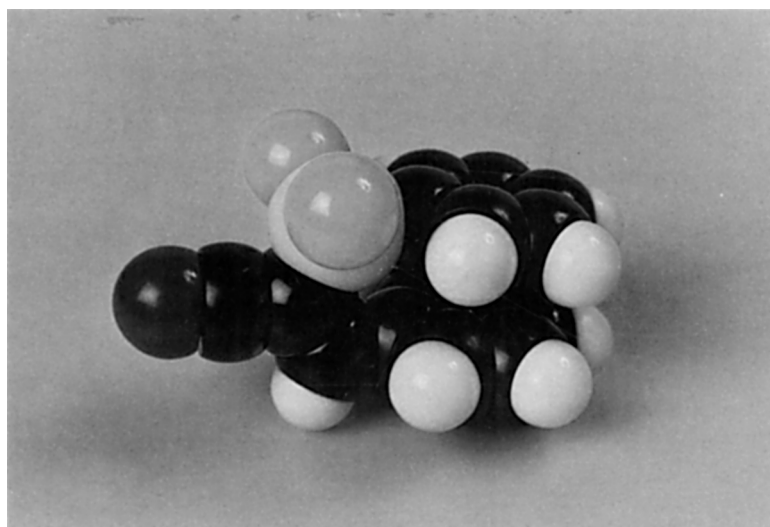
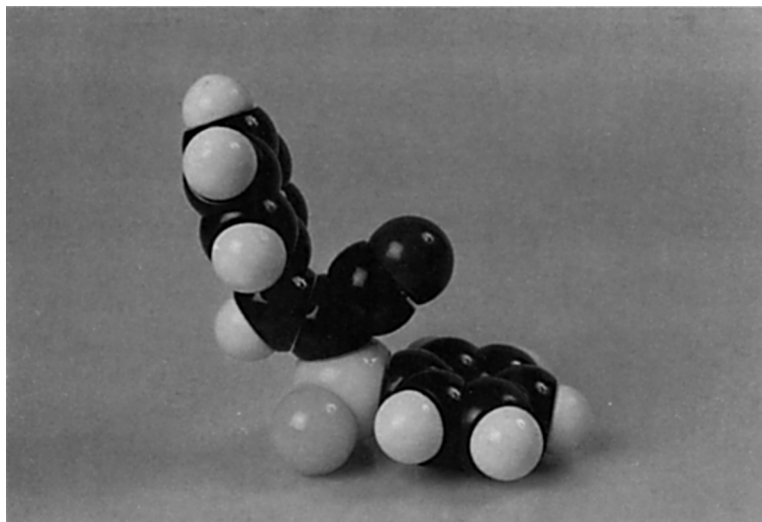


Figure 1 The monomer PSC—model of the cis isomer.



**Figure 2** The monomer PSC—model of the trans isomer.

### **Thermal Measurements**

The melting range,  $T_m$ , of the copolymers, defined as the range of temperature when the shape of the polymer particles starts to change and the temperature when drops are formed, was determined on a hot-stage microscope with a heating rate of  $4^\circ\text{C}/\text{min}$ . The glass transition temperature,  $T_g$ , was determined by the calorimetric method on a Mettler TA-3000 or on a Perkin-Elmer DSC-1B apparatus.

### **Viscosity**

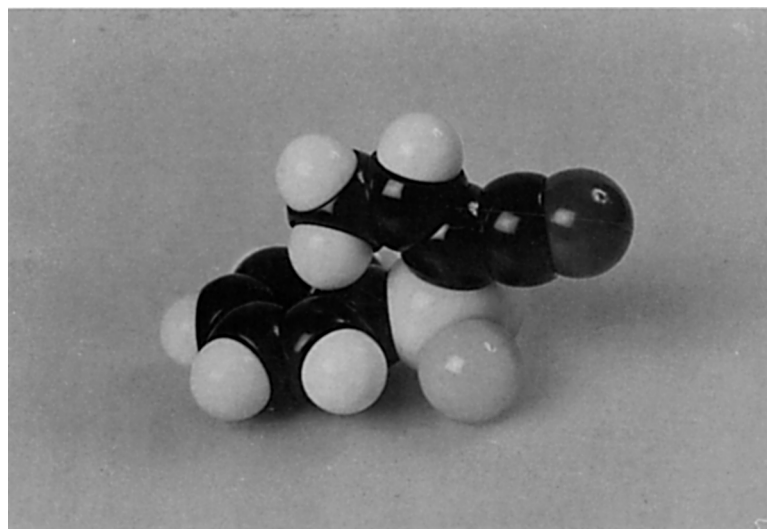
The intrinsic viscosity of the copolymers was determined from the viscosity measurements of their

