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Radical Copolymerization of Sulfur Dioxide and Styrene. II. Sequence Distribution in Poly(styrene sulfone)

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ABSTRACT: As an extension of our previous work on the radical copolymerization of sulfur dioxide and styrene the sequence distribution in poly(styrene sulfone) has been investigated from nmr spectra, using styrene-α-d or styrene-β-d_2 monomer. From the triad distribution and the distribution of styrene sequence [the probability of a sequence of styrene units (1, 2, and $\geq$3) bounded by sulfur dioxide units], it has been concluded that our propagation mechanism proposed in the preceding paper is most probable if a antepenultimate unit effect for the growing sulfonyl radical is taken into consideration.

In our preceding paper,[1] a new propagation mechanism was proposed for the radical copolymerization of sulfur dioxide and styrene. In this mechanism, in addition to usual propagation and depropagation steps, the reaction step of a new type, in which sulfur dioxide is eliminated from a growing sulfonyl radical under the attack of styrene monomer (second-order depropagation of growing sulfonyl radical), is assumed, and it seems possible to rule out propagation mechanism involving a participation of a charge-transfer complex of sulfur dioxide and styrene, which has often been assumed by many investigators. This proposal is based on the following experimental results: the copolymer composition varies mainly with total monomer concentration and temperature but little with feed composition; at the lower temperature (0°) it does not depend even on total monomer concentration, and the overall rate of copolymerization hardly depends on the concentration of sulfur dioxide.

The present work is concerned with the sequence distribution in poly(styrene sulfone), since it seems possible to examine the validity of our mechanism from this study. Ivin, Navrâtil, and Walker[2,3] have studied extensively the tacticity and the mode of the addition in propagation reaction from the nmr spectra of alternate polysulfones obtained by the radical copolymerization of sulfur dioxide and aliphatic olefins, and Schaefer, Kern, and Katnik[4] have reported the sequence distribution of poly(sulfite ether) prepared from polymerization of sulfur dioxide and propylene oxide, but as far as we know, there is no investigation about sequence distribution of polysulfone consisting of various copolymer compositions.

Experimental Section

Materials. Styrene-β-d_2 was prepared according to the following reactions described by Mross and Zundel.[5]

$$O{=}C(C_6H_5)CD_3 \xrightarrow{LiAlH_4} H(HO)C(C_6H_5)CD_3 \xrightarrow{ClCO_2C_2H_5} H(C_2H_5O_2CO)C(C_6H_5)CD_3 \xrightarrow{300°} C_6H_5CH{=}CD_2$$

Acetophenone-d_3 was prepared by repetition (at least five times) of the reaction of acetophenone with NaOD in D_2O (99.75%) at 70–80° in nitrogen atmosphere for 0.5 hr. Its nmr spectrum shows it to be 97% deuterated at methyl position. The nmr spectrum of styrene-β-d_2 so obtained shows a peak at 7.0–7.4 ppm (aromatic protons), that at 6.5–6.7 ppm (α protons), and very low absorption at 5.0–5.8 ppm (β protons). Integration gives a ratio of 835:170:15 for the areas of the aromatic, α and β protons, respectively, implying that it is 95% deuterated at the β position. Styrene-α-d was prepared from α-bromostyrene using the Grignard reaction in tetrahydrofuran.[6] α-Bromostyrene was prepared from the reaction of styrene dibromide with KOH in ethanol. The nmr spectrum of this monomer so obtained shows a peak at 7.0–7.4 ppm (aromatic protons), two peaks at 5.1 and 5.6 ppm (β protons), and very low peaks at 6.3–6.9 ppm (α protons) and integration (730:295:7) indicated it to be 95% deuterated at the α position.

Polymerization. Radical copolymerization of sulfur dioxide and styrene has been carried out at 30–80° with 2,2′-azobis(isobutyronitrile) (AIBN) using dichloromethane as a diluent. For the copolymerization at 30–50° it has been found useful to include a very small quantity of trichlorobromomethane in the reaction mixture in order to limit the molecular weight of polymer and so to make it more readily soluble in the nmr solvent ($CDCl_3$), thus well-resolved spectra could be obtained.[3] The quantity of trichlorobromomethane was adjusted to give the polymer having the molecular weight of 5000–10,000 (measured by vapor pressure osmometer). The molecular weights of the polymers prepared at 70–80° without addition of the transfer agent were within the same molecular weight range. For the copolymerization at 0° phenyl phenyl azosulfone, a more efficient initiator[7] than AIBN at a low temperature, was used.

