Copolymerization of Styrene with Sulfur Dioxide. Determination of the Monomer Sequence Distribution by Carbon-13 NMR

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ABSTRACT: We have prepared poly(styrene sulfone)'s containing 57 to 86 mol % styrene by free-radical copolymerization of styrene with sulfur dioxide at temperatures from 0 to 60 °C. The ^{13}C spectra of these copolymers are reported for the first time, and the multiple resonances observed for the methine, methylene, and quaternary carbons are assigned to monomer triad sequences. These spectra allow an accurate determination of the monomer sequence distribution, which shows that 1:1 alternating sequences are not formed above about 40 °C. Poly(styrene sulfone)'s prepared above this temperature have variable-length styrene sequences, containing a minimum of two styrene units. Those prepared near room temperature have a highly regular monomer sequence distribution, with a macroscopic compositional average of two styrene units for every sulfur dioxide unit. These results cannot be explained by a simple first-order Markov copolymerization mechanism, and an alternative mechanism involving depropagation reactions is proposed.

Sulfur dioxide, although it does not homopolymerize, participates in a wide variety of free-radical copolymerizations with unsaturated monomers to form polysulfones.[3] Because olefins do not homopropagate under conditions suitable for polysulfone formation, poly(olefin sulfone)'s have a regular alternating 1:1 composition which is independent of the copolymerization temperature and monomer feed ratio. Ethylene will form a nonalternating polysulfone, but only at very high pressures (typically greater than 800 atmospheres), which favor the formation of sequences of ethylene units.[4]

In contrast, several vinyl monomers form polysulfones of variable composition, i.e., the composition depends on temperature and the monomer feed ratio. These monomers can compete effectively with sulfur dioxide for addition to their own radicals during copolymerization. Such monomers are styrene[5,6] and several of its para derivatives,[7-10] acrylamide,[11] chloroprene,[12] vinyl bromide,[13] and vinyl chloride.[13,15] Some vinyl monomers apparently do not form polysulfones, notably methyl acrylate,[3a] methyl methacrylate, acrylonitrile and α-methylstyrene,[16] and 2- and 4-vinylpyridine.[14] In fact, these monomers may homopolymerize in liquid sulfur dioxide solvent by radical or cationic mechanisms.

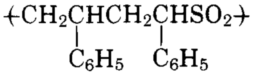
Olefin–sulfur dioxide polymerizations provide a striking demonstration of the ceiling temperature phenomenon.[17] The ceiling temperature (T_c) is defined as that temperature at which the free-energy change for polymerization is zero. In kinetic terms, the rate for propagation exceeds that for depropagation below T_c but becomes equal to it at T_c (the activation energy for propagation is usually much smaller than that for depropagation), so that the net rate of polymerization is zero. This effect was first observed in 1938 for the copolymerization of isobutene with sulfur dioxide[18] but was not correctly explained in terms of the position of the propagation–depropagation equilibrium until 10 years later.[19] Although depropagation reactions can strongly affect the rate of formation of poly(α-olefin sulfone)'s, they obviously play no part in determining copolymer composition in these systems, since this is invariant.

The kinetics of the copolymerization of olefins with sulfur dioxide, as well as the formation of strictly alternating 1:1 polysulfones, have suggested to several authors that propagation proceeds by equimolar olefin–sulfur dioxide complexes.[20-23] For those vinyl monomers which form variable-composition polysulfones, however, depropagation reactions and the possible participation of complexes can affect not only the rate of copolymerization but also the copolymer composition. In this regard, the dependence of the compositions of styrene and vinyl chloride polysulfones, for example, on the monomer feed ratio at various temperatures is not explicable by the simple first-order Markov (Lewis–Mayo[24]) copolymerization scheme, a clear indication that more complex mechanisms are involved. These may include penultimate effects, the participation of complexes, depropagation reactions, or a combination of these.

The first detailed kinetic investigation of the styrene–sulfur dioxide copolymerization was made by Barb in 1952.[5,25] The data were interpreted by a mechanism involving complex participation, although in a later paper Barb modified this scheme to include depropagation reactions.[26] Subsequently, Walling showed that the same kinetic features were compatible with a copolymerization scheme involving depropagation without complex participation.[27] In their early publications in the field, Matsuda and co-workers claimed that poly(styrene sulfone) had a 2:1 composition irrespective of copolymerization conditions; they attributed this to an effective homopolymerization of a 2:1 styrene–sulfur dioxide complex.[28,29] However, they showed in a later paper that an equimolar complex was formed and they ruled out propagation reactions involving this complex. Rather, they proposed a novel depropagation step for sulfonyl radicals involving the concerted addition of styrene with loss of the terminal sulfur dioxide unit, for which they coined the term "second-order" depropagation.[30]

Several groups have used γ radiation to initiate the formation of poly(styrene sulfone). Hummel et al. investigated the copolymerization over the temperature range −78 to 30 °C.[6] They found that at low temperatures a concurrent ionic homopolymerization of styrene also took place, which could be selectively inhibited by a number of compounds. At −78 °C, the copolymers were nearly equimolar (52 mol % styrene content), and this composition varied little with monomer feed ratio. However, at higher copolymerization temperatures, the polysulfones contained larger proportions of styrene, which showed a dependence on the monomer feed ratio. The data were consistent with either Barb's[5] or Walling's[27] mechanisms but could not distinguish the two. Yemin and Martin[31] also studied the radiation-induced copolymerization over a range of temperatures and monomer feed ratios and used Walling's scheme to interpret their kinetic and compositional data. It has also been claimed that γ radiation will initiate the copolymerization in the solid state.[32]

