(33) The catalytic role of the metal promoter is especially required where the temperature of the reaction is substantially lower than that required for the first-order homolysis of the peroxydisulfate to proceed at comparable rates (i.e., $T > 100$ °C).[34]

(34) For the purely thermal reaction of peroxydisulfate with tetrafluoroethylene, compare entry 2 in Table I. The *increase* in pressure noted may be tentatively ascribed to the formation of $XCF_2CF_2X$, and hence, oxalic acid, which is known to afford $CO_2$ with peroxydisulfate [Po, H. N.; Allen, T. L. *J. Am. Chem. Soc.* **1968**, *90*, 1127]. It is noteworthy that no or little insoluble polymeric material was formed.

(35) For a review, see: (a) Kochi, J. K. "Free Radicals"; Wiley: New York, 1973; Vol. I, Chapter 11; (b) Nonhebel, D. C.; Walton, J. C. "Free Radical Chemistry"; Cambridge University Press: London, 1974; p 305ff. (c) Such a facile oxidation of perfluoroalkyl radicals by iron(III) species is interesting and merits further study.

(36) Tanner, D. D.; Osman, S. A. A. *J. Am. Chem. Soc.* **1968**, *90*, 6572.

(37) Anderson, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 1651. For a discussion, see also ref 35a, p 651ff.

(38) The absence of perfluorsuberic, -pimelic, or -adipic acids in the oxidative decarboxylation of perfluoroglutaric acid in eq 4 suggests that radical coupling does not compete with radical oxidation in these systems. It is also possible that some hypervalent iron species can lead to carboxy radicals in eq 11. Compare: Groves, J. T.; Van De Puy, M. *J. Am. Chem. Soc.* **1975**, *97*, 7118.

(39) Hamilton, J. M. *Ind. Eng. Chem.* **1953**, *45*, 1347.

(40) From J & W Scientific, Inc.

# Polymerization Behavior of 7,7,8,8-Tetrakis(ethylsulfonyl)quinodimethane with Donor Monomers

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ABSTRACT: It was found from the charge-transfer transition with hexamethylbenzene that 7,7,8,8-tetrakis(ethylsulfonyl)quinodimethane (TESQ) (EA = 1.17 eV) is much lower in electron affinity than 7,7,8,8-tetracyanoquinodimethane (TCNQ) (EA = 2.84 eV). TESQ and styrene underwent spontaneous alternating copolymerization in nitromethane, but when *p*-dioxane or dichloromethane was used instead of nitromethane, the copolymer obtained was not alternating and the styrene unit content was greater than 50 mol %, supposedly indicating that cationic polymerization of styrene takes place simultaneously. Additionally, when the TESQ fraction was above about 0.4, no copolymer was produced, and only 1:1 adduct was obtained in high yield. It was found that TESQ is able to induce the cationic oligomerization of isobutyl vinyl ether, *n*-butyl vinyl ether, 2-chloroethyl vinyl ether, and phenyl vinyl ether. However, reaction with vinyl acetate did not take place at all. Hydrogen-transfer reactions of TESQ and some alcohols, e.g., cinnamyl alcohol, 1-phenyl-1-propanol, and 1-phenylethanol, were attempted. Dehydration of the alcohols took place in addition to the intended hydrogen-transfer reaction, especially in the case of the latter two alcohols. It is pointed out that TESQ behaves more like an acidic compound than TCNQ although TESQ is much weaker in electron-accepting character than TCNQ.

So far the polymerization behavior of some quinodimethane derivatives with electron-accepting character has been studied. 7,7,8,8-Tetracyanoquinodimethane (TCNQ) can be copolymerized in an alternating fashion in acetonitrile with so-called donor monomers such as styrene (St),[1] 2-chloroethyl vinyl ether (CEVE),[2] phenyl vinyl ether (PhVE),[2] and vinyl acetate (VAc)[2] and is able to induce the cationic polymerizations of *n*-butyl vinyl ether (*n*-BVE) and isobutyl vinyl ether (*i*-BVE) in acetonitrile.[2,3] The mode of polymerization between TCNQ and CEVE was found to change from the alternating copolymerization to the cationic polymerization of CEVE upon replacement of the solvent from acetonitrile, with a low dielectric constant, to ethylene carbonate, with a high dielectric constant.[4] 7,7,8,8-Tetrakis(methoxycarbonyl)quinodimethane (TMCQ) can be copolymerized in an alternating amphoteric fashion; it reacts as an acceptor monomer with donor monomers such as St, VAc, PhVE, CEVE, and *i*-BVE while it reacts as a donor monomer with the very powerful electron-accepting monomer TCNQ.[5] 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$) can be copolymerized in an alternating fashion not only with donor monomers such as St, PhVE, and VAc but also with so-called acceptor monomers with small positive *e* values such as methyl methacrylate and methyl acrylate.[6] 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) is copolymerized alternatingly with St and induces the cationic polymerization of *i*-BVE and CEVE.[7] These interesting and unusual polymerization behaviors had not been found in conventional vinyl polymerizations.

In a series of studies of quinodimethane compounds at the Experimental Station of the du Pont Co. in the 1960's, 7,7,8,8-tetrakis(ethylsulfonyl)quinodimethane (TESQ) was reported by Hertler and Benson,[8] but its polymerization behavior has not been described yet. In Hammett substituent constants,[9] the ethylsulfonyl group ($\sigma_p = 0.68$) is as electron withdrawing as the cyano group ($\sigma_p = 0.66$), indicating a similar electron-withdrawing inductive effect, so TESQ was expected to be similar to TCNQ in its polymerization behavior as an acceptor monomer. Thus it seemed interesting to study in detail its polymerization behavior, as an acceptor monomer.

In this paper we study the spontaneous reactions between TESQ and donor monomers such as St, *n*-BVE, *i*-BVE, CEVE, PhVE, and VAc. In addition, we study the hydrogen-transfer reaction and dehydration of some alcohols with TESQ in connection with some unusual phenomena in the above reactions.