The method of copolymerization was similar to that described in the preceding paper.[1] For all experiments the conversions were no more than 10 wt % and the copolymers in chloroform were precipitated by methanol. The copolymers consisting of various compositions were obtained by changing the polymerization temperature, keeping the total monomer concentration constant at 6.0 mol/l., since, as described in the introduction, copolymer composition hardly depends on the feed composition and to change the total monomer concentration requires a large quantity of the deuterated styrene. The compositions of the copolymers were determined from the elementary analyses of sulfur.

Nmr of the Copolymers. The nmr spectra were measured in 10% (wt %/vol) deuteriochloroform solutions of the copolymers at room temperature using Jeol C-60HL (60 MHz) with tetramethylsilane as the internal reference. The resolutions of the spectra

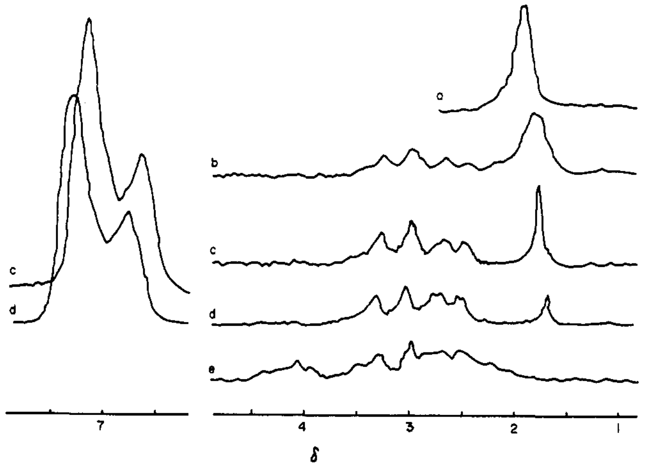

Figure 1. Nmr spectra of poly(styrene-β-d_2 sulfones) and polystyrene-β-d_2: (a) polystyrene-β-d_2; (b)-(e) poly(styrene-β-d_2 sulfones) consisting of following copolymer compositions (styrene mol % in copolymer): (b) 81.4 mol %; (c) 70.6 mol %; (d) 64.6 mol %; (e) 60.4 mol %. Polymerization temperatures for the copolymers (b)-(e) are 80, 50, 30, and 0°, respectively.

measured at higher temperatures or using 100-MHz were not very much better than those described above.

Syntheses of the Model Compounds. α,β-Methanesulfonyl-α'-phenylethane-α-d and -β-d_2 were prepared by the following reactions, respectively.

$$CH_2{=}CDC_6H_5 \xrightarrow{CH_3SSCH_3,\ I_2} CH_3SCH_2CD(C_6H_5)SCH_3 \xrightarrow{H_2O_2} CH_3SO_2CH_2CD(C_6H_5)SO_2CH_3$$

$$CD_2{=}CHC_6H_5 \xrightarrow{Br_2} BrCD_2CH(C_6H_5)Br \xrightarrow{NaSCH_3} CH_3SCD_2CH(C_6H_5)SCH_3 \xrightarrow{H_2O_2} CH_3SO_2CD_2CH(C_6H_5)SO_2CH_3$$

α-d compound: mp 204°; nmr [$(CD_3)_2SO$] δ 7.2–7.6 (m, aromatic), 3.8–4.2 (q, methylene), 2.75 (s, methyl), 2.9 (s, methyl). *Anal.* Calcd for $C_{10}DH_{13}O_4S_2$: C, 45.61; H, 5.74; S, 24.35. Found: C, 45.85; H, 5.57. β-d_2 compound: mp 204–205°; nmr [$(CD_3)_2SO$] δ 7.3–7.7 (m, aromatic), 4.95 (s, methyne), 2.75 (s, methyl), 2.9 (s, methyl). *Anal.* Calcd for $C_{10}D_2H_{12}O_4S_2$: C, 45.44; H, 6.10; S, 24.26. Found: C, 45.14; H, 6.17.