solutions in THF in an Ubbelohde viscometer at  $30 \pm 0.1^\circ\text{C}$ .

## **RESULTS AND DISCUSSION**

### **Monomers—Synthesis and Structure**

The two trisubstituted comonomers, PSCR and PSC<sup>7</sup> were prepared by Knoevenagel condensations of acetaldehyde and benzaldehyde, respectively, with phenylsulfonyl acetonitrile.<sup>6</sup> For PSCR, the method of Popp and Catala<sup>8</sup> to prepare ethyl  $\alpha$ -cyanocrotonate was applied. Considering the formation of



**Figure 3** The monomer PSCR—model of the cis isomer.

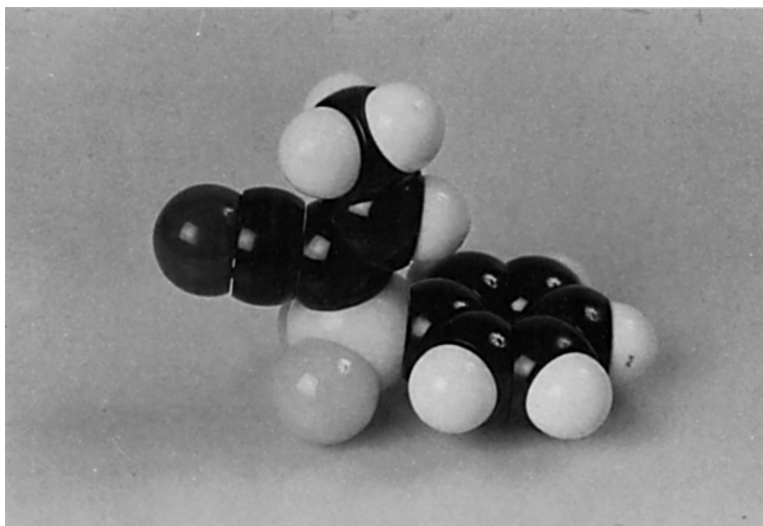


Figure 4 The monomer PSCR—model of the *trans* isomer.

*trans* isomers of  $\alpha,\beta$ -unsaturated sulfones<sup>9a,b</sup> and the steric hindrance in the *cis* isomers of both comonomers due to  $\beta$ -substitution by the methyl and especially by the phenyl group in PSCR and PSC, respectively (Figs. 1-4), the formation of the *trans* isomers of the phenylsulfonyl group against the  $\beta$ -substituents can be assumed. Further, the <sup>13</sup>C-NMR spectra point to the presence of one isomer only for each comonomer, as there are eight absorption lines for eight carbon types in PSCR and 11 lines for 11 carbons in PSC (Table III).

### Copolymerizations

The copolymerization parameters  $r_1$  and  $r_2$  of the two monomer pairs, styrene with PSC and styrene with PSCR, were determined by the Kelen and Tüdös graphical method<sup>10</sup> (Figs. 5-7) according to the equation