The above investigations show that kinetic and compositional data alone cannot distinguish and test alternative copolymerization models involving more complex steps than those in the Lewis–Mayo model. More stringent tests of these models can be made with monomer sequence distribution information,[33-35] which can be obtained from high-resolution NMR studies. To date, the only variable-composition polysulfones which have been examined in this way are those formed by ethylene,[36] vinyl chloride[37] and styrene.[10,38] Iino et al.[10] reported the first NMR spectra of poly(styrene sulfone)'s having several compositions, but these were ^1H spectra obtained at 60 MHz and were poorly resolved, providing no detailed sequence information. An alternative approach adopted by these authors was to subject a 2:1 copolymer to random degradation by potassium *tert*-butoxide, which gave products indicating that this copolymer consisted predominantly of the repeat sequence



$$-\!\!\left(CH_2\underset{C_6H_5}{CH}CH_2\underset{C_6H_5}{CH}SO_2\right)\!\!-$$

This finding was independently confirmed by Hummel and Schüddemage from results obtained by pyrolysis gas chromatography and mass spectrometry.[39] Such a regular monomer sequence distribution is unusual for free-radical copolymers, which normally have a broad distribution of sequence lengths, and is further evidence that a first-order Markov description of the styrene–sulfur dioxide copolymerization is inappropriate.

In a more recent paper, Iino et al. were able to obtain some monomer sequence information from 60 MHz ^1H spectra of poly(styrene sulfone)'s which had been selectively deuterated.[38] Replacement of either the methylene or methine protons by deuterium allowed better resolution of the backbone region than that observed in the spectra of fully protonated copolymers, but nevertheless peak overlap persisted and the poor signal-to-noise ratio for these single-scan CW spectra did not allow accurate quantitative analysis.

In this paper we report the first examination of the monomer sequence distribution in poly(styrene sulfone)'s by ^{13}C NMR. Triad monomer sequences are clearly resolved and unambiguously assigned, allowing a reliable determination of the sequence distribution. Configurational sequence effects are also observed, and spectra obtained at 90.52 MHz show a distinct improvement in resolution over those at 25.16 MHz. A striking feature is the absence of alternating SMS sequences (S = sulfur dioxide, M = styrene) in all copolymers prepared at temperatures above approximately 40 °C; this finding has a significant bearing on the choice of the appropriate copolymerization scheme. We have also obtained the 360 MHz ^1H spectrum of poly(styrene-β,β-d_2 sulfone), which is sufficiently well resolved to provide both monomer and configurational sequence information.

Experimental Section

Materials. Styrene was distilled at reduced pressure in a nitrogen atmosphere. Sulfur dioxide (Matheson Gas Products, anhydrous grade) was passed through a phosphorus pentoxide column and distilled under vacuum. Styrene-β,β-d_2 was obtained from Merck and Co. and vacuum distilled. Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried in a vacuum desiccator.

Copolymerization. All copolymerizations were carried out in bulk, with the monomer mixture sealed in glass ampules. A weighed amount of AIBN was added to the ampules (where appropriate) and the required volume of styrene was pipetted in. The ampule was then attached to a vacuum manifold and its contents were outgassed by several freeze–thaw cycles. A known quantity of sulfur dioxide (measured by the pressure exerted in a calibrated bulb and by the liquid volume at −78 °C) was distilled into the ampule, which was then sealed. The contents were mixed by shaking and the ampule was placed in a thermostatted water bath at the desired temperature. The copolymerizations at 0 °C were conducted in an ice–water bath and initiated by ^{60}Co γ radiation. These mixtures contained ca. 4 mol % acetone to inhibit the ionic homopolymerization of styrene. After a suitable reaction time, the ampules were chilled in liquid nitrogen and cut open, and the homogeneous contents were transferred to a large excess of methanol, from which the polysulfone was recovered. The polysulfone was reprecipitated from dioxane or chloroform solution and dried under vacuum at ambient temperature. Table I lists the details of the copolymerizations.

Table I
Details for the Preparation of Poly(styrene sulfone)'s

Copolymer No.	Mol % styrene in monomer feed[a]	Temp, °C	Mol % AIBN	Dose, Mrad	Yield, wt %
1	29[b]	0		21	30
2	30	0		4.3	1.7
3	68	40	0.1		10
4	69	60	2.0		29
5	90	60	2.8		26

[a] Arithmetic mean of initial and final comonomer compositions. [b] Styrene-β,β-d_2.