Results and Discussion

Nmr Spectra of Poly(styrene sulfone). Figure 1 shows the nmr spectra of polystyrene-β-d_2 and poly(styrene-β-d_2 sulfone) of various compositions. Each peak at 1.6–1.8 ppm in the spectra of the copolymers, of which position is nearly coinciding with that of α protons in polystyrene-β-d_2, is assigned to the α protons of styrene units which have styrene units on both sides, namely, St*St*St triads (St represents a styrene unit, $-CH_2CH(C_6H_5)-$, and italic type indicates a monomer unit under consideration) and the peaks at 2.0–4.5 ppm are assigned to the α protons of styrene units which have sulfur dioxide units on one side or both sides, namely, St*St*SO_2, SO_2*St*St, or SO_2*St*SO_2 triads, for the reason described below.

It is well known that the peak position of α or β protons to sulfonyl group shifts to downfield because of strong electron-attracting character of this group. Of course, α-proton resonance experiences greater shift to downfield than β protons. It has been reported[3] that in the nmr spectrum of poly(hexene-1 sulfone) in $CDCl_3$, which is an alternate copolymer such as $\sim SO_2CH_2CH(n\text{-}C_4H_9)SO_2\sim$, the peaks at 3.2–4.1 ppm correspond to main-chain methyne and methylene protons (α protons to sulfonyl group) and the broad peak at 2.0 ppm to α-methylene protons of side chain (β to sulfonyl group) and the broad peak at 1.4 ppm to β- and γ-methylene protons of side chain (γ and δ to sulfonyl group). From the facts that there is no detectable difference between nmr shifts due to γ and δ protons to sulfonyl group and that this peak position (1.4 ppm) is almost the same as that of methylene protons of *n*-hexane or *n*-octane (1.3 ppm), it is suggested that γ and more remote protons for sulfonyl group are hardly affected by sulfonyl group. This result seems to be reasonable since electron attractive character of sulfonyl group in such a nonconjugative system may be attributed to the inductive effect and this effect falls off with distance from the attracting group. Thus, the peak at 1.6–1.8 ppm, whose position is nearly coincident with that of α protons in polystyrene-β-d_2, is assigned to α protons in St*St*St triads, since in these triads there is no sulfonyl group, *i.e.*, no α and β protons to sulfonyl group, although this triad has γ or more remote protons.

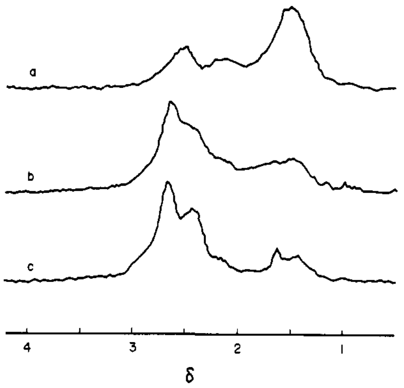

Figure 2. Nmr spectra of poly(styrene-α-d sulfones) consisting of following copolymer compositions (styrene mol % in copolymer): (a) 81.5 mol %; (b) 73.3 mol %; (c) 69.7 mol %. Polymerization temperatures for the copolymers (a)-(c) are 80, 50, and 30°, respectively.