$$\eta = r_1\xi - r_2/\alpha(1 - \xi) \quad (1)$$

and also by the least squares method<sup>10</sup> and they are

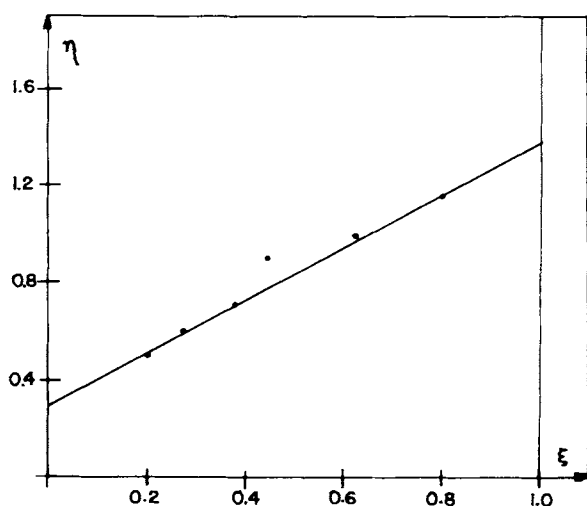


Figure 5 Copolymerization of styrene ( $M_1$ ) with PSC ( $M_2$ ) in THF solution. Determination of  $r_1$  and  $r_2$  according to Kelen and Tüdös.

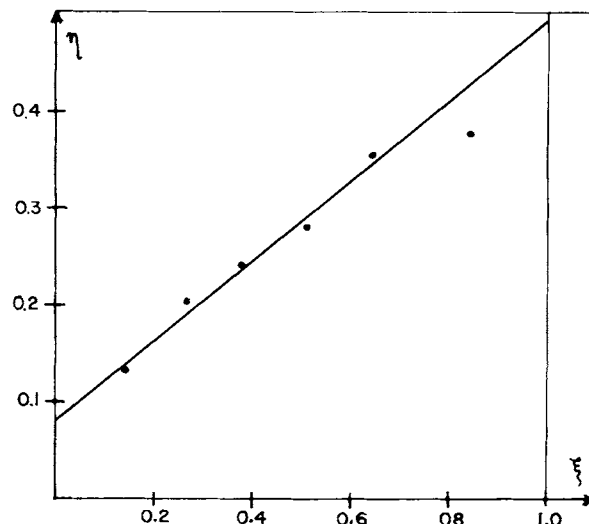
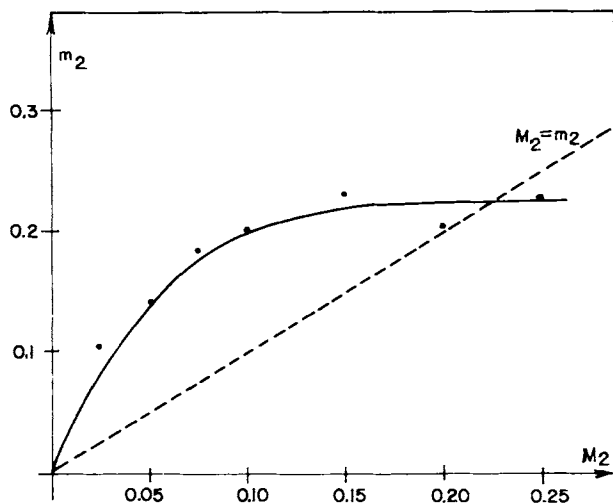


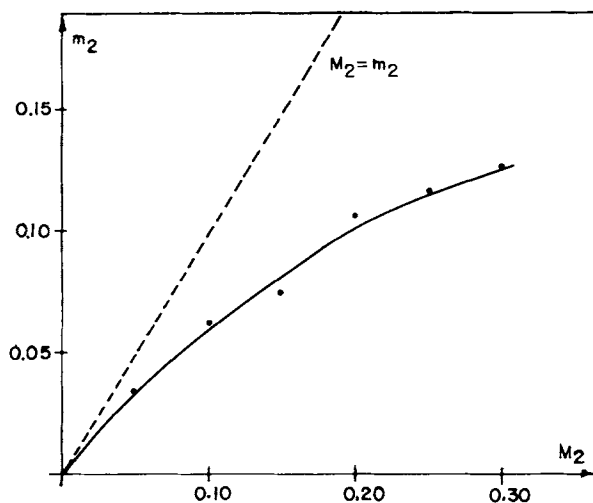
Figure 6 Copolymerization of styrene ( $M_1$ ) with PSCR ( $M_2$ ) in THF solution. Determination of  $r_1$  and  $r_2$  according to Kelen and Tüdös.







