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Spontaneous Cohabitory Anionic Polymerization of Vinylidene Cyanide and Cationic Polymerization of Cyclic Ethers on Mixing the Two Monomers at 25°

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ABSTRACT: Mixing vinylidene cyanide with any one of the cyclic ethers tetrahydrofuran, oxetane, 2,2-dimethyloxirane, 2-chloromethyloxirane, and 2-phenyloxirane, either in bulk or in toluene, resulted in the polymerization of both the vinylidene cyanide and cyclic ether to afford homopolymers of both. The cyclic ethers trioxane, 3,3-bis(chloromethyl)oxetane, and oxirane initiated the polymerization of vinylidene cyanide but did not undergo ring-opening polymerization themselves. Other ethers such as 1,3-dioxolane, tetrahydropyran, and diethyl ether did not initiate the polymerization of vinylidene cyanide. In these polymerizations, vinylidene cyanide and the cyclic ethers polymerize *via* anionic and cationic propagation reactions, respectively. The rate of polymerization of vinylidene cyanide is rapid; polymerization of the cyclic ethers, when observed, takes place much more slowly. An initiation mechanism involving polar interaction between the vinylidene cyanide and the cyclic ether is proposed.

The polymerization of vinylidene cyanide takes place with anionic initiation, even with weak bases such as water and dimethylformamide at −78°. Vinyl ethers readily polymerize by cationic initiation, yet the mixing of these two kinds of monomers in solution (benzene) at 25° yields essentially homopolymers of the vinyl ethers and polymer containing high contents of vinylidene cyanide,[1] regardless of molar ratio of the vinyl ether to the vinylidene cyanide charged (5:1 to 1:5).[2] These results and the information[1] that the addition of trihydroxyethylamine inhibits the polymerization of the vinyl ethers and the addition of phosphorous pentoxide inhibits the polymerization of vinylidene cyanide in this system suggest simultaneous cationic and anionic polymerizations, respectively. These extraordinary results prompted us to explore the possibility that other monomers such as cyclic ethers, which are both electron donors and are susceptible to polymerization *via* cationic mechanisms, would also lead to the formation of homopolymers of each type of monomers (vinylidene cyanide and cyclic ether) when the two are mixed.[3]

Experimental Section

Materials. Vinylidene cyanide was prepared by the thermal decomposition of 1,1,3,3-tetracyanopropane,[1] bp 51° (10 mm) [lit.[1] bp 50.5° (10 mm)]. Tetrahydrofuran was heated to reflux over potassium hydroxide for 10 hr, distilled, and redistilled from a metallic sodium mirror. Purified material was stored over a metallic sodium mirror after the removal of air from the H_4furan by several freeze–thaw cycles under reduced pressure. Oxiranes and oxetanes were heated to reflux over potassium hydroxide, distilled, and then redistilled from calcium hydride. Trioxane was melted over calcium hydride and sublimed under reduced pressure. Toluene and dichloromethane were purified by the usual methods.

Polymerization Procedures for Vinylidene Cyanide and Cyclic Ethers (Table I). Polymerizations were carried out in the absence of light in Pyrex glass ampoules under reduced pressure. The dried monomers and solvents were transfered in a vacuum system by trap-to-trap distillation into ampoules, and then the ampoules were sealed and allowed to stand for definite periods of time at 25°. The ampoule was opened and the polymer produced was isolated by evaporating the volatile materials. The raw polymer was fractionated into the insoluble and soluble part in toluene at room temperature. Ir spectra and elemental analyses of these fractions showed that the insoluble fraction was a polymer predominantly consisting of poly(vinylidene cyanide), while the soluble fraction was essentially a homopolymer of cyclic ether.

The solution viscosities of the polymers were determined at 30° in benzene for the polymers of cyclic ethers, and in dimethylformamide containing 1% of acetic anhydride for the polymers of vinylidene cyanide.