## Experimental Section

**Materials.** TESQ (mp 190 °C dec) and $\alpha,\alpha,\alpha',\alpha'$-tetrakis(ethylsulfonyl)-*p*-xylene ($TESQH_2$) (mp 257–258 °C) were prepared according to the method of Hertler and Benson.[8] TCNQ and *p*-phenylenedimalononitrile ($TCNQH_2$) were obtained by the process of Acker and Hertler.[10] TCNQ was purified by recrystallization from ethyl acetate and sublimation (twice) (mp 293.5–296 °C). PhVE was prepared from phenol and dibromomethane (bp 51.5–52.0 °C (17 mmHg)).[11] St (bp 58 °C (32 mmHg)), *n*-BVE (bp 92.5 °C), *i*-BVE (bp 81 °C), CEVE (bp 109

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Table I
Solvents for TESQ

| group | solubility for TESQ and decoloration | solvent |
|---|---|---|
| 1 | high solubility and rapid decoloration | dimethyl sulfoxide, *N,N*-dimethylformamide, formamide tetrahydrofuran, ethylenechlorohydrin |
| 2 | high solubility and decoloration within two days | *p*-dioxane, 1,2-dibromoethane, chloroform, dichloromethane, 1,1,2,2-tetrachloroethane |
| 3 | high solubility and slow decoloration (about a week) | cyclohexanone, benzonitrile, nitromethane, nitroethane |
| 4 | slight (swollen) solubility | benzene, monochlorobenzene, acetic acid, acetone, 1,2-dichloroethane, formic acid, acetonitrile, *m*-cresol |
| 5 | no solubility | carbon tetrachloride, *m*-xylene, toluene, carbon disulfide, trichloroethylene, ethyl acetate, *o*-dichlorobenzene, monoglyme, isopropyl alcohol, 2-ethoxyethanol, methanol, 1,1,2-trichloro-1,2,2-trifluoroethane |

°C), and VAc (72 °C) were purified from commercial products by conventional methods. DDQ was prepared from hydroquinone according to the method of Walker and Waugh[12] and was purified just prior to use by recrystallization using a mixture of chloroform and benzene (4:1 by volume) as solvent and by further sublimation (mp 212–213 °C). 1-Phenyl-1-propanol (bp 74–75 °C (3 mmHg)) and 1-phenylethanol (bp 90–92 °C (10 mm Hg)) were prepared by the reduction reaction of propiophenone and acetophenone, respectively, with lithium aluminum hydride.[13] $\beta$-Methylstyrene as authentic sample for gas chromatography examination was prepared according to the method of Overberger and Tanner.[14] Guaranteed reagent grade hexamethylbenzene (HMB), *p*-chloranil (PCA), diphenylpicrylhydrazyl (DPPH), and cinnamyl alcohol were used without further purification. *p*-Dioxane (bp 101 °C), dichloromethane (bp 39.5 °C), nitromethane (bp 101 °C), and dimethyl sulfoxide ($Me_2SO$) (bp 65–67 °C (10 mmHg)) as solvents were purified from commercial products by conventional methods.

**Solvent for TESQ.** Thirty-four kinds of commercially available solvents were examined in solubility and oxidizing ability toward TESQ. The results are summarized in Table I.

**Polymerization Procedure.** For copolymerization, given amounts of TESQ, comonomer, and solvent were placed in an ampule, which was degassed completely by the freeze–thaw method (repeatedly three times) and sealed. No initiator was added. The ampule was set in a bath thermostated at 60 °C for the time of polymerization and then opened. In the case of St as a comonomer, the reaction mixture was poured into excess methanol containing a small amount of calcium nitrate to give a precipitate. The precipitate obtained was dissolved again in benzene, and the resulting solution was poured into excess methanol to precipitate the copolymer, which was dried under reduced pressure. In the case of *i*-BVE, *n*-BVE, CEVE, or PhVE as a comonomer, the reaction mixture was placed under reduced pressure to remove volatile materials. For *i*-BVE, *n*-BVE, or CEVE, a viscous residue was obtained but PhVE yielded a powdery one. The residue obtained was dissolved in a chloroform. The resulting solution was passed into a silica gel column to remove the unreacted TESQ. The solution treated was placed under reduced pressure to remove chloroform, and the reaction product was obtained.

For the terpolymerization of TESQ, TCNQ, and St, given amounts of the monomers and nitromethane as a solvent were placed in an ampule. The rest of the procedure was carried out similarly to the copolymerization described above. The terpolymer obtained was dissolved in *N,N*-dimethylformamide (DMF), and the resulting solution was poured into excess methanol to precipitate the terpolymer, which then was dried under reduced pressure.

**1:1 Adduct Formation of TESQ and St.** Given amounts (0.8–1.0 mmol) of TESQ and St and 40 mL of dichloromethane, *p*-dioxane, or nitromethane solvent were placed in an ampule, which was set in a bath thermostated at 60 °C for 112 h. The reaction mixture was placed under reduced pressure to remove the solvent. The solid residue was dissolved in a small amount of benzene, and the resulting solution was poured into petroleum ether to precipitate a powdery product. The product was placed on a column packed with silica gel and eluted with a mixture of benzene and methanol (9:1 by volume) as one elution band. The eluate of the one band was poured into hexane to give a precipitate, which then was dried to a constant weight.

**Hydrogen-Transfer Reaction and Dehydration Reaction.** The experimental procedure followed methods described in papers on the hydrogen-transfer reaction of alcohols with tetracyanoethylene[13] and TCNQ.[15]

For the hydrogen-transfer reaction, given amounts of the alcohol, the hydrogen acceptor (DDQ, PCA, TCNQ, and TESQ), and 1 mL of *p*-dioxane were placed into a Pyrex glass tube, which was degassed by the freeze–thaw method and sealed. The tube was set in an oil bath thermostated at 120 °C for a given reaction time. The reaction mixture was analyzed by gas chromatography (GLC) with 12% diethylene glycol succinate on Diasolid L as a packing agent and phenylcyclohexane as an internal standard.

For the dehydration reaction, a given amount of 1-phenylethanol or 1-phenyl-1-propanol and a catalytic amount of TESQ, $TESQH_2$, or $TCNQH_2$ were placed into a Pyrex glass tube, which was degassed by the freeze–thaw method and sealed. The tube was set in an oil bath thermostated at 115 °C for a given reaction time and then opened. The reaction products obtained were analyzed by GLC. In the case of 1-phenylethanol, the reaction product was poured into excess methanol to give a precipitate, which, also, was analyzed by gel permeation chromatography, with tetrahydrofuran as an eluent.

