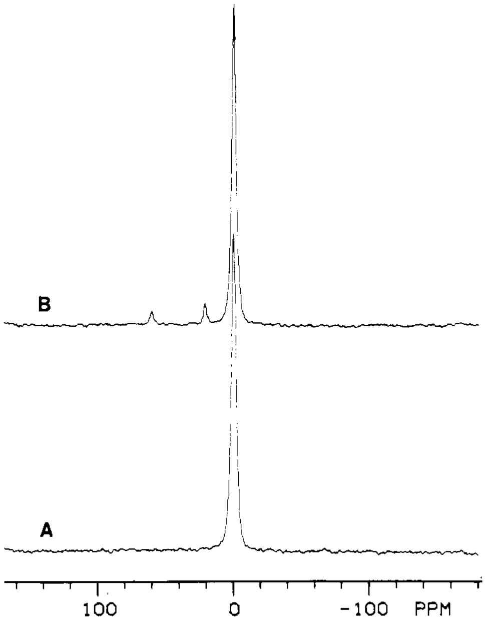

Figure 1. ^{13}C CP/MAS NMR spectra of solid poly(methylsiloxane) polymers. Chemical shifts are in parts per million from liquid Me_4Si; larger values correspond to lower shielding. Contact time, 5.0 ms; 2.0-s repetition time. (A) Sample prepared from CH_3SiCl_3; 4300 repetitions. (B) Sample prepared from $CH_3Si(OCH_2CH_3)_3$; 5000 repetitions.

Figure 1. The single sharp resonance line shown in Figure 1A corresponds to the methyl carbon in a polymer of the general type I. Structural moieties with a $CH_3Si(OH)(OSi{<})_2$ arrangement would not likely be distinguished from a $CH_3Si(OSi{<})_3$ moiety with the ^{13}C NMR resolution obtained by CP/MAS experiments on amorphous polymers such as these.[6] Figure 1B, showing the ^{13}C spectrum of material prepared from $CH_3Si(OCH_2CH_3)_3$, consists of the strong sharp methyl peak occurring in Figure 1A and small peaks that can be identified with $CH_3CH_2OSi{<}$ carbon resonances. The ethoxy resonances imply that the average molecular weight of this polymer is small enough that ethoxy end groups constitute an appreciable fraction of the carbon content.

The ^{29}Si CP/MAS spectra corresponding to spectra 1A and 1B are given in spectra 2A and 2B of Figure 2, respectively. The strong peaks at −65 ppm in spectra 2A and 2B correspond well, on the basis of analogous solution spectra on $CH_3Si^*(OSi{<})_3$ systems,[2b,7] to the general siloxane framework of structure I. The additional peak at −55 ppm in spectrum 2A is assigned on the basis of previous solution work[8] to a moiety of the type $CH_3Si^*(OH)(OSi{<})_2$, not distinguishable from $CH_3Si^*(OSi{<})_3$ in the ^{13}C CP/MAS spectrum. This additional peak shows a substantial quantity of $HOSi{<}$ end groups in the polymer. The small shoulder on the low-shielding side of the peak at −65 ppm in spectrum 2B is probably a manifestation of the $CH_3Si^*(OC_2H_5)(OSi{<})_2$ end-group moieties exhibited by the ethoxy carbon resonances in the ^{13}C spectrum (spectrum 1B). These patterns in the CP/MAS spectra are consistent with differences in the "average" elemental composition data (larger C and H values for B, and larger Si value for A).

In summary, one can see that CP/MAS NMR provides spectra on solid samples of organosiloxane polymers with a degree of resolution that is highly useful for structural characterization. Furthermore, the combination of ^{13}C and ^{29}Si NMR provides considerably more information than would be available from either nuclide in the absence of the other or from elemental analyses. The spectra are sufficiently sharp and intense to permit relaxation studies for exploring submicroscopic motion in these materials and for quantifying the results. Experiments of this nature are under way.

