Radical Copolymerization of Sulfur Dioxide and Styrene. 5.[1] The Styrene Sequence Distribution of Poly(styrene sulfones)

Hun-Jai Bae, Tokuji Miyashita, Masashi Iino, and Minoru Matsuda*

Chemical Research Institute of Nonaqueous Solutions, Tohoku University, Katahira 2-1-1, Sendai, 980 Japan. *Received May 22, 1987*

ABSTRACT: The styrene sequence distribution of poly(styrene sulfones) was determined for various copolymer compositions both from styrene oligomers produced from selective reductive cleavage of the carbon–sulfur bonds in the copolymer chain and from ^{13}C NMR data for the copolymers. The former method could determine the styrene sequences up to nonad sequences, whereas the latter was feasible up to tetrads. The styrene sequence distribution depended only upon the copolymer composition irrespective of copolymerization conditions; in the distribution, the major styrene sequence for each copolymer changed with the copolymer composition; that is, the styrene dyad sequence is the main component in a 2:1 (styrene/SO_2) copolymer and the triad sequence is the main component in a 3:1 copolymer. Some calculations for the distribution were carried out based on Markoffian statistics. However, the characteristic distribution observed could not be explained by a Mayo–Lewis-type propagation mechanism even considering penultimate or pen-penultimate unit effects.

Introduction

Although the free radical copolymerization of sulfur dioxide and styrene has been studied extensively by several research groups,[1–9] the propagation mechanism has not been settled. The behavior of this copolymerization is very interesting. The copolymer composition hardly depends upon feed composition but changes with total monomer concentration ([styrene] + [SO_2]), diluent, and copolymerization temperature.[5,6] The depropagation of styrene from the growing styryl free radical having a sulfonyl group as the penultimate unit has been observed at rather low temperature, 40 °C,[9] and on the basis of the data reported for the free radical copolymerization of sulfur dioxide and olefins by Ivin et al.,[10,11] it is most likely that the growing sulfonyl free radical is also depropagating, forming styryl free radicals.

To solve the propagation mechanism for this copolymerization, the distribution of triad monomer sequences (MMM, MMS, MSM, SMS, and SMM, where M and S are styrene and sulfur dioxide, respectively) of poly(styrene sulfones) has been determined by means of ^{1}H NMR for the copolymers prepared with deuteriostyrenes (styrene-α-d and -β,β-d_2)[7] or ^{13}C NMR for poly(styrene sulfones).[8] It was revealed from the NMR studies that the MMS and SMM triads are contained in a high content in a 2:1 copolymer.

In this paper, the distribution of the styrene sequences in poly(styrene sulfones) with various copolymer compositions has been determined by two methods. First, the styrene sequences were successfully isolated as styrene oligomers after reductive cleavage of the copolymers. The dissociative electron-transfer reaction to the copolymers induced a selective reductive cleavage of C–S bonds in the copolymer chain, forming dianions, $^{-}St(St)_xSt^{-}$. After protonation of the dianions, the HPLC (high-performance liquid chromatography) of the styrene oligomers gave a distribution of styrene sequences. Second, the distribution was determined by ^{13}C NMR of the copolymers. The distribution thus determined has some interesting aspects and shows that the propagation mechanism of the copolymer is quite different from the usual radical copolymerization mechanism.

Experimental Section

Preparation of Poly(styrene sulfones). Copolymers with various copolymer compositions were prepared by free radical copolymerization of sulfur dioxide and styrene varying in feed composition, total monomer concentration ([SO_2] + [styrene]), and temperature in *o*-dichlorobenzene with 2,2′-azobisisobutyronitrile as a thermal initiator. Gravimetrically determined conversions were controlled to be no higher than 5 wt % in order to prepare copolymers having a uniform composition. The copolymer compositions were determined from elemental analyses of carbon. Molecular weights of the copolymers were measured on a Toyo Soda GPC (HLC-802 UR with styragel columns in THF) coupled with a light scattering and a data processing system (HLC-CP8, Model 3).