**Charge-Transfer Absorption Band.** Absorption spectra of the TESQ–St and TESQ–HMB systems in nitromethane and dichloromethane, respectively, at room temperature were recorded on a Shimadzu Model UV-200 spectrometer. The concentrations of solution employed were $[TESQ] = 3.0 \times 10^{-3}$ mol/L and $[St] = [HMB] = 0.3$ mol/L.

**Characterization of the Polymer and the Low Molecular Weight Adduct.** Compositions of the copolymer and the adduct were established by elemental analysis. Their molecular weights were determined by a Knauer vapor pressure osmometer, using benzene or chloroform as a solvent. Solution viscosity of the terpolymer of TCNQ, TESQ, and St was determined at 30 °C by an Ostwald viscometer, using DMF containing 0.1 wt % lithium chloride as a solvent.

## Results and Discussion

Although it is fairly stable in the solid state, TESQ is known to react slowly in solution with oxygen to lead to terephthalic acid.[8] When TESQ was dissolved in $Me_2SO$, the yellow color of its $Me_2SO$ solution disappeared immediately under air or even under nitrogen. The $^1H$ NMR spectrum of the decolored TESQ in dimethyl-$d_6$ sulfoxide ($Me_2SO$-$d_6$) showed a peak at 14 ppm, reasonably assignable to a carboxylic acid proton. The $Me_2SO$ solution of TESQ decolored under nitrogen was placed under reduced pressure to remove volatile materials. The colorless crystalline material obtained was identified as $\alpha,\alpha$-bis(ethylsulfonyl)-*p*-toluic acid by its IR, $^1H$ NMR, and elemental analysis data. Since TESQ is readily subject to oxidation in such a way, solvents in the third group of Table I are preferable as reaction solvents for TESQ, and ones in the second group also may be used if the reaction is carried out with great care.

**Charge-Transfer Transitions between TESQ and St or HMB.** The difference spectrum in nitromethane between the mixture of TESQ with St and TESQ, attrib-

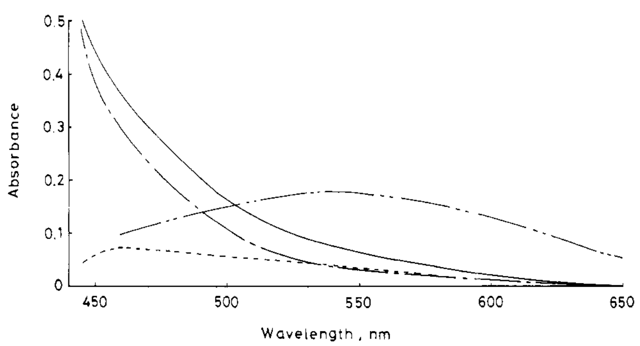

**Figure 1.** UV–vis spectra of a mixture of TESQ with HMB in dichloromethane: (—) spectrum of a mixture of TESQ with HMB; (- - -) spectrum of TESQ; (- · -) difference spectrum between the preceding two spectra, corresponding to that of the complex; (- - - ·) difference spectrum between TCNQ and a mixture of TCNQ with HMB in acetonitrile. Concentrations of solutions employed are [TESQ] = $3.0 \times 10^{-3}$ mol/L and [HMB] = 0.3 mol/L.

utable probably to the charge-transfer complex between TESQ and St, appears only as a shoulder (an increase in intensity) at the longer wavelength side of an absorption band of TESQ rather than as a definite peak. Thus the absorption maximum of the lowest intermolecular charge-transfer transition between TESQ and St could not be determined numerically for this complex. Since HMB is much more electron donating than St and the charge-transfer transition band between HMB and TCNQ was observed at 540 nm[5] as a definite peak, the charge-transfer transition band between TESQ and HMB was measured in dichloromethane. HMB does not absorb any light at wavelengths longer than 440 nm. The spectrum of the mixture of HMB and TESQ is shown in Figure 1, where the peak position is roughly read as 460 nm, due to its very broad absorption band. From the well-known relationship[16] among the absorption wavelength of the charge-transfer transition band, electron affinity of acceptor compound, and ionization potential of donor compound, the electron affinity of TESQ could be estimated numerically as 1.17 eV since the electron affinity of TCNQ may be taken as 2.84 eV.[17] It is noteworthy that TESQ is much weaker in electron-accepting character than TCNQ, irrespective of similar Hummett constant values for the ethylsulfonyl and cyano groups,[9] suggesting that they would have a similar inductive effect on the quinodimethane part.

**Copolymerization between TESQ and St.** Table II summarizes the results of the copolymerizations of TESQ and St in the three kinds of solvents, *p*-dioxane (dielectric constant $\epsilon = 2.21$[18] and electron-donating power $\Delta\nu_D = 77$ cm$^{-1}$),[19] dichloromethane ($\epsilon = 8.93$[18] and $\Delta\nu_D = -12$ cm$^{-1}$),[19] and nitromethane ($\epsilon = 35{,}87$[18] and $\Delta\nu_D = 6$ cm$^{-1}$),[19] and Figure 2 shows the composition diagram for these copolymerizations. The copolymers were obtained as pale yellow powders. The molecular weights of the copolymers obtained were found to be as low as 2400–4800. DPPH was found to inhibit the copolymerization in nitromethane, indicating that the copolymerization proceeds via a free radical intermediate.

The copolymers obtained in nitromethane were found to show fixed found values in elemental analysis, regardless of monomer feed ratio. The found values for the copolymers are in good agreement with the calculated values for the alternating copolymer composed of eight TESQ units and nine St units with St units at both terminals. The $^1$H NMR spectrum of the copolymer is shown in Figure 3, where it can be seen that the methine and methylene protons of the St unit, appearing at $\delta$ 2.5–3.5 ppm, are much more subject to deshielding than the corresponding ones of homopolystyrene, appearing at $\delta$ 1–2 ppm.[20] It can be pointed out that the deshielding arises from a powerful electron withdrawal by the neighboring bis(ethylsulfonyl)methylene group when the St unit is sandwiched between TESQ units. On the other hand, the compositions of copolymer obtained in *p*-dioxane and dichloromethane were found to be dependent upon the monomer feed ratio, different from that in nitromethane, as shown in Figure 2. The copolymers obtained were examined by column and gel permeation chromatography and their spectra allowed only one band, conclusively showing that a polymer mixture, for example, that of the alternating copolymer and the polymer with a TESQ unit content less than 50 mol %, did not form. At the moment, the solvent effect observed in this copolymerization was found to be complicated and could not be explained consistently in terms of polarity and basicity. However, from the dehydration reaction of 1-phenylethanol with TESQ to give polystyrene as described later, it might be proposed that TESQ and its hydrogenation product may initiate the cationic polymerization of St simultaneously with the alternating copolymerization.