A typical polymerization was carried out as follows. Vinylidene cyanide (1.0 g, 12.8 mmol) which had been dried over phosphorous pentoxide was distilled under reduced pressure (0.1 mm) into an ampoule cooled to −78° and then toluene (2.0 ml) was distilled into the same ampoule. The ampoule was warmed to room temperature, shaken, and then cooled to −78°. Oxetane (0.62 g, 12.8 mmol) which had been dried over sodium mirror was distilled into the ampoule under reduced pressure. The ampoule was sealed and shaken until the mixture was a clear solution and then was allowed to stand for 24 hr at 25°. The ampoule was opened and the volatile materials were distilled under reduced pressure (0.1 mm). The residue was extracted with toluene (20 ml). The insoluble fraction, dried *in vacuo*, was essentially a homopolymer of vinylidene cyanide as determined by its ir spectrum and elemental analysis. *Anal.* Calcd for $(C_4H_2N_2)_n$: C, 61.53; H, 2.58; N, 35.89. Found: C, 59.34; H, 2.61; N, 33.15.

The soluble fraction recovered by evaporation of toluene was a copolymer composed of poly(vinylidene cyanide) (∼5%) and polyoxetane (∼95%) as determined by elemental analysis. *Anal.* Found: C, 62.02; H, 9.82; N, 2.37.

Cyclic Dimers. In the spontaneous homopolymerization of vinylidene cyanide and either ethylene oxide or styrene oxide, cyclic dimers (dioxane or its derivatives) were found in the polymerization mixtures. In the case of ethylene oxide, 1,4-dioxane was isolated by glc of the distillate in yields of 42, 37, and 35% where the initial mol ratios of vinylidene cyanide to ethylene oxide were 1:5, 1:1.5, and 2.5:1, respectively. In the case of styrene oxide, *cis*- and *trans*-2,5-diphenyl-1,4-dioxanes were sepa-

Table I
Polymerization of Vinylidene Cyanide (VC) and Cyclic Ethers at 25°[a]

Cyclic Ether	Mol Ratio VC:Ether	Solvent	Insoluble Fraction			Soluble Fraction		
			% VC	% Conv	[η][d]	% Ether	% Conv[a]	[η][e]
Trioxane	1:1	CH_2Cl_2[b]	86	62			0	
	5:1	CH_2Cl_2[b]	86	32			0	
Tetrahydrofuran	1:10	Bulk[c]		Trace		86	25	1.28
	1:1	Bulk[c]	92	54	0.85	93	65	0.74
	5:1	Bulk[c]	93	36	1.36	95	100	0.27
Oxetane	1:5	Toluene	68	37	0.12	97	79	1.22
	1:1	Toluene	78	64	0.40	95	100	0.24
	5:1	Toluene	90	33	0.52	94	100	0.10
3,3-Bis(chloromethyl)-oxetane	1:5	Toluene	86	34			0	
	1:1	Toluene	86	56			0	
	1:1	Acetonitrile	88	56			0	
2,2-Dimethyloxirane	1:5	Toluene	87	100	0.21	90	3	2.10
	1:1	Toluene	90	84	0.77	88	7	0.90
	5:1	Toluene	85	61	1.39	70	44	0.14
2-Chloromethyloxirane (epichlorohydrin)	1:10	Toluene	86	73			2	
	1:1	Toluene	92	94		80	69	
	10:1	Toluene	94	79			4	
2-Phenyloxirane (styrene oxide)	1:5	Toluene	79	100		91	3[f]	
	1:1	Toluene	87	100		83	45[f]	
	5:1	Toluene	99	54		80	67[f]	
Oxirane (ethylene oxide)	1:5	Toluene	87	16			1[g]	
	1:1.5	Toluene	93	100			5[g]	
	2.5:1	Toluene	92	84			2.5[g]	
	1:10	Bulk	82	90		51[h]	1.5[g]	

[a] Polymerizations were carried out for 96 hr, except with tetrahydrofuran, in which case the polymerizations were allowed to continue for 168 hr. Conversions are calculated on the basis of the respective monomer charged. [b] Cyclic ether is insoluble in toluene. [c] Polymerization of cyclic ether in toluene takes place only very slowly. [d] Measured in dimethylformamide at 25°. [e] Measured in benzene at 25°. [f] A mixture of two diphenyl-1,4-dioxane isomers was obtained in each example. [g] In each case, 1,4-dioxane was obtained from the reaction. [h] Block copolymer as evidenced by its nmr spectrum and solubility in toluene. The nmr spectrum was identical with that of the two homopolymers.