It may be expected that in the copolymer shown in Figure 1d both St*St*SO_2 ($-CD_2CH(C_6H_5)CD_2CH(C_6H_5SO_2-$) and SO_2*St*ST ($-SO_2CD_2CH(C_6H_5)CD_2CH(C_6H_5)-$) triads are predominant as compared to both St*St*St and SO_2*St*SO_2 triads, since the molar ratio of St:SO_2 in this copolymer is 1.8 and furthermore as shown in Figure 1d the area of the peak (1.6–1.8 ppm) due to St*St*St triads is very small compared with that at 2.0–4.5 ppm. Thus, the peaks at 2.4–3.3 ppm may be assigned to SO_2*St*St and St*St*SO_2 triads; two peaks appearing at higher field may be assigned to SO_2*St*St triads, namely, β protons to sulfonyl group and those appearing at lower field to St*St*SO_2 triads, namely, α protons to sulfonyl group, by assuming head-to-tail structure of the pair of styrene units, since the area ratio is approximately 1:1 [integration; 11 (higher field):10 (lower field) in Figure 1d)] and in the long-chain polymer SO_2*St*St and St*St*SO_2 triads should be the same population. The reason for the separation of each signal into two peaks is unclear at present, but the similar separation has been found[3] in the spectrum of main-chain methyne protons in poly(hexene-1 sulfone) in $CDCl_3$; it is probably due to the tacticity of a StSt unit. As shown in Figure 1e, with the increase of sulfur dioxide content in copolymer all the peaks become very broad probably because of the hindered segmental motion due to the increase of sulfur dioxide content. α protons in the model compound of α,β-methanesulfonyl-α'-phenylethane-β-d_2 for a SO_2*St*SO_2 triad have the peak at 4.95 ppm and β protons in α-d model compound at 3.8–4.2 ppm but in copolymer these peaks are expected to shift to higher field, as in the case of polystyrene[8] (α protons in polystyrene have the peak at about 1.1 ppm higher field than that in cumene). Applying this condition (1.1 ppm) to poly(styrene sulfone), the peak position of α protons in SO_2*St*SO_2

triads should be about 3.85 ppm. The compound, thought to be an alternate poly(styrene sulfone) prepared from polymerization of styrene sulfide followed by oxidation,[9] shows the very broad peaks at around 3 ppm (probably due to β protons) and around 4 ppm (probably due to α protons) in the nmr spectrum in liquid sulfur dioxide, in accordance with the above result. Thus, the broad peak at around 4 ppm in Figure 1e may be assigned to α protons in SO_2*St*SO_2 triads, although, as described later, for the purpose of calculation of triad and styrene sequence distribution only the area ratio of the peak at 1.6–1.8 ppm (St*St*St) *vs.* the peaks at 2.0–4.5 ppm (SO_2*St*St + St*St*SO_2 + SO_2*St*SO_2) is necessary.

Figure 2 shows the nmr spectra of poly(styrene-α-*d* sulfone). For the same reason as in the case of styrene-β-d_2 the peak at 1.2–1.9 ppm corresponds to β protons of St*St*St triads, and other peaks at lower field, to the other triads, though the separation between the two regions is poor as compared to that in Figure 1.

Triad and Styrene Sequence Distributions. It is well known that in polysulfone prepared from radical copolymerization of sulfur dioxide with olefine there is no SO_2SO_2 sequence. The equation for normalization for triad distribution is as follows.

$$T_{\mathrm{StStSt}} + T_{\mathrm{StStSO_2}} + T_{\mathrm{StSO_2St}} + T_{\mathrm{SO_2StSt}} + T_{\mathrm{SO_2StSO_2}} = 1 \quad (1)$$

T_{StStSt} is given by

$$T_{\mathrm{StStSt}} = Am_1/(A + B) \quad (2)$$

where A is the peak area due to the St*St*St triads and B is the sum of those due to the SO_2*St*St, St*St*SO_2, and SO_2*St*SO_2 triads and m_1 is styrene mole fraction in copolymer. In eq 2 $A/(A + B)$ is the fraction of St*St*St triads based on styrene units ($T'_{\mathrm{StStSt}} + T'_{\mathrm{StStSO_2}} + T'_{\mathrm{SO_2StSt}} + T'_{\mathrm{SO_2StSO_2}} = 1$) and $Am_1/(A + B)$ is that based on eq 1.