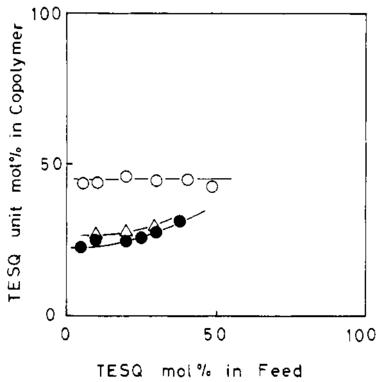

**Figure 2.** Composition diagram of the copolymerization of TESQ with St in dichloromethane (●), nitromethane (○), and *p*-dioxane (△).

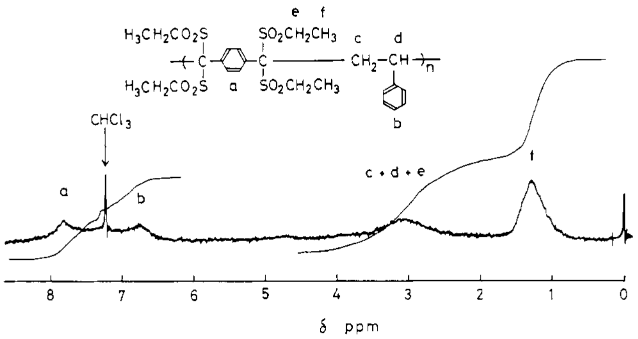

**Figure 3.** $^1$H NMR spectrum in chloroform-*d* of the copolymer of TESQ and St obtained in nitromethane.

In order to obtain the relative reactivities of TESQ and TCNQ as acceptor monomers, terpolymerization of TESQ, TCNQ, and St was carried out in nitromethane at 60 °C. Nitromethane was chosen as a polymerization solvent because both the TCNQ–St system and the TESQ–St system give alternating copolymers in this solvent. The results of the terpolymerization of TESQ, TCNQ, and St are summarized in Table III. The products were obtained as white powders. Compositions of the monomer mixture and the terpolymer obtained are shown as open and closed circles, respectively, in the triangular diagram of Figure 4. The terpolymers obtained always contain each about 50 mol % St and TCNQ units, regardless of monomer feed ratio, and TESQ unit content is very low. Both TESQ and TCNQ were considered as acceptor monomers toward St.

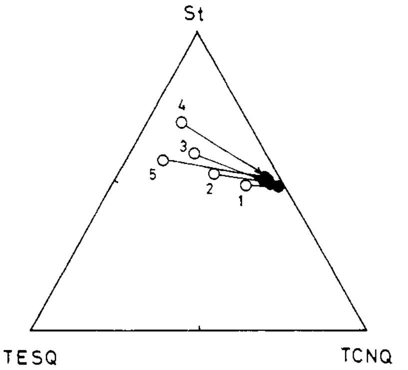

**Figure 4.** Triangular composition diagram of the terpolymerization of TESQ, TCNQ, and St: (○) feed composition; (●) terpolymer composition. Arrows show change in composition from the feed to the terpolymer obtained.

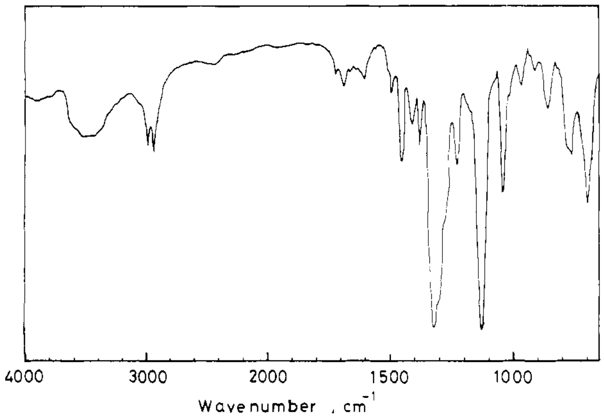

**Figure 5.** IR spectrum of the adduct of TESQ and St obtained in dichloromethane (KBr disk).

Thus, the experimental results imply that TCNQ is incorporated much more rapidly into the terpolymer than TESQ and that TESQ is much less reactive as an acceptor monomer than TCNQ.

**1:1 Adduct between TESQ and St.** As another characteristic point of the copolymerization between TESQ and St, it could be pointed out that the yield of the copolymer obtained decreased remarkably with TESQ fraction in the monomer feed, and no copolymer was obtained in the monomer feed region above about 0.4 of TESQ mole fraction. In addition, neither monomer could be recovered, but a low molecular weight product composed of TESQ and St units was obtained in fairly high yield. In Table IV are shown the results of the reaction of almost equimolar amounts of TESQ and St. The product was obtained as a pale yellow powder. The IR and $^1$H NMR spectra of the product obtained in dichloromethane are shown in Figures 5 and 6a, respectively. The compound with structural formula A illustrated in Figure 6a could explain well these spectra and the found values in the elemental analysis. The absorption peaks in the NMR spectrum could be assigned to protons marked with the corresponding letters in formula A and the ratios in peak area were found as a/b/c/d/e = 9/1/10/2/13, agreeing well with the calculated values of 9/1/10/2/12. It was concluded, therefore, that the reaction product is the 1:1 adduct with structural formula A. The products obtain in *p*-dioxane and nitromethane were found to have IR and $^1$H NMR spectra, elemental analysis, and molecular weight similar to those of the product obtained in dichloromethane, indicating the same 1:1 adduct.