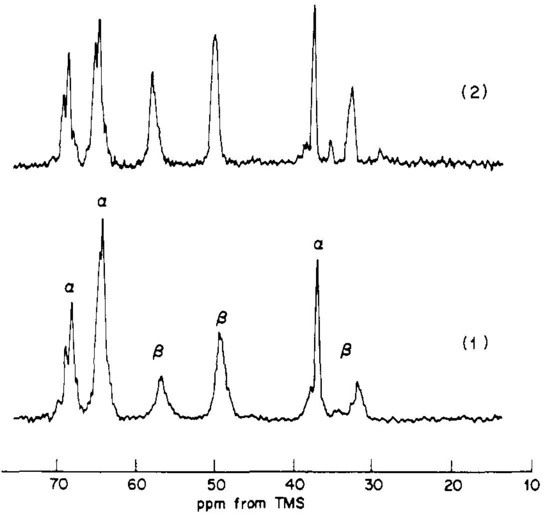


Figure 1. $^{13}C\{^1H\}$ spectra (25.16 MHz) showing backbone resonances in poly(styrene sulfone)'s 1 and 2. Spectra observed at 55 °C for 25% w/v solutions in chloroform-*d*. Pulse width 65 μs (60° flip angle), pulse delay 1.2 s, 4 kHz spectral window with pulse positioned 70 Hz upfield from TMS, 8K data points (FID), 13 000 and 20 000 scans, respectively, 1.5 Hz digital broadening. Copolymer compositions: **1**, 57 mol % styrene-β,β-d_2, and **2**, 58 mol % styrene.

NMR Spectra. The NMR spectra were recorded in the pulsed Fourier transform mode, using a modified Varian XL-100[40] and a Bruker HX-360 spectrometer. The polysulfones were observed as 10 to 25 wt % solutions in chloroform-*d* at 55 °C. All chemical shifts are referenced to internal tetramethylsilane (TMS). Further details are given in the appropriate figure captions. Peak areas for the sequence distribution analysis were measured by cutting out and weighing peaks which had been traced onto drawing paper.

Results and Discussion

Carbon-13 Spectra. Figure 1 shows the 25.16 MHz backbone ^{13}C resonances of copolymers 1 and 2, i.e., those prepared at 0 °C by γ irradiation of mixtures containing styrene-β,β-d_2 and styrene, respectively. The areas of all methylene carbons in the spectrum of the poly(styrene-β,β-d_2 sulfone) are smaller than those for the methine carbons, owing to a reduced Overhauser enhancement. The peak heights of the methylene carbons are also reduced somewhat by broadening due to deuterium coupling.[41] These observations provide a convenient means of assigning the backbone resonances.

Monomer Sequences. The assignments of these peaks to particular monomer sequences are based on their relative intensities as a function of the macroscopic copolymer com-

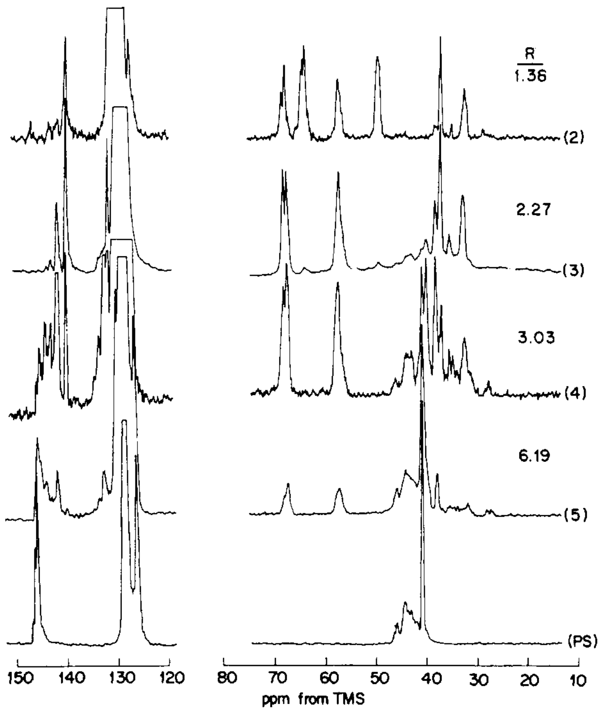


Figure 2. $^{13}C\ \{^1H\}$ spectra (25.16 MHz) of poly(styrene sulfone)'s with compositions as shown by the *R* values (styrene/sulfur dioxide in the copolymer). Spectra observed with the instrumental settings given in the caption to Figure 1, with chloroform-*d* as solvent at 55 °C. ^{13}C spectrum of atactic polystyrene (PS) observed as a 20 wt % solution in cyclohexane-d_{12} at 77 °C (3000 scans, 4 kHz window, 16K data points for FID, 2.5 s pulse delay).

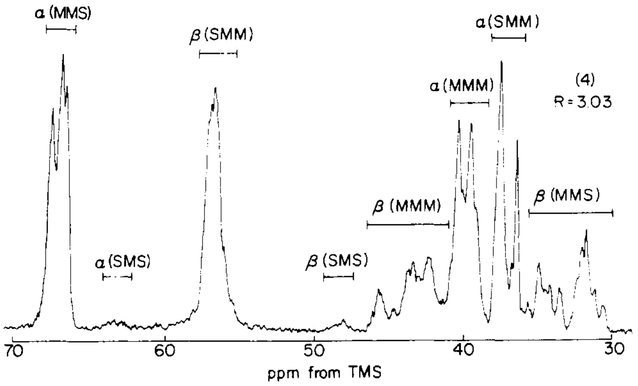


Figure 3. Assignment of the triad monomer sequences for the methine (α) and methylene (β) backbone carbons in the 90.52 MHz ^{13}C spectrum of poly(styrene sulfone) with $R = 3.03$ (sample 4). Spectrum observed at 55 °C for a 30% w/v solution in chloroform-*d*; 40 000 scans, 15 μs pulse width (90° flip angle), 10.869 kHz spectral window, 8K data points (FID), zero digital broadening, 1.5 s pulse interval. The spectrum shown represents a 4.2 kHz expansion of the backbone resonances. S = SO_2, M = styrene in the directional sense $C_\beta \rightarrow C_\alpha$.