Reductive Cleavage of Poly(styrene sulfones). The reductive cleavage of the C–S bonds in the copolymers due to dissociative electron transfer forming the dianions of styrene oligomers was conducted according to a method reported by Reggel et al.;[12] sodium metal (ca. 2.0 g) was added to an ethylenediamine (EDA) solution of the copolymer (ca. 1.0 g of copolymer/120 mL of EDA). To avoid reaction of CO_2 or O_2 with dianions or intermediates (radical anions) formed from the reductive cleavage, nitrogen gas was admitted into the vessel throughout the reduction. The reduction was conducted at low temperature (10 °C) over a period of more than 10 days. The progress of the reductive cleavage was followed by observing the development of a deep reddish color due to formation of the sodium metal salt of styryl carbanion. After the protonation of the carbanion, styrene oligomers were formed. Unreacted excess sodium metal and remaining dianions were quenched by addition of ice water under stirring to avoid raising the temperature.

The styrene oligomers were fractionated by a Waters Associates HPLC with Radial Pak C-18 column in a Z-Module (Radial compression separation system). Fractionation by GPC was carried out using a μ-Styragel column (Waters, 500Ax2 + 200A + 100Ax3 in series). ^{13}C NMR spectra were measured by JEOL FX-90Q FT-NMR at 22.5 MHz with complete decoupling of proton (solvent, $CDCl_3$; temperature, 55 °C; accumulation, 20000 times).

Results

Copolymer Compositions of Poly(styrene sulfones). The copolymer compositions of the copolymers used for the present study and the copolymerization conditions were summarized in Table I. To obtain the copolymers with various copolymer compositions, copolymerization temperature and total monomer concentration were changed; the dependency of the composition upon both the feed and total monomer concentration is very similar to that reported elsewhere.[6] The number-average molecular weight increased almost linearly in the range 1.5×10^4 to 1.4×10^5 with increasing styrene concentration in feed or total monomer concentration. Molecular weight ratios, M_w/M_n, were found to be 1.6–1.7 for copolymers prepared with *o*-dichlorobenzene as a diluent, but in bulk copolymerization, the copolymer more commonly showed a M_w/M_n value of 4.

Styrene Sequences from Reductive Cleavage of the Copolymers. Various reduction methods have been examined to find the conditions for the selective cleavage of the C–S bond in the copolymer chain. In the reduction

Table I
Copolymerization Conditions and Copolymer Compositions of Poly(styrene sulfones)

sample	[St], mol %[a]	copolymerization conditions: [St], mol % in feed	[St] + [SO_2],[b] mol/L	temp, °C	solvent
30–B	65	60	11.6	30	
50–B	67	60	11.6	50	
C–03	70	30	9.0	60	DCB[c]
C–02	71	50	9.0	60	DCB
M–06	71	70	10.0	60	DCB
M–05	71	70	9.0	60	DCB
M–04	72	70	7.0	60	DCB
M–13	73	30	5.0	60	DCB
M–03	75	70	5.0	60	DCB
M–12	77	30	3.0	60	DCB
N–3–B	77	80	1.0	30	DCB
C–05	78	90	9.0	60	DCB
M–23	79	90	5.0	60	DCB
M–02	83	70	3.0	60	DCB
N–3–A	83	90	1.0	30	DCB

[a] In copolymer; determined by elemental analysis. [b] Total monomer concentration in feed. [c] *o*-Dichlorobenzene.

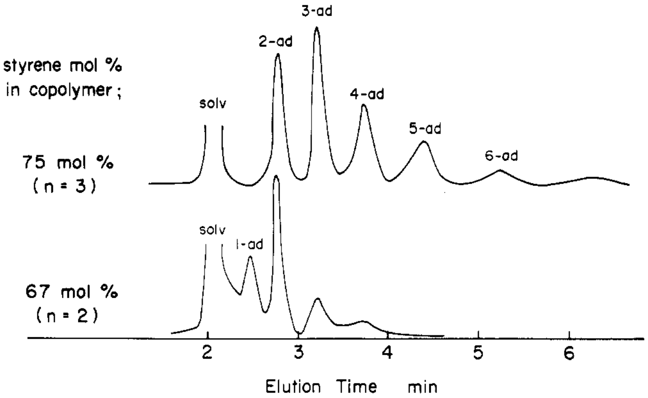

Figure 1. HPLC fraction of styrene oligomers produced from reductive cleavage of poly(styrene sulfones).