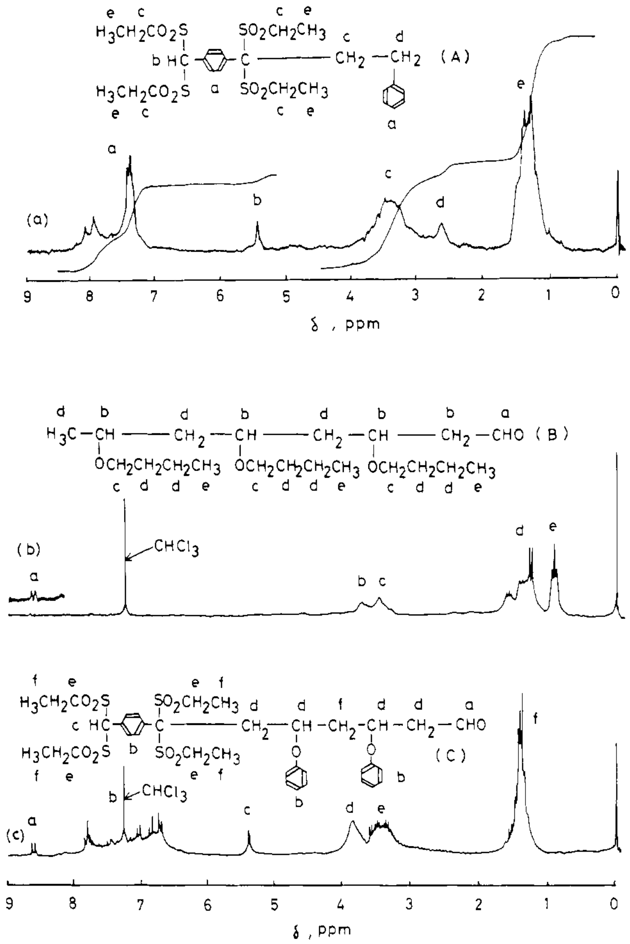

**Figure 6.** $^1$H NMR spectra in chloroform-*d* of (a) the adduct of TESQ and St obtained in dichloromethane, (b) the cationic oligomer of *n*-BVE initiated by TESQ, and (c) the cationic oligomer of PhVE initiated by TESQ.

**Polymerization Modes between TESQ and Vinyloxy Compounds.** In Table V are shown the results of the polymerization of TESQ with *i*-BVE, *n*-BVE, CEVE, PhVE, and VAc in dichloromethane. The reaction products of TESQ with *i*-BVE, *n*-BVE, and CEVE showed neither IR absorptions at 1600 cm$^{-1}$ due to the benzene nucleus nor ones at 1110 and 1320 cm$^{-1}$ due to the sulfone group, but they did give an absorption at 1740 cm$^{-1}$, which is assignable to the carbonyl group of aldehyde because their FT $^1$H NMR spectra carried an absorption at 8.6 ppm, probably due to aldehyde proton, as shown in Figure 6 b. Their found values in elemental analysis were in good agreement with the calculated ones for structural formula B illustrated in Figure 6b. Therefore, it is conceivable that they may be oligomers of the respective vinyloxy compounds with an aldehyde group as a terminal group and three to five degrees of polymerization. The reaction product of TESQ with PhVE showed absorptions at 1740 cm$^{-1}$ due to the aldehyde group and ones at 1110 and 1320 cm$^{-1}$ due to the sulfone group. Its found values in elemental analysis were in good agreement with the calculated ones for structural formula C illustrated in Figure 6c. In addition, its $^1$H NMR, shown in Figure 6c, and IR spectra were explained well in terms of structure C. Therefore, it is probable that the reaction product of TESQ with PhVE also is an oligomer of PhVE with the TESQ unit as one terminal and the aldehyde group as the other one. Reaction of TESQ with VAc was not found to take place under the reaction conditions and TESQ could be recovered quantitatively.

It can be pointed out that reactions of TESQ with vinyloxy compounds do not give any alternating copolymer and all vinyloxy compounds employed except VAc undergo

Table II
Copolymerization[a] of TESQ with St in Various Solvents at 60 °C

| solvent | monomer feed, mmol TESQ | monomer feed, mmol St | amt of TESQ, mol % | vol of solvent, mL | time, h | polymn yield, mg | conv, % | anal. % C | anal. % H | copolymer comp, mol % TESQ | $\overline{M}_n$[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $p$-dioxane ($\epsilon$ = 2.21) | 0.236 | 2.09 | 10.2 | 10 | 27 | 40.9 | 12.4 | 59.96 | 5.83 | 26.8 | 2700 |
| | 0.870 | 3.46 | 20.1 | 40 | 97 | 86.7 | 11.2 | 59.28 | 5.59 | 27.9 | 2400 |
| | 0.869 | 2.07 | 29.5 | 40 | 124.5 | 30.5 | 4.9 | 58.29 | 5.74 | 29.7 | 1900 |
| | 0.876 | 0.97 | 47.5 | 40 | 310 | | | | | | |
| | | | | | | I[c] 260.3 | 50.6 | 50.28 | 5.68 | | 640 |
| dichloromethane ($\epsilon$ = 8.93) | 0.236 | 4.41 | 5.1 | 10 | 21 | 32.3 | 5.7 | 63.22 | 6.07 | 22.1 | |
| | 0.759 | 6.83 | 10.0 | 40 | 46 | 73.9 | 6.9 | 60.66 | 5.75 | 25.8 | 4500 |
| | 0.758 | 3.12 | 19.6 | 40 | 93 | 69.5 | 10.2 | 61.53 | 6.49 | 24.5 | 4200 |
| | 0.869 | 2.62 | 24.9 | 40 | 10 | 19.2 | 2.8 | 60.60 | 6.19 | 25.9 | |
| | 0.769 | 1.81 | 29.9 | 40 | 165 | 31.5 | 5.7 | 59.69 | 5.89 | 27.4 | 3900 |
| | 0.857 | 1.44 | 37.4 | 40 | 292 | 36.5 | 6.6 | 57.63 | 5.78 | 31.0 | |
| | | | | | | I[c] 382.2 | 60.9 | 50.32 | 5.56 | | 670 |
| nitromethane ($\epsilon$ = 35.87) | 0 | 3.59 | 0 | 6 | 19 | 0 | 0 | | | | |
| | 0.251 | 4.52 | 5.3 | 10 | 22 | 16.4 | 2.8 | 52.17 | 5.70 | 43.4 | |
| | 0.856 | 7.69 | 10.0 | 40 | 22 | 63.2 | 5.2 | 52.01 | 5.81 | 43.9 | 4800 |
| | 0.864 | 3.49 | 19.9 | 40 | 91 | 40.3 | 5.2 | 51.79 | 5.76 | 45.9 | 4800 |
| | 0.868 | 2.06 | 29.7 | 40 | 147 | 19.6 | 3.1 | 51.86 | 5.30 | 44.3 | |
| | 0.864 | 1.29 | 40.2 | 40 | 360 | 9.1 | 1.7 | 51.68 | 5.29 | 44.8 | |
| | 0.876 | 0.93 | 48.6 | 40 | 145 | 7.9 | 1.6 | 52.57 | 5.44 | 42.4 | |
| | | | | | | I[c] 397.0 | 77.8 | 50.55 | 5.83 | | 670 |
| | 0.213[d] | 1.91 | 10.0 | 10 | 26 | | 0 | | | | |