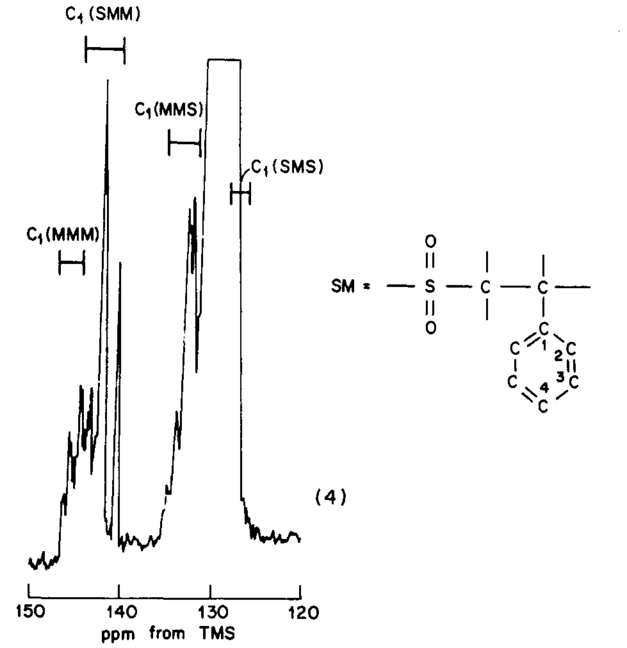


Figure 4. Assignments for the quaternary carbon resonances to triad monomer sequences in the 25.16 MHz ^{13}C spectrum of polysulfone 4. Instrumental settings given in the caption to Figure 1.

position *R*; *R* is the ratio of total styrene to total sulfur dioxide in the copolymer. Figure 2 shows the complete ^{13}C spectra of copolymers 2 to 5, with the ^{13}C spectrum of atactic polystyrene (PS) for comparison. The multiplicity of peaks observed in the backbone region for the α and β carbons (α = methine, β = methylene) indicates that monomer triad sequences are resolved.[42]

The positions of MMM triad resonances (M = styrene in the directional sense $C_\beta \rightarrow C_\alpha$) are established from the spectrum of polystyrene, the sharp peak at high field being due to the α carbon.[43] Owing to the inductive effect of the sulfone group, all α-carbon resonances in monomer sequences derived from MS dyads and all β-carbon resonances derived from SM dyads appear at lower field than those derived from SM and MS dyads, respectively. Further, with increasing *R*, the areas of these resonances must decrease relative to those for MMM triads. These considerations allow us to make the assignments shown in Figure 3 for the backbone region, using the 90.52 MHz ^{13}C spectrum of polysulfone 4 as a convenient example. The quaternary (aromatic C_1) carbon resonances were assigned by a similar rationale and are shown in Figure 4 for polysulfone 4 at 25.16 MHz. The spectra show that a sulfone group in the β position exerts a shielding influence compared to a carbon in this position.[44] The above assignments are summarized in Table II.

From these assignments we can derive the unconditional probabilities of occurrence of the five possible monomer triad sequences, as shown in Table III. Only the backbone carbon resonances were employed for quantitative purposes, as the T_1 values of the quaternary carbons are considerably longer, making differential saturation effects likely with the pulse intervals employed. The statistical analysis of the monomer sequence distribution was carried out following standard theory.[34,46,47] Denoting the unconditional probability of occurrence of any sequence of *n* monomer units, X^n, by $p(X^n)$, the following relations must apply:

$$p(M) + p(S) = 1 \tag{1}$$

$$p(X^nM) + p(X^nS) = p(X^n) \tag{2}$$

$$p(MX^n) + p(SX^n) = p(X^n) \tag{3}$$

From (2) and (3), letting $X^n = M$:

$$p(MS) = p(SM) \tag{4}$$

$$p(MMS) = p(SMM) \tag{5}$$

In all copolymerizations with sulfur dioxide:[48]

$$p(SS) = p(SSS) = p(SSS\ldots) = 0 \tag{6}$$

Therefore, from eq 2:

$$p(M) = p(MM) + p(MS) = p(MMM) + p(MMS) + p(MSM) \tag{7}$$

Table II
Chemical Shift Range for the Methine, Methylene, and Quaternary Carbon Resonances in Various Monomer Triad Sequences in Poly(styrene sulfone)'s

Monomer sequence	Chemical shift range, ppm from TMS C_α	C_β	C_1
SMS	62.46–65.72	48.24–50.44	126.55–127.66
SMM	35.94–38.61	55.45–57.93	139.59–143.75
MMS	66.27–69.05	30.21–35.94	131.32–134.88
MMM	38.61–40.56	40.56–48.15	143.75–147.12