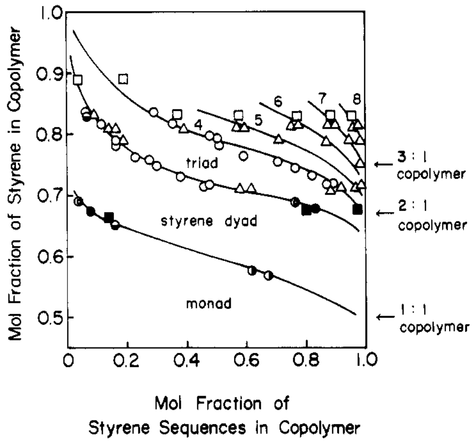

Figure 2. Relationship between mole fraction of styrene sequences and copolymer composition in poly(styrene sulfones): (□ and △) determined by HPLC method; (◒, ●, and ○) determined by ^{13}C NMR method; (⊙ and ◑) from Cais et al.'s data. Polymerization temperatures: (□) 30 °C; (△) 60 °C; (◒) 30 °C; (●) 50 °C; (○) 60 °C; (⊙) 0 °C; (◑) 40 °C.

with lithium metal, the various products derived from the cleavage of the C–C bond in the polymer chain or the hydrogen abstraction from the polymer methylene chain were produced, and the reduction of phenyl rings also occurred. For example, in the reduction of a 2:1 copolymer by lithium metal in ethylenediamine at 118 °C (boiling point), 1,3-dicyclohexylpropane, 1,3-dicyclohexylbutane, and olefinic compounds (butane or cyclohexene derivatives) were formed. Sodium metal reduction at 30–110 °C gave mainly 1,3-diphenylbutane (40–50 mol %, based on styrene units in a 2:1 copolymer), 1,3-diphenylbut-2-ene (ca. 15 mol %), and 1,3-diphenylbut-1-ene (ca. 10 mol%); the phenyl rings were not reduced but hydrogen abstraction occurred, forming olefinic compounds. Reductions with sodium metal in liquid ammonia and with lithium aluminum hydride, sodium naphthalenide, and Raney nickel in tetrahydrofuran were also examined, but these reduction methods were not suitable, judging from both the structure of the products and the yield; that is, the selective cleavage of only the C–S bond did not proceed quantitatively under these conditions.

We finally chose mild reduction conditions which effectively suppressed the C–C bond scission and hydrogen abstraction from the copolymer chains. Reduction with sodium metal at low temperature (10 °C) over a long reduction time was adopted. The reduction proceeded very slowly. The color of the solution changed gradually, i.e., slight yellow (1–2 days after) and then deep red (7–10 days), indicating completion of the formation of the sodium metal salt of styrene carbanions.

Fractionation of the reduction products using a GPC column was insufficient judged by the separation of the peaks; especially, the oligomers longer than tetramer were not separated. On the other hand, fractionation by HPLC (C-18 column) gave sufficient results on the basis of peak separation; for example, those for the reduction products obtained with 75 and 67 styrene mol % copolymers are shown in Figure 1. It is clearly shown that the sequences up to the styrene heptamer were contained in the former copolymer, but the styrene monad did not exist, and the latter copolymer, that is, a 2:1 copolymer, consisted of styrene monad, dyad, and triad and a trace of tetramer. Similarly, we could obtain the HPLC fractionation data

Table II
Mole Fraction of Styrene Sequences in Poly(styrene sulfones) Determined by Reductive Cleavage of the C–S Bond

	mole fraction of styrene sequences									[St], mol % in copolymers	
sample	monad	dyad	triad	tetrad	pentad	hexad	heptad	octad	nonad	HPLC[a]	EA[b]
30–B	0.03	0.89	0.06	0.02	0	0	0	0	0	67	65
50–B	0.14	0.67	0.16	0.03	0	0	0	0	0	67	67
C–02	0	0.57	0.30	0.10	0.03	0	0	0	0	71	71
M–06	0	0.60	0.32	0.06	0.02	0	0	0	0	71	71
M–04	0	0.24	0.32	0.25	0.17	0.02	0.002	0	0	75	72
C–05	0	0.20	0.26	0.24	0.15	0.09	0.04	0.02	0	79	78
M–12	0	0.14	0.20	0.22	0.20	0.14	0.07	0.03	0.002	81	77
N–3–B	0	0.16	0.23	0.20	0.18	0.09	0.06	0.04	0.04	81	77
M–02	0	0.15	0.21	0.21	0.18	0.12	0.07	0.04	0.02	82	83
N–3–A	0	0.03	0.20	0.24	0.20	0.10	0.09	0.08	0.06	83	83

[a] Calculated from the distribution of styrene sequences determined by HPLC. [b] Obtained from elemental analysis.