As described above, there is no SO_2SO_2 sequence, thus

$$T_{\mathrm{StSO_2St}} = 1 - m_1 \quad (3)$$

If $T_{\mathrm{SO_2StSO_2}} = 0$, the following equation can be derived from the fact of no presence of SO_2SO_2 sequence.

$$2(1 - m_1) = Bm_1/(A + B) \quad (4)$$

Therefore, subtraction of the left-hand term from the right-hand term gives $T_{\mathrm{SO_2StSO_2}}$.

$$T_{\mathrm{SO_2StSO_2}} = 2(1 - m_1) - Bm_1/(A + B) \quad (5)$$

Then, as $2T_{\mathrm{SO_2StSt}} = 2T_{\mathrm{StStSO_2}} = 1 -$ (other T's) we can get the following equation.

$$T_{\mathrm{SO_2StSt}} + T_{\mathrm{StStSO_2}} = 2Bm_1/(A + B) - 2(1 - m_1) \quad (6)$$

Figures 3 and 4 show the plot of A/B *vs.* copolymer composition for the poly(styrene-β-d_2 sulfone) and poly(styrene-α-*d* sulfone), respectively. The agreement between both A/B values is fairly good (within less than 15%), but we have calculated the distribution only from A/B value of poly(styrene-β-d_2 sulfone) since the peak separation between A and B is clearer than that in the case of α-*d* polymer. The triad distributions so obtained are summarized in Table I, in which the probability of a sequence of styrene units having the unit length n (n = 1, 2, and $\geq$3) bounded by sulfur dioxide units, N_n, is also shown for m_1 range of 0.60–0.66. The values of N_2 and $N_{\geq 3}$ are minimum and maximum values, respectively, and so, at high m_1 value, these values become meaningless, as described in the footnote of Table I.

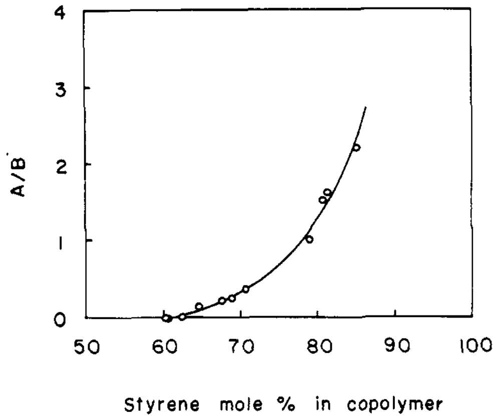

Figure 3. Relationship between A/B values and styrene mol % in copolymer for poly(styrene-β-d_2 sulfones).

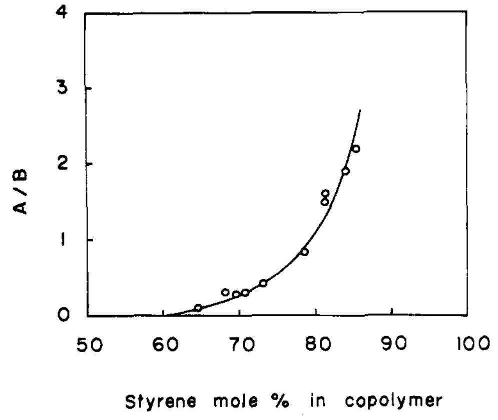

Figure 4. Relationship between A/B values and styrene mol % in copolymer for poly(styrene-α-*d* sulfones).

From Table I it is seen that these results cannot be explained by the ordinary copolymerization mechanism, in that in the low-temperature polymerization (m_1 = 0.60–0.65 at polymerization temperature of 0–30°) there is an abrupt change from N_2 to $N_{\geq 3}$, corresponding to the very large value of $T_{\mathrm{StStSO_2}}$ ($T_{\mathrm{SO_2StSt}}$) and the very small value of T_{StStSt}. For example, in the copolymer for which $m_1 = 0.62$, the values, $N_2 = 0.63$ and $N_{\geq 3} = 0$, corresponding to $2T_{\mathrm{StStSO_2}} = 0.48$ and $T_{\mathrm{StStSt}} = 0$, respectively, are obtained.