Table III
Analysis of Macroscopic Composition and Triad Monomer Sequence Distribution in Poly(styrene sulfone)'s from ^{13}C NMR Results

Copolymer No.	Triad monomer sequence Unconditional probability SMS	MSM[b]	SMM	MMS	MMM	p(M)	R[a]
1	0.289	0.430	0.141	0.141	0.000	0.57	1.33
2	0.260	0.420	0.160	0.160	0.000	0.58	1.38
3	0.013	0.306	0.293	0.293	0.095	0.69	2.27[c]
4	0.000	0.248	0.248	0.248	0.255	0.75	3.03
5	0.000	0.139	0.139	0.139	0.582	0.86	6.19

[a] $R = p(\mathrm{M})/p(\mathrm{S}) = p(\mathrm{M})/\{1 - p(\mathrm{M})\}$. [b] Not observable by ^{13}C NMR. However, $p(\mathrm{MSM}) = p(\mathrm{MS}) = p(\mathrm{SMS}) + p(\mathrm{MMS})$. [c] Microanalysis: 11.2, S; 6.1, H; from which $R = 2.2$.

The ratio of styrene to sulfur dioxide in the copolymer is given by:

$$R = p(\mathrm{M})/p(\mathrm{S}) = p(\mathrm{M})/\{1 - p(\mathrm{M})\} \quad (8)$$

and the mole percent of styrene content is equal to $100p(\mathrm{M})$.

Values of p(M) and R derived by eq 7 and 8 are also shown in Table III. The monomer sequence assignments for the backbone region are supported by two results: (i) the adherence of the data to eq 5, and (ii) the excellent agreement between the derived R values and those obtained from copolymer composition–monomer feed composition curves drawn at the appropriate temperatures from literature data. The comparison of the macroscopic composition data from this work with that from the literature is shown in Table IV.

Proton Spectra. The 360 MHz ^{1}H spectrum of poly(styrene-β,β-d_2 sulfone) with $R = 1.33$ (i.e., sample 1) is shown in Figure 5. The signal-to-noise ratio and resolution of this spectrum are much greater than reported at 60 MHz for an equivalent copolymer (Figure 1, spectrum e in ref 38). The assignments shown in Figure 4 are the same as those given by Iino et al.,[38] from which we obtain the following unconditional sequence probabilities: $p(\mathrm{SMS}) = 0.280$, $p(\mathrm{MSM}) = 0.427$, $p(\mathrm{SMM}) = p(\mathrm{MMS}) = 0.147$, and $p(\mathrm{MMM}) = 0$. These values are in excellent agreement with those derived from the corresponding ^{13}C spectrum (Table III), providing a further measure of self-consistency in the assignments and analysis. It is evident that for sequence analysis the ^{13}C spectra are superior to the ^{1}H spectra, even when the latter are obtained from selectively deuterated polysulfones at high observing frequency, due to the greater separation of carbon resonances in the various monomer sequences.

Fine Structure. The resonances assigned to monomer triad sequences show considerable fine structure or broadening in both the ^{13}C and ^{1}H spectra of the poly(styrene sulfone)'s. This is due to configurational sequence effects, higher order monomer sequences (tetrads, pentads, etc.), or to a combination of these.

Table IV
Comparison of Composition of Poly(styrene sulfone)'s as Measured by ^{13}C NMR with Literature Values for Copolymers Prepared under Identical Conditions

Copolymer No.	Copolymer Composition,[a] mol % styrene This work[b]	Lit.[c]	Lit. Ref
2	58	58	6
3	69	69[d]	6, 10, 29
4	75	74	25, 26
5	86	81	25, 26

[a] $100p(\mathrm{M})$. [b] From ^{13}C NMR analysis. [c] Literature data plotted as composition curves. [d] Value interpolated from literature data at room temperature and at 50 °C.

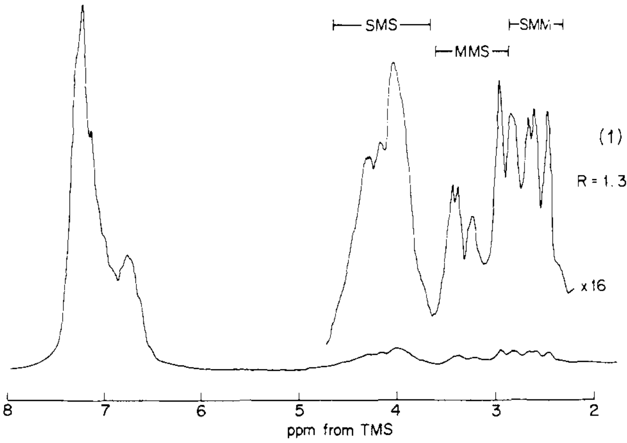


Figure 5. ^{1}H Spectrum (360 MHz) of poly(styrene-β,β-d_2 sulfone) with $R = 1.3$ (sample 1). Spectrum observed at 55 °C for a 10% w/v solution in chloroform-d. FT mode, 100 scans, 13 μs pulse width (90° flip angle), 3623 Hz spectral window, 16K points (FID), zero digital broadening.