**Figure 8** Copolymerization of styrene ( $M_1$ ) with PSCR ( $M_2$ ) in bulk. Copolymer composition  $m_2$  vs. the mole fraction  $M_2$  of monomer feed.



**Figure 10** Copolymerization of styrene ( $M_1$ ) with PSCR ( $M_2$ ) in THF solution. Copolymer composition ( $m_2$ ) vs. the mole fraction  $M_2$  of monomer feed.

PSCR, the comonomer PSCR content ( $m_2$ ) in the copolymer is always lower than in the feed (Fig. 10). This behavior is surprisingly different from the copolymers of styrene with various esters of  $\alpha$ -cyano-cinnamic acid,<sup>1,2</sup> which all form azeotropes at an ester content of about 30 mol %, although there is definitely a structural resemblance between these esters and PSCR.

The rate of copolymerization of the two comonomers with styrene is lower in comparison with the homopolymerization rate of styrene. The rate re-

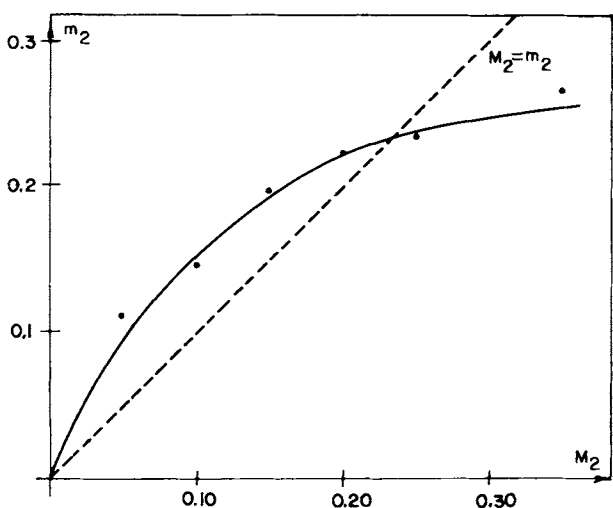
duction for the 2 three-substituted monomers PSCR and PSCR in THF solution is quite similar and should be ascribed to steric hindrance in addition to the rate-reducing effect of sulfur-containing monomers.<sup>15</sup> Yet, the rate for the pair styrene-PSCR in bulk is, as expected, higher than when performed in THF solution. In both systems, the rate decreases with rising sulfonyl-comonomer content.

## Characterization of the Copolymers

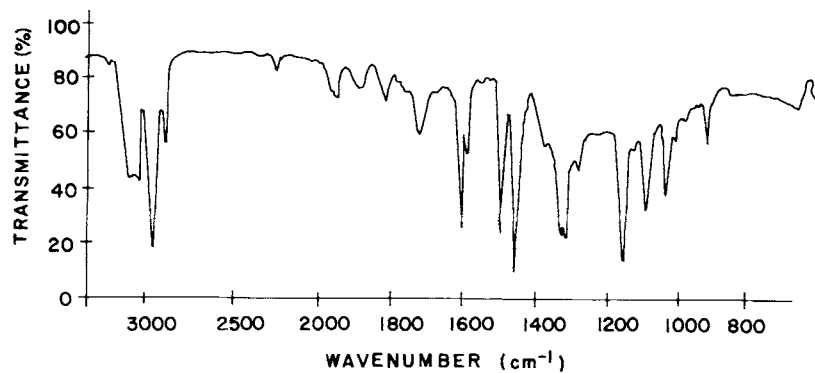
### IR and Proton NMR Spectra

The IR spectra of the two copolymers (Figs. 11 and 12) show all the typical absorptions of the phenyl group at 1600, 1585, and 1500  $\text{cm}^{-1}$  and of the methylene and methine groups at 2960–2850  $\text{cm}^{-1}$  of polystyrene.<sup>16</sup> The peaks at 2240  $\text{cm}^{-1}$  of the nitrile group and at 1320–1340  $\text{cm}^{-1}$  of the sulfone group prove the presence of the nitrile-sulfonyl comonomers in the respective copolymers. Their intensities rise with increasing comonomer content. The peak at 1390  $\text{cm}^{-1}$  in the styrene-PSCR system (Fig. 12) is attributed to the methyl group in the PSCR comonomer.