rated from the soluble fraction of the polymerization mixture by column chromatography on alumina to yield *cis*-2,5-diphenyl-1,4-dioxane, mp 118° (lit.[4] 122°), and *trans*-2,5-diphenyl-1,4-dioxane, mp 167° (lit.[4] 173°). Yields of 28% (ratio of cis to trans isomer, 0.25), 20% (ratio of cis to trans isomer, 0.24), and 12% (ratio of cis to trans isomer, 0.31) were obtained when the ratios of vinylidene cyanide to styrene oxide were 1:5, 1:1, and 5:1, respectively. Nmr spectra (60 MHz) of these compounds were identical with those reported.[5]

Kinetic Studies. The kinetic studies for the polymerization of vinylidene cyanide and tetrahydrofuran were carried out directly in nmr tubes. The spectra of the polymerization mixture were observed in the initial stages [less than 40% conversion of poly(vinylidene cyanide)] by following the disappearance of the absorptions originating from methylene protons of vinylidene cyanide at 6.95 ppm and those of tetrahydrofuran at 1.85 and 3.75 ppm.[6] A small amount of benzene added to the system was used as the internal standard (7.37 ppm), and the disappearance of the absorptions originating from both monomers was measured in comparison with the intensity of benzene. The data in the latter stage of the polymerization were carried out by separating and isolating both polymers as described above, since all the absorptions in the nmr spectra were broadened by the precipitation of poly(vinylidene cyanide).

Results and Discussion

Polymerization. The reaction of vinylidene cyanide with polymerizable cyclic ethers in toluene at 25° gave an insoluble fraction of polymer which precipitated immediately or dispersed in the solution, and a soluble polymer fraction which was produced more slowly (Table I). The insoluble fraction, as it was obtained from the reaction without further fractionation, was essentially a homopolymer of vinylidene cyanide; the polymer remaining in solution, when obtained, was essentially a homopolymer of the cyclic ether. Room temperature appeared to be approximately the threshold temperature for polymerization, since in most cases no polymer of either monomer was obtained at 0° or below.

The ethers which were studied can be divided into three categories: (1) those which induced the polymerization of vinylidene cyanide and polymerized themselves—tetrahydrofuran, oxetane, 2,2-dimethyloxirane, epichlorohydrin, and styrene oxide. Of these only tetrahydrofuran and oxetane reproducibly gave high yields of polymer, regardless of the monomer ratio; (2) those which induce the polymerization of vinylidene cyanide but do not polymerize themselves—trioxane, 3,3-bis(chloromethyl)oxetane, and oxirane; (3) those which do not polymerize vinylidene cyanide (not given in Table I) 1,3-dioxolane, tetrahydropyran, and diethyl ether. In this category, neither 1,3-dioxolane nor vinylidene cyanide polymerized.

As shown in Table I, the molecular weight of polymers obtained from vinylidene cyanide and the cyclic ethers tetrahydrofuran, oxetane, and 2,2-dimethyloxetane varied with the ratio of both monomers charged. Increasing of the molar ratio of cyclic ethers to vinylidene cyanide in the feed decreased the molecular weight of poly(vinylidene cyanide) and conversely increased the molecular weight of polyethers.

Styrene oxide and ethylene oxide are the only two cyclic ethers in this series which also are known to afford polymer by anionic initiation and propagation mechanisms, and therefore the poly(ethylene oxide) and poly(styrene oxide) could have been produced anionically. In both cases, however, dioxane derivatives were isolated from the polymerization mixture containing polyether and poly(vinylidene cyanide); dioxane was obtained from the ethylene oxide polymerization and two of the diphenyl dioxanes (*cis*- and *trans*-2,5-diphenyl-1,4-dioxane) were obtained from the styrene oxide polymerization. These products are characteristic of cationic polymerization of these monomers,[7] and are not produced during the course of an anionic polymerization. When vinylidene cyanide and ethylene oxide were polymerized in a ratio 1:10 in bulk, a small