Table III
Chemical Shift Range for the Methine, Methylene, and Quaternary Carbon Resonances in Monomer Sequences in Poly(styrene sulfones)

monomer seq	chemical shift range, ppm from TMS: methine	methylene	quaternary
SMS	62.46–65.72	48.24–50.44	126.55–127.66
SMM	35.90–38.50	55.45–57.93	139.59–143.75
SMMM	37.32–38.50		
SMMS	35.90–37.32		
MMS	66.27–69.05	30.21–35.94	131.32–134.88
MMM	38.50–41.52	41.52–48.15	143.75–147.12
MMMS	38.50–40.15		
MMMM	40.15–41.52		

for the reductive products from the copolymers with various copolymer compositions. The distributions of styrene sequences are summarized in Table II. Figure 2 shows the variation of the mole fraction of styrene sequences with copolymer composition.

The Determination of Styrene Sequences by ^{13}C NMR. The analysis by ^{13}C NMR for the copolymers was also carried out in the same manner as the method of Cais et al.[8] They determined the triad sequence from the multiple resonances observed for the methine (α carbon) and methylene carbons (β carbon). The tetrad sequence can be also determined by more precise analysis of the multiple resonance as they suggested. For the doublet of α(MMM) resonance in the range 38.61–40.56 ppm, the high-field component of the doublet decreases in intensity with increasing styrene mole fraction, while the low-field component increases with the mole fraction. Therefore α(MMMM) is assigned to 40.49 ppm and α(MMMS) to 39.62 ppm. The same analysis can be applied to α(SMM). The chemical shift range determined for the methine carbon resonance in tetrad sequences is shown in Table III. Typical spectra obtained with 65 and 75 mol % styrene copolymers are shown in Figure 3; in the former copolymer, the styrene monad, i.e., SMS, is clear present, whereas there are no monads in the latter. This is consistent with the results of the reductive cleavage method. The distribution of styrene sequences determined by ^{13}C NMR is shown in Table IV and Figure 2.

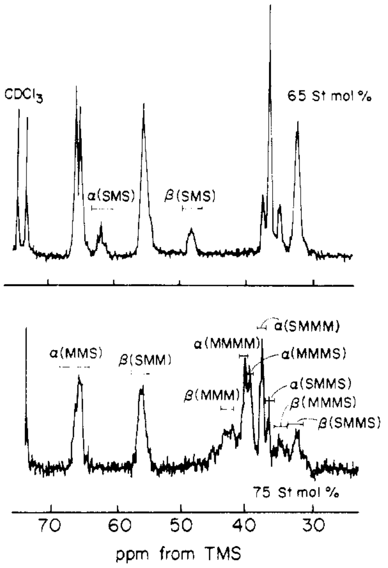

Figure 3. ^{13}C NMR spectra for methine (α) and methylene (β) backbone carbons of poly(styrene sulfones) with different styrene mole percent: (a) 65 mol % (30-B); (b) 75 mol % (M-03).

Discussion

Organic sulfones, sulfides, and ethers are subject to reductive cleavage by alkali metals in amine solvents.[13] However, the application to high polymers has not been reported. The reductive cleavage of a 2:1 poly(styrene sulfone) was carried out with lithium and sodium metals in ethylenediamine; at high temperature (100–110 °C) lithium induced bond scission even for C–C bonds, giving 1,3-dicyclohexylpropane. A pronounced difference in behavior between lithium and sodium metal is that when the former is used, the phenyl ring was also reduced and hydrogen atoms were abstracted from the copolymer chain, forming olefinic compounds. Thus, it is most likely that the lithium metal reduction is more vigorous. We finally chose mild reduction conditions: at low temperature (10 °C) using sodium metal. Under these conditions, poly(styrene sulfones) with various copolymer compositions were reductively cleaved giving the desired products, i.e., styrene oligomers derived from C–S bond scission only without C–C bond scission or reduction of phenyl rings. A longer reduction time, however, was necessary to get oligomers in a quantitative yield.