[a] Without added initiator. [b] Determined by vapor pressure osmometry. Solvent, benzene. [c] When the copolymer yield was low, the methanol solution left after removal of the precipitate of the copolymer was treated in the procedure for the 1:1 adduct to give the product I. [d] In the presence of 6.5 mg of DPPH.

Table III
Terpolymerization[a] of TESQ, TCNQ, and St in Nitromethane at 60 °C

| run no. | monomer feed, mol % TESQ | monomer feed, mol % TCNQ | monomer feed, mol % St | total amt of monomer, mmol | vol of solvent, mL | time, min | conv, % | anal. % C | anal. % H | anal. % N | terpolymer comp, mol % TESQ | terpolymer comp, mol % TCNQ | terpolymer comp, mol % St | $\eta_{sp}/C$,[b] dL·g$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 10.9 | 40.3 | 48.9 | 0.992 | 10 | 30 | 13.3 | 75.85 | 4.00 | 17.36 | 1.8 | 49.7 | 48.5 | |
| 2 | 18.8 | 28.2 | 53.0 | 0.703 | 10 | 28 | 12.2 | 73.90 | 4.01 | 15.97 | 3.9 | 47.3 | 48.8 | |
| 3 | 20.1 | 19.8 | 60.1 | 0.775 | 10 | 35 | 20.9 | 72.52 | 3.61 | 14.77 | 5.6 | 44.7 | 49.7 | 0.645 |
| 4 | 19.9 | 9.9 | 70.2 | 1.793 | 20 | 45 | 17.6 | 73.62 | 4.16 | 15.04 | 4.6 | 44.4 | 51.0 | 0.535 |
| 5 | 31.5 | 10.4 | 58.0 | 2.207 | 40 | 70 | 15.0 | 74.67 | 4.21 | 15.84 | 3.4 | 46.0 | 50.6 | 0.526 |

[a] Without added initiator. [b] DMF containing 0.1 wt % lithium chloride solvent; $t$ = 30 °C.

Table IV
Reaction of TESQ with St at 60 °C[a]

| solvent | monomer feed, mmol TESQ | monomer feed, mmol St | amt of TESQ, mol % | adduct yield, mg | conv, % | anal.[b] % C | anal.[b] % H | $\overline{M}_n$[c] |
|---|---|---|---|---|---|---|---|---|
| dichloromethane | 0.768 | 0.79 | 49.5 | 290 | 65.3 | 50.11 | 6.20 | 670 |
| $p$-dioxane | 0.876 | 0.97 | 47.5 | 260 | 50.6 | 50.28 | 5.68 | 640 |
| nitromethane | 0.876 | 0.93 | 48.6 | 397 | 77.8 | 50.55 | 5.83 | 670 |

[a] Without added initiator. Solvent volume 40 mL. [b] Calculated values for the 1:1 adduct of TESQ and St: C, 49.80; H, 5.93. [c] Determined by vapor pressure osmometry. Solvent, benzene. Calculated molecular weight for the 1:1 adduct of TESQ and St: 578.8.

Table V
Reaction of TESQ with Vinyloxy Compounds in Dichloromethane[a] at 60 °C

| run no. | monomer feed, mg: TESQ | monomer feed, mg: comonomer | time, h | oligomer yield, mg | conv, % | anal.: % H | anal.: % C | $\overline{M}_n$[b] | remark |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 10.1 | *i*-BVE, 199.4 | 7.5 | 19.0 | 9.1 | 11.16 | 70.09 | 440 | $\nu_{C=O}$ 1740 cm$^{-1}$ |
| 2 | 9.7 | *n*-BVE, 207.3 | 7.4 | 23.7 | 10.0 | 11.31 | 69.88 | 340 | $\nu_{C=O}$ 1740 cm$^{-1}$ |
| 3 | 11.2 | CEVE, 219.6 | 24.0 | 33.4 | 15.2 | 6.14 | 46.10 | 350 | $\nu_{C=O}$ 1740 cm$^{-1}$ |
| 4 | 10.3 | PhVE, 210.2 | 24.0 | 12.5 | 5.9 | 5.9 | 53.26 | 720 | $\nu_{C=O}$ 1740 cm$^{-1}$;<br>$\nu_{S-O}$ 1110, 1320 cm$^{-1}$ |
| 5[c] | 10.3 | VAc, 201.3 | 24.0 | 0 | 0 | | | | |

[a] Without added initiator. Solvent volume, 10 mL. [b] Determined by vapor pressure osmometry. Solvent, chloroform. [c] TESQ was recovered quantitatively.