It is known that the quaternary and methylene carbons in polystyrene are stereosensitive, while the methine is not. The quaternary carbon shows pentad splitting,[49] and the methylene carbon shows hexad splitting.[50] This stereosensitivity is responsible for the observed fine structure of the C_1(MMM) and β(MMM) ^{13}C resonances in poly(styrene sulfone)'s. The fine structure of the backbone ^{13}C resonances is particularly well resolved at 90.52 MHz, as shown by Figure 3. Here we observe that the α(MMM) resonance is a doublet, and since this carbon is stereoinsensitive in polystyrene, this doublet splitting is very probably due to higher order monomer sequences in the polysulfone. This is supported by the observation that the high-field component of this doublet (39.62 ppm) decreases in intensity with increasing R, while the low-field component (40.49 ppm) increases in intensity (Figure 2). A reasonable assignment therefore is M*M*MS at 39.62 ppm and M*M*MM at 40.49 ppm (the styrene unit containing the observed α carbon is *underlined*).

Figure 3 also shows that α(SMM), α(MMS), and β(MMS) are split mainly into doublets. The α(SMM) doublet components at 36.48 and 37.64 ppm can be assigned to S*M*MS and S*M*MM, respectively, following the same rationale used to assign the components of the α(MMM) doublet. The relative intensities of the components of the α(MMS) doublet do not change sufficiently with R to be due to higher order monomer sequences and can therefore be assigned to configurational dyad sequences. The dyads must involve the asymmetric centers in either the MM or MSM sequences, although we cannot decide which from the present evidence. The fact that three lines are clearly resolved at 90.52 MHz may indicate that triad stereosequences (in the monomer sequence M*M*SM) need to be considered, although some effect of tetrad monomer sequences cannot be excluded. A similar conclusion can be drawn regarding the β(MMS) resonance. Although the main doublet is probably due to the two configurational placements in the MM dyad, the observation of at least nine resolved lines at 90.52 MHz indicates a complex combination of monomer and stereosequence splittings of this resonance.

The quaternary carbon resonances (Figure 4) show considerable splitting, although this is masked to a large extent in the MMS and SMS sequences by overlap with the intense resonances of the other aromatic carbons (i.e., ortho, meta, and para). However, the SMM resonance is principally a doublet which changes in relative intensity in a regular manner with changing R. This suggests the assignment S*M*MS at 139.90 ppm and S*M*MM at 141.72 ppm. The quaternary MMM resonance is split mainly by stereosequential effects, as discussed above, although the fact that the dispersion of chemical shifts is greater than in polystyrene shows that monomer sequences also have some influence.

The 360 MHz ^{1}H spectrum of poly(styrene-β,β-d_2 sulfone) also shows splitting beyond the triad monomer sequence level (Figure 5). Whereas the SMS resonance is mainly broadened, undoubtedly due to configurational dyad and higher monomer sequence effects, both the MMS and SMM resonances are each well resolved into four components. We did not have copolymers of poly(styrene-β,β-d_2 sulfone)'s with R other than 1.33 and so have not examined the effect of this variable on the relative intensities of these components. We are therefore unable to make any definite assignments beyond those for the monomer triad sequences in the ^{1}H spectrum.

Copolymerization Mechanism. The number fraction of M sequences with length n is defined as:[34]

$$N_{\mathrm{M}}(n) = \frac{p(\mathrm{SM}^n\mathrm{S})}{\sum_{n=1}^{\infty} p(\mathrm{SM}^n\mathrm{S})} \qquad (9)$$

from which

$$R = \sum_{n=1}^{\infty} nN_{\mathrm{M}}(n) \qquad (10)$$

It can be shown[46] that $\sum_{n=1}^{\infty} p(\mathrm{SM}^n\mathrm{S}) = p(\mathrm{MS})$; hence, in the present case where $p(\mathrm{MS}) = p(\mathrm{S})$, we have

$$N_{\mathrm{M}}(n) = p(\mathrm{SM}^n\mathrm{S})/p(\mathrm{S}) \qquad (11)$$

The values of $N_{\mathrm{M}}(1)$ derived by eq 11 are plotted as a function of the polymerization temperature T_{p} in Figure 6.[51]

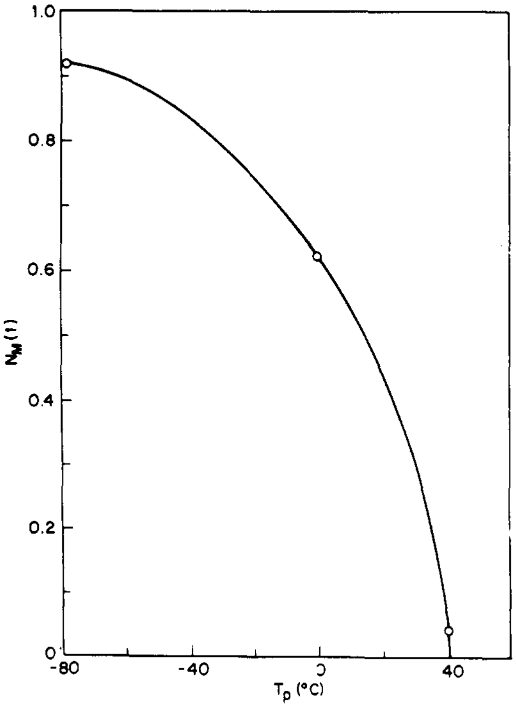


Figure 6. Plot of the number fraction of SMS sequences, $N_{\mathrm{M}}(1)$, as a function of the polymerization temperature for poly(styrene sulfone)'s.