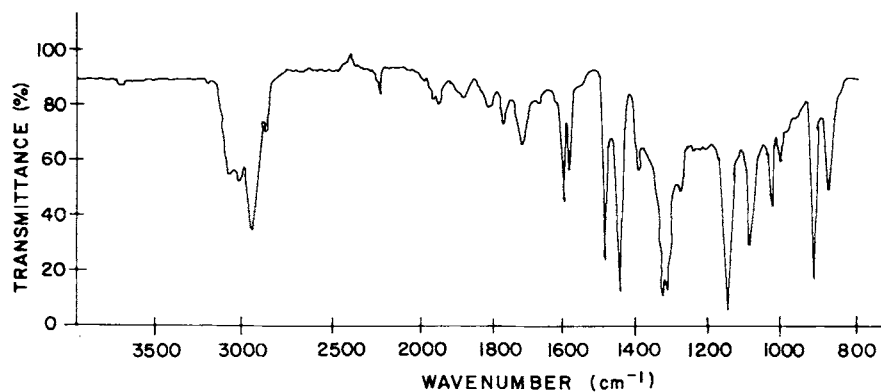
The proton NMR spectra of the two copolymers (Figs. 13 and 14) show superposition and widening of the absorptions of the aromatic and of the aliphatic regions from both styrene and each comonomer, respectively. Thus, the aromatic absorptions of the copolymers appear in a wider range (7.8–6.2 ppm) than in homopolystyrene (7.2–6.2 ppm).<sup>17</sup> The absorption of the methyl group (0.9 ppm) in the



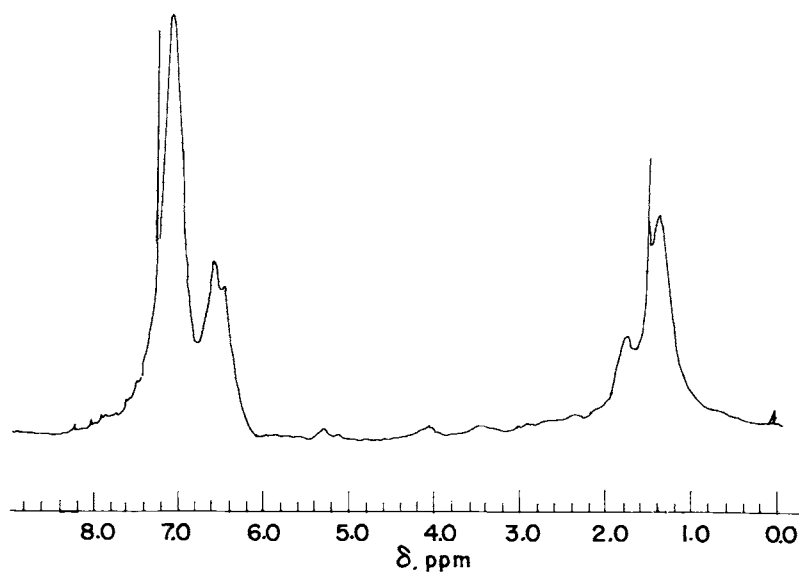
**Figure 9** Copolymerization of styrene ( $M_1$ ) with PSCR ( $M_2$ ) in THF solution. Copolymer composition ( $m_2$ ) vs. the mole fraction  $M_2$  of monomer feed.