Table II
Polymerization of Vinylidene Cyanide (VC) and Tetrahydrofuran (H_4furan) in Bulk (Mol Ratio, 1:1) at 25° in the Presence of Additives[a]

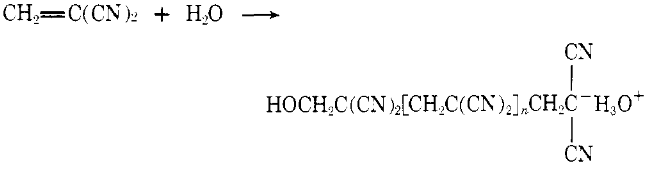
Additives	Mol Ratio Additives:VC	Insoluble Fraction % VC	Insoluble Fraction % Conv	Insoluble Fraction [η]	Soluble Fraction % H_4furan	Soluble Fraction % Conv	Soluble Fraction [η]
Benzoyl peroxide	0	95	46	0.85	98	15	0.32
	0.01	91	55	1.57	97	12	0.08
	0.02	90	24	1.27		0	
P_2O_5	1		0		100	58	Low
Water	0.00004	94	100	0.54		Trace	
	0.0002	94	76	0.36		0	
	0.001	93	73	0.38		0	
Pyridine	1	100	100	*b*		0	
Oxygen	10 ml to 2 g of VC	88	60	0.68		0	

[a] All polymerizations were carried out for 96 hr. [b] The polymerization was explosive; a low molecular weight powder was obtained.

amount of block copolymer was formed, presumably by the anionic initiation of ethylene oxide by poly(vinylidene cyanide) anion.

Effect of Additives on the Polymerization (Table II). When phosphorus pentoxide, a typical inhibitor for anionic polymerization, was present in the tetrahydrofuran or oxetane polymerization, vinylidene cyanide did not polymerize. When pyridine, a typical inhibitor for cationic polymerization, was present, no polyethers were obtained.[8] Similar results were obtained in the case of the spontaneous polymerization of mixtures of vinylidene cyanide and vinyl ethers.[1,2] In the case of the tetrahydrofuran polymerization, benzoyl peroxide and oxygen affected neither the yield nor the composition of the vinylidene cyanide polymer, but both effectively inhibited the formation of polytetrahydrofuran.

The effect of water on the polymerization was studied, since water is a common impurity, and could react with vinylidene cyanide to provide poly(vinylidene cyanide) and also serve as a cationic catalyst. A small amount of



$$CH_2{=}C(CN)_2 + H_2O \longrightarrow HOCH_2C(CN)_2[CH_2C(CN)_2]_nCH_2\overset{CN}{\underset{CN}{C^-}}H_3O^+$$

water effectively inhibited the polymerization of tetrahydrofuran. The highest yields and molecular weights of polytetrahydrofuran were obtained when the polymerization system had been very carefully dried. Poly(vinylidene cyanide) did not initiate the polymerization of tetrahydrofuran or oxetane under the reaction conditions, thus excluding the possibility that hydrogen cyanide eliminated from poly(vinylidene cyanide) was serving as the initiator.

Kinetic Studies. The time-conversion curves for the polymerization of vinylidene cyanide and tetrahydrofuran at a molar ratio 1:1, which have been constructed on the basis of the nmr spectra of the polymerization mixtures at 25°, are shown in Figure 1. Vinylidene cyanide is consumed rapidly in an early stage of the polymerization, and within experimental observations, little polymerization of tetrahydrofuran takes place before the completion of the polymerization of vinylidene cyanide. The rate of propagation of vinylidene cyanide is extremely rapid compared to that of tetrahydrofuran, which has a relatively slow cationic propagation rate.[9] The plots of the consumption of both monomers *vs.* time at various ratios of vinylidene cyanide to tetrahydrofuran are shown in Figures 2 and 3. The rates of disappearance of vinylidene cyanide in these polymerizations increased with the increasing amount of tetrahydrofuran charged initially. Similar results were obtained in the case of the polymerization of tetrahydrofuran.