The styrene oligomers can be fractionated satisfactorily by using an HPLC column, as shown in Figure 1. The distribution of styrene sequences can be determined by this method, including longer sequences than can be seen by C^{13} NMR. This is the first report on the distribution of the styrene sequences including longer sequences up to nonad. As can be seen from Figure 2, each styrene se-

Table IV
Mole Fraction of Styrene Sequences in Poly(styrene sulfones) by ^{13}C NMR Spectra

sample	mole fraction of styrene sequences: monad	dyad	triad	tetrad	[St], mol % in copolymers: ^{13}C NMR[a]	EA[b]
30-B	0.16	0.84	0	0	65	65
50-B	0.008	0.75	0.17	0	68	67
C-03	0	0.46	0.41	0.13	72	70
C-02	0	0.48	0.36	0.15	72	71
M-06	0	0.47	0.42	0.11	72	71
M-05	0	0.37	0.46	0.17	73	71
M-04	0	0.30	0.46	0.24	74	72
M-13	0	0.28	0.42	0.30	75	73
M-03	0	0.23	0.37	0.40	76	75
C-05	0	0.17	0.34	0.49	78	78
M-12	0	0.14	0.34	0.52	80	77
N-3-B	0	0.10	0.24	0.66	82	77
M-23	0	0.10	0.25	0.65	82	79
M-02	0	0.07	0.22	0.71	83	83
N-3-A	0	0.04	0.15	0.81	87	83

[a] Calculated from the distribution of styrene sequences determined by ^{13}C NMR. [b] Obtained from elemental analysis.

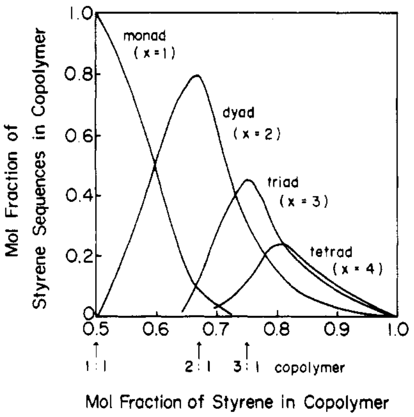

Figure 4. Styrene sequence distribution up to tetrad derived from experimental data in Figure 2.

quence peak is clearly resolved, the areas becoming smaller on going to longer sequences. It may be concluded that the styrene sequence distribution obtained depends only on copolymer composition irrespective of copolymerization conditions, such as temperature and feed composition. For example, copolymers M-12 and N-3-B were polymerized under different conditions (Table I) but have the same copolymer composition resulting in similar distributions (Table II). The styrene sequence distribution in Figure 4 was derived from the results in Figure 2. It should be stressed that in the distribution the major styrene sequence for each copolymer varied with copolymer composition and coincided with the average copolymer compositions determined by elemental analyses; that is, in a 2:1 copolymer, the styrene diad sequence is the main component (80 mol %), and the monad and triad are in equivalent amount (10 mol % each); while for a 3:1 copolymer, the styrene triad sequence is the main component (45 mol %), and the dyad and tetrad are 30 and 11 mol %, respectively, and a residue (14 mol %) consisting of styrene sequences longer than pentad. Moreover, we find that the regularity of styrene sequences becomes greater with decreasing styrene content. In the 2:1 copolymer, the styrene dyad sequence constitutes 80 mol % while in the 3:1 copolymer, the triad, which is the main component, decreases to 45 mol % (the styrene monad constitutes 100 mol % in the 1:1 copolymer, since sulfur dioxide does not propagate itself). Here, it is also of interest that styrene monad (SMS sequence) is never present in styrene-rich copolymers higher than the 3:1 copolymer. This was confirmed in the ^{13}C NMR spectra observed for such copolymers: the signals at 48.24–50.44 (methylene), 62.46–65.72 (methine), and 126.55–127.66 (quaternary carbon) ppm due to the SMS sequence do not appear.