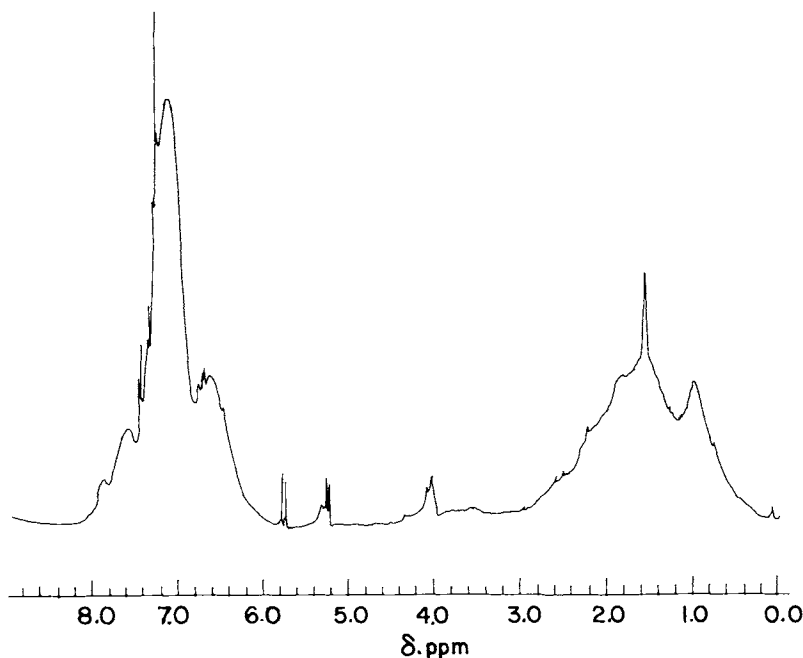
**Figure 11** Copolymerization of styrene with PSC. Infrared spectrum of the copolymer NSB (13).



**Figure 12** Copolymerization of styrene with PSCR. Infrared spectrum of the copolymer NSM (26).



**Figure 13** Copolymerization of styrene with PSC. Proton NMR spectrum of the copolymer NSB (13).



**Figure 14** Copolymerization of styrene with PSCR. Proton NMR spectrum of the copolymer NSM (26).

copolymer styrene-PSCR (Fig. 14) affects a widening of the aliphatic band (2.4–0.8 ppm) in comparison to the aliphatic ranges of the copolymer styrene-PSC (Fig. 13) and of homopolystyrene (2.4–1.2 ppm).<sup>17</sup>

### Thermal Behavior

The melting ranges of the copolymers of styrene with the two trisubstituted comonomers PSC and PSCR are somewhat higher than that of homopolystyrene (115–145°C) and rise with increasing comonomer content. For the pair styrene-PSCR copolymerized in bulk,  $T_m$  reaches up to 155–175°C, at a  $m_2$  content of about 23 mol % and up to 120–160°C for  $m_2 = 27$  mol % when made in solution; in the system styrene-PSC,  $T_m$  of 143–155°C was obtained for an  $m_2$  content of about 13 mol %. The glass transition temperature for the pair styrene-PSC increases with increasing PSC content up to 120°C at about 13 mol % PSC against a  $T_g = 103$ °C for homopolystyrene. This increase can be attributed mainly to the bulkiness of the comonomer and to steric hindrance. Yet, this value is rather low in comparison to those of the copolymers of styrene with two trisubstituted comonomers of similar “size”—benzyl cyanocinnamate, having a  $T_g$  of about 140°C for 18 mol % comonomer or *n*-butyl cyanocinnamate (13 mol %) with a  $T_g = 130$ °C (Ref. 2)—and is probably due to

the rather low molecular weight of the copolymer, as indicated by its low intrinsic viscosity. For the copolymer styrene-PSCR made in THF solution, the increase of  $T_g$  is, as expected, still smaller—114–116°C for up to 26 mol % PSCR, as this comonomer is less hindered than is PSC—but when made in bulk, a  $T_g$  of 126°C for  $m_2 = 20$  mol % was measured.

### Intrinsic Viscosity

The generally low values of the intrinsic viscosity of the investigated systems in comparison to homopolystyrene (Tables V–VII) are to be ascribed to transfer reactions of styrene radicals with the sulfonyl group.<sup>5a</sup>

Summarizing, the two sulfonyl-containing monomers of this investigation affect a rate reduction in the free radical-initiated copolymerization with styrene in comparison with the homopolymerization of styrene. The resulting copolymers have rather low molecular weights, as derived from their intrinsic viscosity, which may be ascribed mainly to transfer reactions by the sulfonyl group.

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