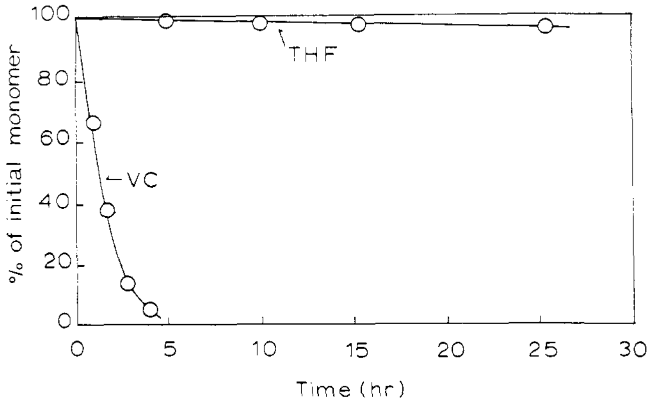


Figure 1. Rates of the vinylidene cyanide (VC) and tetrahydrofuran (THF, H_4furan) disappearance in bulk at 25° (mol ratio of 1:1).

The observation that the consumption of tetrahydrofuran is nearly 100% at high molar ratios of vinylidene cyanide to tetrahydrofuran is somewhat unusual. (See Table I, line 5 and Figure 3.) In the polymerization of tetrahydrofuran in bulk at 25° with Lewis acid catalysts, an equilibrium is established with monomer at 75% conversion to polymer.[10] In the vinylidene cyanide–tetrahydrofuran system, there are two differences which could account for this observation. The polymerization mixture rapidly produces a gel, remaining as such during the tetrahydrofuran polymerization. Also, the counterion, which is not known for this propagation, could protect the oxonium ion more effectively from intramolecular attack.

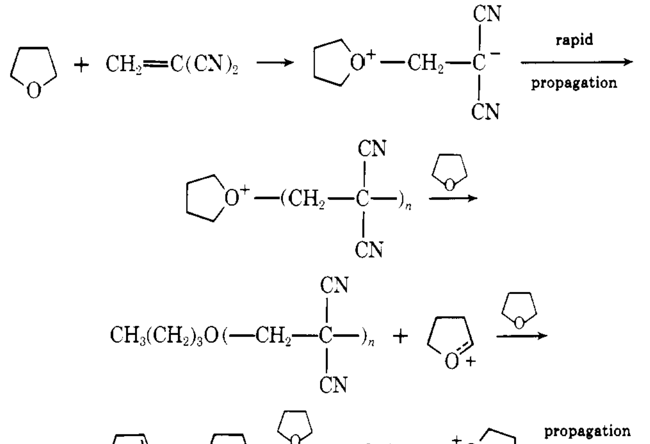
Mechanism. With the exception that propylene sulfide is polymerized by various electron acceptors,[11] these results are without precedent. Oxetane will polymerize in tetranitromethane in the presence of an electron donor olefin, but the initiator for its polymerization is the acid, trinitromethane.[12,13]

Polymerizations which are initiated *via* donor–acceptor complexes have been observed with a strong donor monomer (*N*-vinylcarbazole) and a weak acceptor monomer (methyl methacrylate or acrylonitrile).[14,15] In these cases, little or no color was observed in the polymerization. Tetrahydrofuran forms a complex with maleic anhydride, a weak acceptor, but undergoes the one-electron transfer only on irradiation.[16] Under these conditions, certain cyclic ethers will undergo ring-opening polymerization.[17]

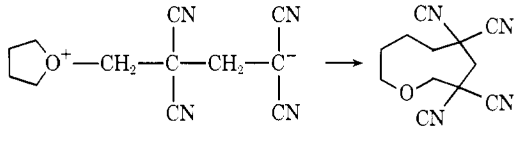
In the polymerization of vinylidene cyanide and the cyclic ethers, weak donors[18] and a strong electron acceptor are involved, but no color, however transient, was observed in the visible region. In addition, all our attempts to initiate polymerization of oxetane or tetrahydrofuran with the strong acceptors such as dichlorodicyano-*p*-benzoquinone, tetracyanoethylene, and tetracyanoquinodimethan produced only a trace of polymer. Thus, a charge-transfer mechanism for initiation is not consistent with these observations.