Table VI
Hydrogen-Transfer Reaction at 120 °C[a]

| hydrogen donor | hydrogen acceptor | reaction time, h | yield of dehydrogenation product,[b] % | | recovery of hydrogen donor,[b] % | unknown other product, % |
|---|---|---|---|---|---|---|
| cinnamyl alcohol | DDQ | 24 | cinnamaldehyde | 99 | 3 | 0 |
| | PCA | 24 | | 100 | 0 | 0 |
| | TCNQ | 24 | | 77 | 18 | 0 |
| | TESQ | 24 | | 52 | 6 | ~40 |
| 1-phenyl-1-propanol | DDQ | 24 | propiophenone | 75 | 17 | 0 |
| | PCA | 24 | | 22 | 29 | ~50 |
| | TCNQ | 24 | | 34 | 73 | 0 |
| | TESQ | 24 | | 8 | 3 | ~90[c] |
| | $TESQH_2$ | 24 | | 0 | 20 | ~80[c] |
| 1-phenylethanol | DDQ | 21 | acetophenone | 76 | 28 | 0 |
| | PCA | 21 | | 8 | 90 | 0 |
| | TCNQ | 21 | | 19 | 84 | 0 |
| | TESQ | 21 | | 16 | 68 | ~15[c] |
| | $TESQH_2$ | 21 | | 0 | 54 | ~45[c] |

[a] Solvent, *p*-dioxane (1 mL). Concentrations of solutions employed are [hydrogen donor] = [hydrogen acceptor] = 0.1 mol/L. [b] Product yield was determined by GLC with phenylcyclohexane as internal standard. [c] Dehydrated products.

cationic oligomerization with TESQ. On the other hand, when TCNQ was used instead of TESQ, vinyloxy compounds such as CEVE, PhVE, and VAc copolymerize alternatingly with TCNQ, and *i*-BVE and *n*-BVE undergo cationic polymerization.[2] It is noteworthy that TESQ can initiate cationic polymerization of vinyloxy compounds with fairly low electron-donating character such as CEVE and PhVE although TESQ was found from its charge-transfer transition with HMB to be much lower in electron affinity than TCNQ.

**Hydrogen-Transfer Reaction and Dehydration of Alcohols with TESQ.** TESQ was supposed from its chemical structure to function as a powerful hydrogen acceptor in a hydrogen-transfer reaction similarly to DDQ, PCA, and TCNQ. In Table VI are shown results of hydrogen-transfer reactions in *p*-dioxane between the hydrogen acceptors TESQ, DDQ, PCA, and TCNQ, and the hydrogen donors cinnamyl alcohol, 1-phenyl-1-propanol, and 1-phenylethanol. In the case of cinnamyl alcohol as a hydrogen donor, cinnamaldehyde was obtained in almost quantitative yield for DDQ, PCA, and TCNQ, while an unknown compound boiling at temperatures lower than 100 °C was formed as a byproduct in considerable yield for TESQ, indicating that some reactions other than the hydrogen-transfer reaction were occurring to nearly an equivalent extent. In the case of 1-phenyl-1-propanol, DDQ and TCNQ gave only propiophenone as a dehydrogenation product, PCA yielded propiophenone and an unknown volatile compound other than β-methylstyrene, and TESQ afforded a small amount of propiophenone and a large amount of β-methylstyrene, the latter of which is thought to be the dehydration product of 1-phenyl-1-propanol, indicating that the dehydration reaction took place preferentially rather than the expected hydrogen-transfer reaction. In the case of 1-phenylethanol, DDQ, PCA, and TCNQ gave only acetophenone, while TESQ afforded almost equivalent amounts of acetophenone and St. This formation of St could not be confirmed directly by GLC because St has the same retention time as *p*-dioxane, which was used as a solvent, but it was presumed reasonably from the results of the dehydration reactions described later. Therefore, it is conceivable that TESQ serves not only as a hydrogen acceptor compound in the hydrogen-transfer reaction but also as a catalyst in the dehydration of alcohol. To verify the catalytic action, the dehydration of alcohols such as 1-phenyl-1-propanol and 1-phenylethanol was carried out in the presence of a small amount of TESQ or $TESQH_2$ without solvent at 115–120 °C. $TESQH_2$, regarded as the hydrogenation product of TESQ, was expected from its chemical structure to be a strong Brønsted acid, which may act as a good catalyst in the dehydration of the alcohols. The results obtained are summarized in Table VII. It is obvious that the dehydration of the alcohols is promoted effectively with TESQ or $TESQH_2$ to give dehydration products such as β-methylstyrene and St in quantitative yield. The gel permeation chromatogram of the product of the dehydration reaction of 1-phenylethanol in the presence of catalytic amounts of TESQ is shown in Figure 7, which shows the formation of St as a dehydration product and further its cationic polymerization products such as dimer, trimer, tetramer, and polymer of St, indicating that TESQ manifests a powerful catalytic action in the dehydration of alcohol and also induces a cationic polymerization of St, the dehydration product of 1-phenylethanol.

It is likely that $TESQH_2$ is a very effective catalyst for the dehydration of the alcohols rather than TESQ. Thus it is conceivable that when TESQ is used as a hydrogen

Table VII
Dehydration[a] by TESQ, $TESQH_2$, and $TCNQH_2$

| catalyst, mmol | | alcohol, mmol | | [alcohol]/[catalyst] | time, h | product | yield,[b] % | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | monomeric form | polymeric form |
| TESQ | 0.053 | 1-phenyl- | 2.24 | 42 | 25 | β-methyl- | 53 | 43 |
| | 0.037 | 1-propanol | 1.97 | 53 | 3 | styrene | 32 | 62 |
| | 0.039 | | 3.04 | 80 | 6 | | 29 | 62 |
| $TESQH_2$ | 0.045 | | 1.68 | 37 | 3.5 | | 40 | 59 |
| $TCNQH_2$ | 0.052 | | 2.19 | 42 | 24 | | 0 | 0 |
| TESQ | 0.009 | 1-phenyl- | 1.56 | 176 | 24 | styrene | 16 | 83 |
| $TESQH_2$ | 0.011 | ethanol | 1.66 | 158 | 24 | | 14 | 85 |

[a] Without solvent. Reaction temperature, 115-120 °C. [b] Product yield was determined by GLC.

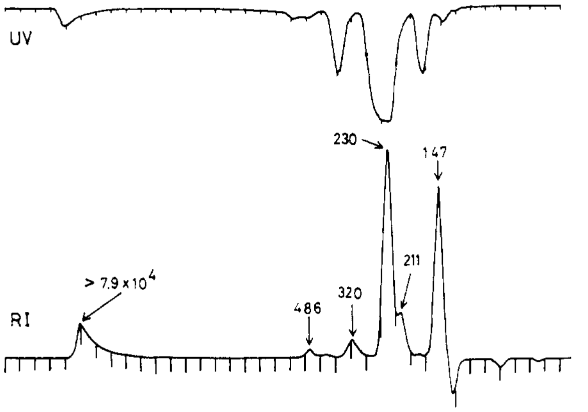

**Figure 7.** Gel permeation chromatogram of the dehydration product of 1-phenylethanol with TESQ. Eluent, tetrahydrofuran; internal standard, phenylcyclohexane (MW = 150.3).

acceptor for the hydrogen-transfer reaction, TESQ is reacts with the alcohols to yield its hydrogenation product, $TESQH_2$, which immediately accelerates the dehydration of the alcohol and interferes with the intended hydrogen-transfer reaction.