Bovey, Tiers, and Filipovich[8] have reported that aromatic proton resonance of polystyrene consists of two well-resolved peaks with an integrated intensity ratio of 3:2 due to the para and two meta protons and to the two ortho protons, respectively, and in the styrene-butadiene copolymer (emulsion polymerization), as the styrene sequence length becomes small, the peak of the ortho protons becomes small and at last disappears (the ortho proton resonance experiences a greater shift to upfield than the ordinary aromatic resonance due to a ring-current effect of neighboring styrene units). Mochel[10] has reported that in the same copolymer it is not until the average styrene sequence length of 5.45 is reached that the ortho proton peak becomes resolved and the minimum styrene sequence length which will cause the ortho proton shift is two or three units. Figure 1d shows that in sulfur dioxide-styrene copolymer the ortho proton peak is well resolved although the average styrene sequence length is only 1.8 [namely, at $m_1 = 0.646$ the value of $m_1/(1 - m_1) = 1.8$ because of the absence of a SO_2SO_2 sequence] and T_{StStSt}

Table I
Triad and Styrene Sequence Distribution of Poly(styrene sulfone)

Copolymer Composition (mol fraction)			Triad				Sequence[a]		
Styrene (m_1)	SO_2 (m_2)	A/B	T_{StSO_2St}	T_{StStSt}	T_{StStSO_2} + $T_{SO_2StSO_2}$	T_{SO_2StSt}	N_1	N_2	$N_{\geq 3}$
0.60	0.40	$\simeq$0	0.40	0	0.40	0.20	0.50	0.50	0
0.62	0.38	$\simeq$0	0.38	0	0.48	0.14	0.37	0.63	0
0.64	0.36	0.05	0.36	0.03	0.49	0.12	0.33	>0.59	<0.08
0.66	0.34	0.12	0.34	0.07	0.50	0.09	0.26	>0.53	<0.21
0.68	0.32	0.21	0.32	0.12	0.49	0.07			
0.70	0.30	0.30	0.30	0.16	0.48	0.06			
0.75	0.25	0.67	0.25	0.30	0.40	0.05			
0.80	0.20	1.3	0.20	0.45	0.30	0.05			
0.646[b]	0.354	0.08	0.35	0.05	0.49	0.11			
				(0.07)[d]	(0.76)[d]	(0.17)[d]			
0.706[c]	0.294	0.33	0.29	0.18	0.47	0.06			
				(0.25)[d]	(0.67)[d]	(0.08)[d]			

[a] $N_1 = T_{SO_2StSO_2}/SO_2$ mol fraction; $N_{\geq 3} \leq T_{StStSt}/SO_2$ mole fraction; $N_2 = 1 - N_1 - N_{\geq 3}$. [b,c] The copolymer compositions in Figures 1d and 1c, respectively. [d] The value which is based on styrene unit.

value is very small (0.05 from Table I). This indicates that the minimum styrene sequence length which will cause the ortho proton shift is two styrene units and, therefore, among the triads based on styrene units ($T'_{StStSt} + T'_{SO_2StSt} + T'_{StStSO_2} + T'_{SO_2StSO_2} = 1$) only $T'_{SO_2StSO_2}$ has the ortho protons which indicates the ordinary aromatic resonance. From this result the value of $T'_{SO_2StSO_2}$ can be obtained from the area ratio of the shifted ortho protons *vs.* total aromatic protons. Namely, the area ratios above described are found to be about 0.37 for the copolymer in Figure 1c and 0.33 for that in Figure 1d, respectively, and these values so obtained give the values of $T'_{SO_2StSO_2}$ of 0.08 and 0.18, respectively. These values so obtained are in good agreement with those of $T'_{SO_2StSO_2}$ of 0.08 and 0.17 (Table I) obtained from A/B value for the copolymer in Figures 1c and 1d, respectively.

In our preceding paper,[1] we have proposed the following mechanism that assumes the novel reaction of eq 7 in order to explain the rate and the copolymer composition in the low-temperature (below 0°) copolymerization.

$$\sim\mathrm{StSO_2}\cdot + \mathrm{St} \begin{array}{l} \overset{k_{SM}}{\nearrow} \sim\mathrm{SO_2St}\cdot \qquad (7) \\ \underset{k_{d2}}{\searrow} \sim\mathrm{StSt}\cdot + \mathrm{SO_2} \qquad (8) \end{array}$$

$$\sim\mathrm{St}\cdot + \mathrm{SO_2} \xrightarrow{k_{MS}} \sim\mathrm{StSO_2}\cdot \tag{9}$$