This plot illustrates the most significant result from this study with regard to the elucidation of the copolymerization mechanism, i.e., the rapid decrease in $N_{\mathrm{M}}(1)$ with an increase in T_{p} to a value of zero for all poly(styrene sulfone)'s prepared above about 40 °C. This result is in apparent disagreement with the SMS sequence probabilities tabulated by Iino et al. for all poly(styrene sulfone)'s prepared at 50 °C or above (ref 38, Table I[52]). However, a close examination of their published ^{1}H spectra reveals that SMS sequences (as monitored by the methine proton resonance at 4 ppm; ref 38, Figure 1) are absent for poly(styrene sulfones)'s prepared above 30 °C, as we have observed by ^{13}C NMR.

A second interesting result from the present study is the high degree of regularity in the monomer sequence distribution in the poly(styrene sulfone) prepared at 40 °C (sample 3). The ^{13}C data demonstrate that this polysulfone, with a macroscopic compositional average of 2.27:1, contains a number fraction of SMMS sequences of 0.72, with the number fractions of SMS and SMMMS sequences being only 0.04 and 0.24, respectively. This distribution shows a strong bias in favor of the regular structure $\mathrm{+SMM+}_n$. It can be expected that this bias is even stronger for the poly(styrene sulfone) with R exactly equal to two, as reported from pyrolytic[39] or chemical degradation[10] studies of this material. In this respect, styrene is closely analogous to vinyl chloride, which forms a 2:1 polysulfone in which the number fraction of SVVS sequences (V = vinyl chloride) approaches unity.[53]

The copolymerization scheme we favor on the basis of our results is:

$$\sim\mathrm{SM}\cdot + \mathrm{S} \overset{K_1}{\rightleftharpoons} \sim\mathrm{SMS}\cdot \qquad (12)$$

$$\sim\mathrm{MS}\cdot + \mathrm{M} \overset{K_2}{\rightleftharpoons} \sim\mathrm{SM}\cdot \qquad (13)$$

$$\sim\mathrm{SM}\cdot + \mathrm{M} \xrightarrow{k_{\mathrm{p}}} \sim\mathrm{MM}\cdot \qquad (14)$$

$$\sim\mathrm{MM}\cdot + \mathrm{M} \xrightarrow{k_{\mathrm{p}}'} \sim\mathrm{MM}\cdot \qquad (15)$$

$$\sim\mathrm{MM}\cdot + \mathrm{S} \overset{K_3}{\rightleftharpoons} \sim\mathrm{MMS}\cdot \qquad (16)$$

Steps 12 and 13 are those which produce an alternating 1:1 polysulfone and occur exclusively in copolymerizations of α-olefins with sulfur dioxide.[3a] The K values are the equilibrium constants which describe the position of the propagation–depropagation equilibria and are equal to the ratio of the propagation rate constant k_{p} to the depropagation rate constant k_{d}, i.e.,

$$K = k_{\mathrm{p}}/k_{\mathrm{d}} \qquad (17)$$

Because K describes the position of equilibrium, we also have:

$$K_1 = \frac{[\sim\text{SMS}\cdot]}{[\sim\text{SM}\cdot][\text{S}]} \tag{18}$$

and

$$K_2 = \frac{[\sim\text{SM}\cdot]}{[\sim\text{SMS}\cdot][\text{M}]} \tag{19}$$

Therefore, the formation of an alternating polysulfone $+\text{SM}+_n$ from n units each of S and M is represented by a combination of eq 12 and 13, with an overall equilibrium constant $K_{\text{alt}} = K_1K_2$, i.e.,

$$K_{\text{alt}} = 1/[\text{S}][\text{M}] \tag{20}$$

where [S] and [M] are the equilibrium concentations of monomer. At the copolymerization temperature where the equilibrium monomer concentration product is unity, $K_{\text{alt}} = 1$; therefore

$$\Delta G_{\text{alt}} = -RT \ln K_{\text{alt}} = 0 \tag{21}$$

This temperature therefore corresponds to the "standard" T_c for alternating polysulfone formation.

In bulk systems the concentration of monomer is much greater than 1 mol/l., so the observed T_c at which the rate of polymerization is zero is higher (typically by about 50 °C for polysulfones) than the "standard" T_c. For the copolymerization of styrene with sulfur dioxide at −78 °C, R is approximately 1.08,[6] and so with reference to the above copolymerization scheme $K_3 > K_1K_2 \gg 1$ and $k_p \simeq k_p' \simeq 0$ at this temperature. As the temperature is raised, the product K_1K_2 must decrease and the proportion of SMS sequences in the copolymer will be vanishingly small when $K_1K_2 \ll 1$. In the bulk system, our data (Figure 6) show that the T_c at which this occurs is about 40 °C.[54]