In addition, it is clear that TCNQ and $TCNQH_2$, as the hydrogenation product of TCNQ, cannot accelerate the dehydration of the alcohols, implying that $TCNQH_2$ is not a sufficiently strong acid to promote the dehydration of the alcohols; in other words, TCNQ is a very favorable hydrogen acceptor for the hydrogen-transfer reaction, because only the product of the hydrogen-transfer reaction is obtained. It is noteworthy that $TESQH_2$ may act effectively as a proton acid instead of $TCNQH_2$.

In contrast to the expectation based on the Hammett substituent constant values of the ethylsulfonyl and cyano groups that TESQ would manifest a similar character to TCNQ, TESQ was found to be greatly different from TCNQ as follows: (1) In electron affinity, TESQ is much weaker than TCNQ. (2) As an acceptor monomer, TESQ is far more unreactive than TCNQ. (3) In polymerization modes against a series of vinyloxy compounds, TESQ is much more acidic than TCNQ. The product between *i*-BVE and TCNQ was reported to contain the TCNQ unit as a terminal unit,[2,3] while that between *i*-BVE and TESQ does not contain any TESQ unit, indicating a participation of proton in cationic initiation for the *i*-BVE polymerization. (4) TESQ is effective not only as a hydrogen acceptor in the hydrogen-transfer reaction but also as a catalyst in the dehydration of alcohols. The hydrogenation product, $TESQH_2$, is presumed to play an important role as a strong acid for the dehydration reaction. As one of the reasons for the difference between TESQ and TCNQ, it may take into account the type of π valence orbital of the substituent participating in π conjugation with the quinodimethane part. For the ethylsulfonyl group, the 3p orbital of sulfur is operative, while the cyano group of 2p orbital of carbon is operative. Price and Oae[21] described that 2p–3p π bonds are less stable than 2p–2p π bonds. It may be considered, therefore, that π conjugation in TESQ is much weaker than that in TCNQ, meaning that TESQ is a weaker π acid acceptor compound than TCNQ. On the other hand, $TESQH_2$ was considered to be comparable in proton acidity to $TCNQH_2$ on the basis of the Hammett substituent constant and actually $TESQH_2$ should be more acidic than $TCNQH_2$ from the observed catalytic actions in the dehydration of the alcohols.

**Registry No.** TESQ, 84928-90-5; HMB, 87-85-4; TESQ–St copolymer, 84928-91-6; TESQ–TCNQ–St copolymer, 84944-09-2; TESQ–St adduct (1:1), 84944-08-1; *i*-BVE homopolymer, 9003-44-5; *n*-BVE homopolymer, 25232-87-5; CEVE homopolymer, 29160-08-5; PhVE homopolymer, 25588-11-8; cinnamyl alcohol, 104-54-1; 1-phenyl-1-propanol, 93-54-9; 1-phenylethanol, 98-85-1; cinnamaldehyde, 104-55-2; propiophenone, 93-55-0; acetophenone, 98-86-2; β-methylstyrene, 637-50-3; styrene, 100-42-5.

## References and Notes

(1) Iwatsuki, S.; Itoh, T.; Horiuchi, K. *Macromolecules* **1978**, *11*, 497.
(2) Iwatsuki, S.; Itoh, T. *Macromolecules* **1979**, *12*, 208.
(3) Tarvin, R. F.; Aoki, S.; Stille, J. K. *Macromolecules* **1972**, *5*, 663.
(4) Iwatsuki, S.; Itoh, T.; Sakaike, S. *Macromolecules* **1981**, *14*, 1608.
(5) Iwatsuki, S.; Itoh, T. *Macromolecules* **1980**, *13*, 983.
(6) Iwatsuki, S.; Itoh, T. *Macromolecules* **1982**, *15*, 347.
(7) Iwatsuki, S.; Itoh, T. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2971.
(8) Hertler, W. R.; Benson, R. E. *J. Am. Chem. Soc.* **1962**, *84*, 3474.
(9) Gordon, A. J.; Rord, R. D. "The Chemist's Companion"; Wiley: New York, 1972; p 146.
(10) Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370.
(11) McElvain, M.; Pinzon, B. F. *J. Am. Chem. Soc.* **1945**, *67*, 650. Fueno, T.; Matsumura, I.; Okuyama, T.; Furukawa, *J. Bull. Chem. Soc. Jpn.* **1968**, *41*, 818.
(12) Walker, D.; Waugh, T. D. *J. Org. Chem.* **1965**, *30*, 3240.
(13) Nishiguchi, T.; Ohki, A.; Sakakibara, H.; Fukuzumi, K. *J. Org. Chem.* **1978**, *43*, 2803.
(14) Overberger, C. G.; Tanner, D. *J. Am. Chem. Soc.* **1955**, *77*, 369.
(15) Ohki, A.; Nishiguchi, T.; Fukuzumi, K. *J. Org. Chem.* **1979**, *44*, 766.
(16) Foster, R. "Organic Charge-Transfer Complexes"; Academic Press: New York, 1969; p 33.
(17) Chen, E. C. M.; Wentworth, W. E. *J. Chem. Phys.* **1975**, *63*, 3183.
(18) Riddick, J. A.; Bunger, W. B. "Organic Solvent", 3rd ed.; Wiley-Interscience: New York, 1970, pp 536–543.
(19) Kagiya, T.; Sumida, Y.; Inoue, T. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 767. Electron-donating power ($\Delta\nu_D$ in $cm^{-1}$) is defined as the difference in the O–D absorption band of methanol-*d* between the benzene solution and the compound solution: $\Delta\nu_D = \nu_D(\text{benzene}) - \nu_D(\text{compound})$.
(20) Bovey, F. A.; Tiers, G. V. D.; Filipovich, G. *J. Polym. Sci.* **1959**, *38*, 73.
(21) Price, C. C.; Oae, S. "Sulfur Bonding"; Ronald Press: New York, 1962; p 5.