Statistical analysis of the styrene sequence distribution was carried out according to standard theory.[14] $X(\mathrm{M}^n)$ is the probability or number fraction of a styrene sequence of length n among all sequences. The following relations hold:

$$X(\mathrm{M}) + X(\mathrm{S}) = 1 \qquad (1)$$

Since sulfur dioxide (S) does not homopropagate,

$$X(\mathrm{SS}) = X(\mathrm{SSS}) = X(\mathrm{SSS...}) = 0 \qquad (2)$$

and thus

$$X(\mathrm{S}) = X(\mathrm{SM}) + X(\mathrm{SS}) = X(\mathrm{SM}) \qquad (3)$$

By defining the reaction probability with which the growing radical adds to the monomers according to the propagation mechanisms, the number fraction of each styrene sequence can be calculated from Markoffian statistics.

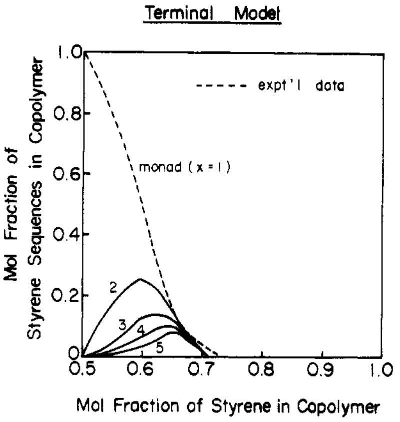

Figure 5. Styrene sequence distribution calculated on the basis of a terminal model; (- - -) experimental data.

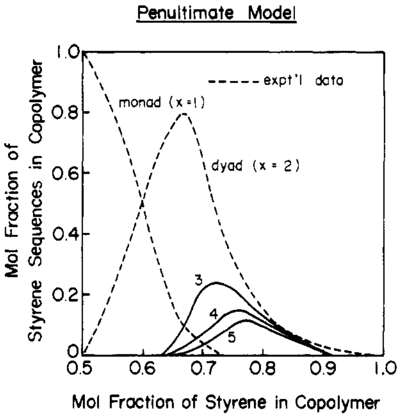

Figure 6. Styrene sequence distribution calculated on the basis of a penultimate model; (- - -) experimental data.

1. **Terminal Model.** P_{mm} defines the probability that the growing styryl radical (-M$^\bullet$) adds to styrene monomer.

$$P_{\mathrm{mm}} + P_{\mathrm{ms}} = 1, \qquad P_{\mathrm{sm}} + P_{\mathrm{ss}}(=0) = P_{\mathrm{sm}} = 1 \qquad (4)$$

The fraction of the styrene sequence is represented as follows:

$$X(\mathrm{SMS}) = X(\mathrm{SM})P_{\mathrm{ms}} = X(\mathrm{S})(1 - P_{\mathrm{mm}}) \qquad (5)$$

$$X(\mathrm{SMMS}) = X(\mathrm{SMM})P_{\mathrm{ms}} = X(\mathrm{SM})P_{\mathrm{mm}}P_{\mathrm{ms}} = X(\mathrm{S})P_{\mathrm{mm}}(1 - P_{\mathrm{mm}}) \qquad (6)$$

$$X(\mathrm{SMMMS}) = X(\mathrm{SM})P_{\mathrm{mm}}P_{\mathrm{mm}}(1 - P_{\mathrm{mm}}) \qquad (7)$$

$$\vdots$$

$$X(\mathrm{SM}^n\mathrm{S}) = X(\mathrm{S})P_{\mathrm{mm}}{}^{n-1}(1 - P_{\mathrm{mm}}) \qquad (8)$$

Figure 5 shows the distribution calculated from eq 8, where P_{mm} was determined from the experimental monad fraction.

2. **Penultimate Model.** The reaction probability is defined, considering a penultimate unit effect. P_{mms} defines the probability that the growing -MM$^\bullet$ radical adds to sulfur dioxide.

$$P_{\mathrm{mmm}} + P_{\mathrm{mms}} = 1, \qquad P_{\mathrm{smm}} + P_{\mathrm{sms}} = 1 \qquad (9)$$

$$X(\mathrm{SMS}) = X(\mathrm{S})P_{\mathrm{sms}} \qquad (10)$$

$$X(\mathrm{SMMS}) = X(\mathrm{S})P_{\mathrm{smm}}P_{\mathrm{mms}} \qquad (11)$$

$$\vdots$$

$$X(\mathrm{SM}^n\mathrm{S}) = X(\mathrm{S})P_{\mathrm{smm}}P_{\mathrm{mmm}}{}^{n-2}P_{\mathrm{mms}} \qquad (n > 2) \quad (12)$$