By this mechanism the drastic change between N_2 and $N_{\geq 3}$ cannot be explained, but such a change can be easily explained by assuming a antepenultimate unit effect in reaction 8 as follows.

$$\sim\mathrm{SO_2StSO_2}\cdot + \mathrm{St} \begin{array}{l} \overset{k_{SM}}{\nearrow} \sim\mathrm{SO_2St}\cdot \qquad (10) \\ \underset{k_{d2}}{\searrow} \sim\mathrm{StSt}\cdot + \mathrm{SO_2} \qquad (11) \end{array}$$

$$\sim\mathrm{StStSO_2}\cdot + \mathrm{St} \xrightarrow{k_{SM}} \sim\mathrm{SO_2St}\cdot \tag{12}$$

$$\sim\mathrm{St}\cdot + \mathrm{SO_2} \xrightarrow{k_{MS}} \sim\mathrm{StSO_2}\cdot \tag{13}$$

It is very likely that the effect of remote units is existent in the strong dipolar monomer such as a sulfur dioxide, as Walling[11] assumed it in poly(styrene sulfone) formation. It seems reasonable that sulfur dioxide is rapidly eliminated from $\sim SO_2StSO_2\cdot$ (eq 11), owing to repulsion between electron-poor sulfur atoms of each sulfonyl group (or between electron-rich oxygen atoms), but is not eliminated (or negligible as compared to other steps) from $\sim StStSO_2\cdot$. This mechanism, of course, is consistent with the experimental results in the preceding paper.[1] In this mechanism it is clear that both $N_{\geq 3}$ and T_{StStSt} are zero in agreement with the experimental result.

A distribution of similar type has been found by Ham[12] in the emulsion copolymerization of styrene and fumaronitrile. Ham has reported that, when m_1 (styrene) = 0.6, the values of N_2 and N_3 are 0.472 and 0.035, respectively, and this can be explained by the effect of remote units on the rate constants, namely $k_{111}/k_{112} = 0.08$, $k_{11211}/k_{11212} = 0.3$, and $k_{21211}/k_{21212} = 4.0$, where k_{111} is the rate constant for the propagation of $\sim 11\cdot$ with 1 monomer (styrene), and so on. It may be considered that his mechanism cannot be applied to our system since it is based on the fact that fumaronitrile content in copolymer cannot be increased beyond 40 mol % regardless of feed composition, but in our system sulfur dioxide content approaches to the level of 50 mol % as polymerization temperature decreases, as usually seen in the case of monomers incapable of adding to themselves.

As described in the preceding paper,[1] at higher temperatures (m_1 = 0.65–0.85 at polymerization temperature of 30–80°) the following two reaction steps, which may be considered to be negligible at 0°, are added to the scheme for low-temperature polymerization (eq 10–13) to explain the results at higher temperatures.

$$\sim\mathrm{StSO_2}\cdot \xrightarrow{k_{dMS}} \sim\mathrm{St}\cdot + \mathrm{SO_2} \tag{14}$$

$$\sim\mathrm{St}\cdot + \mathrm{St} \xrightarrow{k_{MM}} \sim\mathrm{StSt}\cdot \tag{15}$$

We could not calculate the values of triad distribution since the reaction mechanism is rather complex and the copolymer compositions were varied by changing the polymerization temperature. However, as can be seen from Table I, by increasing temperature (namely, by increasing the styrene content in copolymer) $T_{SO_2StSO_2}$ decreases and T_{StStSt} increases, respectively, with the increasing contribution of the reaction of eq 14 and 15.

It is concluded that the results obtained for the triad and styrene sequence distribution indicate that our mechanism proposed in the preceding paper[1] must be modified to take account of an antepenultimate unit effect on the reaction $\sim SO_2\cdot + St \rightarrow \sim St\cdot + SO_2$, this reaction proceeding only for $\sim SO_2StSO_2\cdot$ and not for $\sim StStSO_2\cdot$.