However, in the styrene copolymerization, unlike the olefin–sulfur dioxide copolymerizations, the homopropagation steps 14 and 15 can participate to an increasing extent as the temperature is raised.[55] These reactions generate sequences of two or more styrene units, and since there is no reason to expect a significant penultimate effect on the rate of addition of styrene to the styryl radical, it is reasonable that k_p and k_p' are approximately equal. At sufficiently high temperatures it can be expected that K_3 will approach unity; this is manifested in the reduction of the sulfur dioxide content of the copolymers with increasing temperature. In the high-temperature limit, one expects only the free-radical homopolymerization of styrene in liquid sulfur dioxide to take place, as is observed near room temperature for a number of vinyl monomers with polar substituents. The above scheme also accounts for the regular $+\text{SMM}+_n$ sequence structure of the 2:1 polysulfone, which is formed under the conditions that $K_1K_2 \ll 1$ and where reaction 15 does not compete effectively with the propagation step in reaction 16. The result is a monomer sequence distribution in which the number fractions of SMS and SMMMS sequences are much smaller than that for SMMS sequences, as we have seen.

Our copolymerization scheme differs from Barb's[5] by not involving complexes and differs from Walling's[27] in that a penultimate effect for the addition of S to ∼SM· is not necessary to describe the data. It is also different from the scheme proposed by Iino et al.,[38] in that these authors invoked an unlikely depropagation step involving a concerted insertion of styrene with loss of sulfur dioxide[30] (eq 22) and did not consider depropagation of ∼SM·.

$$\sim\text{SMS}\cdot + \text{M} \rightarrow \sim\text{SMM}\cdot + \text{S} \tag{22}$$

The step shown in eq 22 is equivalent to our depropagation step 12, followed by step 14. None of these special proposals is necessary to explain the behavior of this system.

The present ^{13}C data provide the quantitative sequence data which are necessary for testing the copolymerization model. Although an analytical solution of the kinetic scheme defined by eq 12 to 16, relating the monomer feed composition to the copolymer composition and monomer sequence distribution, is quite complex, this scheme can be conveniently simulated by Monte Carlo procedures to provide the necessary results.[56] We are using this approach at present for the copolymerization of vinyl chloride with sulfur dioxide, for which we have considered an identical scheme of reactions.[57] In a future publication we plan to report a study of the solution dynamics of poly(styrene sulfone)'s by ^{13}C NMR, with special regard to the effect of the monomer sequence type on the flexibility of the chain backbone.

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(52) The labeling of the columns in Table I of ref 38 is incorrect. Using the author's notation, the column labeled T_{SO_2StSt} should read $T_{SO_2StSO_2}$, and that labeled $T_{StStSO_2} + T_{SO_2StSO_2}$ should read $T_{StStSO_2} + T_{SO_2StSt}$. The correct headings correspond to p(SMS) and p(MMS) + p(SMM), respectively, in the present notation.

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Asymmetric Induction by Interfacial Emulsion Copolymerization of Styrene with Maleic Acid in the Presence of Lecithin

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ABSTRACT: The copolymerization of styrene (St) with maleic acid (MAc) was carried out in the oil/water interfacial system at 40 °C, using potassium persulfate (KPS) as an initiator in a sealed tube. The addition of lecithin, which is a naturally occurring zwitterionic surface active and optically active substance, to this interfacial copolymerization system resulted in a water in oil type emulsification of the system and substantial changes in the rate of copolymerization. The copolymers obtained from the emulsion system were richer in styrene monomer units than those obtained from tetrahydrofuran (THF) solution system. Furthermore the copolymers obtained from the emulsion system were confirmed to be optically active. From the experimental results, it was concluded that polymer chains are forced to grow in the vicinity of oil/water interface in the copolymerization of St with MAc in the above system. The observed optical rotation indicates that an excess of one configuration in chain backbone was induced by the chirality of lecithin during the propagation step of the copolymerization. This process of asymmetric induction polymerization is regarded as an example of enantioface differentiating reaction using an asymmetric field built up with lecithin micelle.

Many studies on the asymmetric induction polymerizations of vinyl monomers have been undertaken for obtaining information on the mechanism of the polymerization. As the first attempt, optically active diamyl itaconate was polymerized by Walden[1] with a view to changing in optical rotation but the conception ended in failure. Marvel and his coworkers[2] undertook to induce asymmetry in the polymerization of styrene, methyl methacrylate, and acrylonitrile by the use of chiral radical initiators. However, no optical activity was detected in the resulting polymers. Marvel[3] and Overberger[4] polymerized optically active vinyl monomers, but no optical activity remained after removal of their original asymmetric groups.

Copolymerization with α,β-disubstituted olefin such as maleic anhydride overcomes the problem of pseudoasymmetry in homopolymerization of vinyl monomers. Schuerch et al. reported successful asymmetric polymer syntheses: that is, l-α-methylbenzyl methacrylate/maleic anhydride[5] and l-α-methylbenzyl vinyl ether/maleic anhydride[6] systems. These copolymers were optically active even after removal of their l-α-methylbenzyl group. The authors revealed that asymmetric induction can be also effected by alternating copolymerization of optically active α,β-disubstituted olefins with optically inactive vinyl monomers: that is, *N-endo*-bornyl maleimide/styrene,[7] *N*-l-menthyl malemide/styrene,[8] and *N*-l-menthyl maleimide/methyl methacrylate[8] systems.