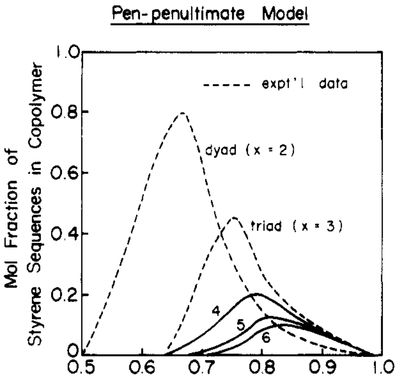

Figure 7. Styrene sequence distribution calculated on the basis of a pen-penultimate model; (---) experimental data.

Figure 6 is the distribution calculated by eq 12, where P_{smm} and P_{mmm} were unknown parameters and determined from the experimental fractions of monad and dyad.

3. Pen-penultimate Model. The distribution can be calculated from the following definition and the equations (Figure 7).

$$P_{\mathrm{mmmm}} + P_{\mathrm{mmms}} = 1, \qquad P_{\mathrm{smmm}} + P_{\mathrm{smms}} = 1 \qquad (13)$$

$$X(\mathrm{SM}^n\mathrm{S}) = X(\mathrm{S})P_{\mathrm{smmm}}P_{\mathrm{mmmm}}^{\,n-3}(1 - P_{\mathrm{mmmm}}) \qquad (n > 3) \quad (14)$$

These distribution curves, shown in Figures 5–7, clearly reveal that the propagation mechanism for the free radical copolymerization of sulfur dioxide and styrene is not explained by a Markoff chain mechanism, even though the penultimate or pen-penultimate unit effect was taken into consideration for it. In the Markoff chain mechanism, the positions of the peak of the distribution curves are never shifted by a change in the copolymer composition. In other words, as reported by many investigators,[14] the predominant component in the copolymer is always the monad irrespective of the copolymer compositions, and the fraction of longer sequence becomes small with sequence length when the Markoff chain mechanism is operative. It is reconfirmed from the data of the distribution of the styrene sequences that Mayo–Lewis-type propagation is never operative in the present copolymerization.

Registry No. (Styrene)(SO_2) (copolymer), 26779-73-7.

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New Polycarbosilane Models. 1. Poly[(methylchlorosilylene)methylene], a Novel, Functional Polycarbosilane

Eric Bacqué, Jean-Paul Pillot,* Marc Birot, and Jacques Dunoguès*

Laboratoire de Chimie Organique et Organométallique (U.A.35 CNRS), Université de Bordeaux I, 351, Cours de la Libération, 33405 Talence Cédex, France.

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ABSTRACT: The aluminium trichloride catalyzed interchange of methyl and chlorine on silicon has been applied for the first time to the polycarbosilane series. Thus, poly[(dimethylsilylene)methylene] ($-(\mathrm{Me_2SiCH_2})_n-$, $\bar{M}_n \simeq 250000$) has been converted into a poly[(methylsilylene)methylene] ($\bar{M}_n \simeq 2300$), the first functional polycarbosilane possessing an unambiguous linear skeleton. The considerable lowering of the average molecular weight, a consequence of the backbone cleavage, was accompanied by the formation of dimethylchlorosilyl groups as the chain terminals. These were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR.

Introduction

Recently, considerable interest has been focused on polycarbosilanes, since Yajima and co-workers demonstrated that these polymers were convenient precursors for silicon carbide fibers.[1] Spinnable polymers were prepared by thermal rearrangement of poly(dimethylsilane), but their structure could not be described accurately by the ideal linear structure $-(\mathrm{MeSiHCH_2})_n-$ which has been originally postulated.[2] More likely, some cyclic framework may arise from side cross-linking reactions proceeding by not yet established mechanisms.[3]

The paucity of information concerning silmethylene polymers prompted us to undertake the synthesis of such derivatives. We report here the preparation and the characterization of the first poly[(methylchlorosilylene)methylene]. Thanks to its highly reactive Si–Cl bonds, it can be regarded as a precursor of a range of novel functional polycarbosilanes.

Results and Discussion

Poly[(dimethylsilylene)methylene] (1) is known to possess an unambiguous linear skeleton and high average molecular weight.[4] This soluble polymer was readily ob-

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* Authors to whom correspondence should be addressed.

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