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Preparation of Six-Branched Polystyrene. Thermodynamic and Hydrodynamic Properties of Four- and Six-Branched Star Polystyrenes

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ABSTRACT: A number of six-branched star polystyrenes have been prepared by an anionic technique. Their dilute solution viscosities were determined in cyclohexane and toluene in order to compare the effect of branching on $[\eta]$ with theoretical predictions. Unperturbed dimensions of these polymers and of the four-branched star polystyrenes prepared earlier were determined and found to be in good agreement with values calculated from Gaussian-chain statistics. Second virial coefficients were measured in a temperature range around Θ (34.5°). They became zero at temperatures increasingly below Θ as the total molecular weight decreased and as the branch number increased. Values of B_0 (or ψ_1) were found to be independent of branching for these samples. The results are discussed in terms of modifications to the smoothed-density Gaussian-coil model of polymer structure.

In a previous publication the synthesis of narrow molecular weight distribution star polystyrenes with four equal branches was described.[1] It was shown that anionic polymerization techniques together with coupling reactions using a tetrafunctional silicon chloride compound led to the desired polymers. The hydrodynamic properties of dilute solutions of a series of four-branched polymers were compared to those of linear polymers. In particular, it was found that $g' = [\eta]_{\mathrm{br}}/[\eta]_{\mathrm{lin}}$ changed from 0.76 in a Θ solvent (cyclohexane 35°) to 0.724 in a good solvent (toluene 35°). These values were compared with two theoretical predictions: $g' = 0.79$ proposed by Zimm and Kilb[2] and $g' = 0.71$ proposed by Stockmayer and Fixman[3] both strictly speaking applying under Θ conditions. To distinguish between these two proposals, which differ by not more than 11%, puts severe demands on the quality of the polymers and the accuracy of the physical measurements. It was thought of interest to investigate the behavior of six-branched polymers. Indeed, for six-branched polymers $g' = 0.666$ according to Zimm–Kilb[2] and 0.51 according to Stockmayer–Fixman[3] a difference of nearly 30%.

This paper describes the synthesis and characterization of a series of six-branched polystyrenes and the measurements of their intrinsic viscosity in the same solvents as were used for the four-branched polymers. There are three references to six-branched polystyrene. The synthesis of one sample by coupling of living polymer with the cyclic trimer of phosphonitrilic chloride has been described.[4] Fractionation and molecular weight determinations have also been reported.[5] For one sample, obtained by coupling with hexachloromethylated benzene, no intrinsic viscosity measurements are available.[6] Two six-branched star polymers, obtained by coupling with hexa[*p*-(chloromethyl)-phenyl]benzene unfortunately contain an important amount of 11-branched material.[7]

We also report on some equilibrium thermodynamic properties of the four- and six-branched polystyrenes and compare them with the properties of linear polymers. Theoretical studies are available that predict the behavior of A_2,[3,8] $\langle S^2\rangle_0$,[3,9,10] and $\alpha^2 = \langle S^2\rangle/\langle S^2\rangle_0$[3,11] for such polymers. Data are available on one four-branched star polymer.[6] Some A_2 values in different solvents for one six-branched polystyrene are also given.[6]

Experimental Section

Polymer Preparation. The preparation of the four-branched star polystyrenes was fully described previously.[1] The six-branched polystyrenes were prepared along the lines described for the synthesis of the four-branched star polymers. 1,2-Bis(trichlorosilyl)ethane was used as the coupling agent. This compound was purchased from Chemicals Procurement Laboratories Inc. and was distilled before use. A middle fraction boiling between 83 and 85° under 16-mm pressure[12] was immediately transferred to a vacuum line system and degassed. All further manipulations were performed under high vacuum. To 25 g of the compound, 15 ml of *n*-hexane was added and three partial crystallizations were performed. At this point the product crystallized at 10°. Six recrystallizations gave a constant melting point at 24° (Literature 25.2[13]). This material (0.67 g) was diluted in *n*-hexane and subdivided into fragile bulbs. The silicon–chlorine bond concentration was determined by acid–base titration.

Polymerization and coupling reactions were carried out in benzene at 30°. All glassware was washed with *n*-butyllithium and rinsed by distilling benzene from a reservoir. Benzene was finally