The observations that the rates of disappearance of the vinylidene cyanide in these polymerizations increased by increasing the amount of tetrahydrofuran initially charged, and that the molecular weight of each polymer increased as the ratio of the other monomer was decreased, indicate mutual initiation by the two monomers. Thus the initiator in the polymerization of vinylidene cyanide is either a cyclic ether, or perhaps a complex of a cyclic ether. Clearly, anionic propagation in the polymerization of vinylidene cyanide and cationic propagation in the polymerization of the cyclic ethers are taking place. The studies of the rates of polymerization indicate, however, that the polymerization of vinylidene cyanide is rapid, and that significant polymerization of cyclic ethers does not take place until the propagation of vinylidene cyanide chains has ceased. Since the poly(vinylidene cyanide) precipitates in the early stages of the polymerization, the anion end may be buried in the polymer chain, fed by vinylidene cyanide monomer, and inaccessable to any terminating species such as a cationically propagating polyether.

A "polar mechanism" similar to that proposed for the polymerization of donor monomers with weak acceptors[13,14] may be responsible for the initiation of polymerization. This mechanism relies on the rapid rate of propagation of vinylidene cyanide compared to the cyclization of the zwitterion.



Models show that cyclization of the dimer is not sterically possible, but cyclization could be accomplished after a second monomer addition. Cyclization at this stage may



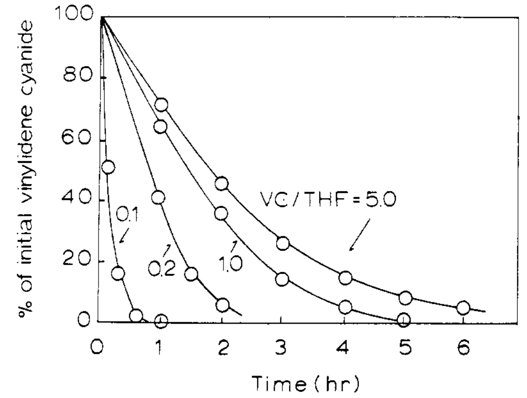


Figure 2. Rate of vinylidene cyanide disappearance on reaction with ratios of vinylidene cyanide (VC) to tetrahydrofuran (THF) in bulk at 25°.

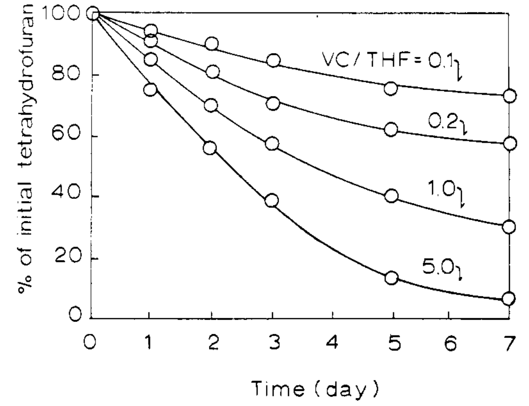


Figure 3. Rate of tetrahydrofuran disappearance on reaction with various ratios of vinylidene cyanide (VC) to tetrahydrofuran (THF) in bulk at 25°.

be precluded both by the rapid propagation rate and the fact that the anionic charge is delocalized over the nitrile, providing resonance stability and a diffuse charge. After the addition of subsequent vinylidene cyanide monomers, cyclization to ring sizes greater than nine becomes relatively more difficult. When the polymerization gets past the oligomer stage, the polymer precipitates, is immobile, and cannot cyclize readily. After precipitation, the chain end can be fed by vinylidene cyanide monomer by diffusion.

The steric bulk surrounding the oxonium ion end could effectively prevent attack of H_4furan at carbon in a propagation step. Hydride transfer from monomer generates the free oxonium ion which is known to decompose to dihydrofuran and provide a proton initiator.[19]

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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 ≥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] Acetophenone-

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

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