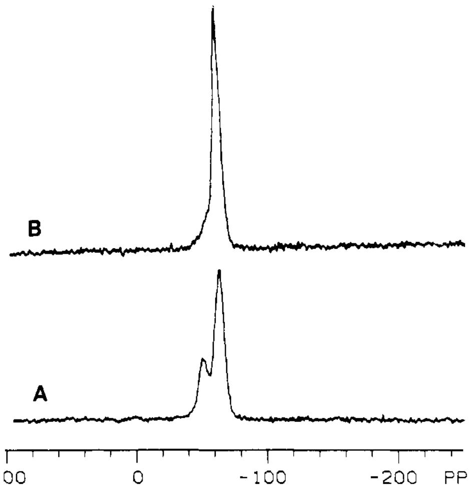

Figure 2. ^{29}Si CP/MAS NMR spectra of solid poly(methylsiloxane) polymers. Chemical shifts are in parts per million from Me_4Si; larger values correspond to lower shielding. Contact time, 10 ms; 4.0-s repetition time. (A) Sample prepared from CH_3SiCl_3; 15964 repetitions. (B) Sample prepared from $CH_3Si(OCH_2CH_3)_3$; 21464 repetitions.

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Change in Polymerization Mode of 7,7,8,8-Tetracyanoquinodimethane and 2-Chloroethyl Vinyl Ether upon Replacement of Solvent

In a previous paper,[1] tetracyanoquinodimethane (TCNQ) was reported to copolymerize alternatingly with vinyl acetate, phenyl vinyl ether, and 2-chloroethyl vinyl ether (CEVE) in acetonitrile but to initiate the cationic polymerization of *n*-butyl vinyl ether (nBVE) and isobutyl vinyl ether (iBVE). It was proposed that the difference in electron character between TCNQ and vinyloxy com-

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pounds is the primary determining factor of the polymerization mode.

In 1972 it was reported by Stille et al.[2] that TCNQ initiates the cationic polymerizations of ethyl vinyl ether, isopropyl vinyl ether, nBVE, iBVE, and *tert*-butyl vinyl ether in acetonitrile and nitromethane. A cationic initiation mechanism was proposed in which charge transfer complexes between TCNQ and alkyl vinyl ethers are subject to a "T-class"[3] (thermal) electron transfer reaction to give a radical cation and a radical anion, which react with each other at free radical ends to yield a zwitterion intermediate, the cationic end of which allows alkyl vinyl ethers to polymerize in a cationic mechanism. In addition, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone is known to initiate the cationic polymerization of alkyl vinyl ethers in a manner similar to that of TCNQ.[2] It is conceivable that an electron transfer reaction between donor and acceptor monomers is very important for the initiation of the cationic polymerization. Thus, it seems likely that a given pair of donor and acceptor monomers can undergo either an alternating copolymerization or a cationic polymerization, depending on whether the polarity of the solvent is low or high.

Shirota et al.[4] observed the following variation in polymerization mode with solvent basicity in the photoinduced polymerizations of *N*-vinylcarbazole (NVZ) in the presence of electron acceptor: in less basic solvents, such as benzene, nitrobenzene, and dichloromethane, cationic polymerization takes place; in moderately basic solvents, such as acetone, acetonitrile, and methanol, cyclodimerization occurs; and in extremely basic solvents, such as hexamethylphosphoric triamide, radical polymerization happens. These differences were explained satisfactorily in terms of solvation of the radical cation species, formed by photoexcitation of NVZ.

It is therefore probable in the case of TCNQ–vinyl ether polymerization that the cationic polymerization is influenced significantly by both the polarity and the basicity of the solvent.

In this paper we report polymerizations of CEVE and TCNQ in solvents more polar than acetonitrile ($\epsilon = 37.5$ at 20 °C).[5] Reasons for selection of CEVE as the comonomer were as follows: In the previous study,[1] CEVE in acetonitrile spontaneously and alternatingly copolymerized with TCNQ and was also the highest electron-donating monomer among the donor monomers alternatingly copolymerizing with TCNQ. Three solvents were employed: dimethyl sulfoxide (Me_2SO) ($\epsilon = 46.68$ at 25 °C),[5] ethylene carbonate ($\epsilon = 89.6$ at 40 °C),[5] and *N*-methylformamide ($\epsilon = 182.4$ at 25 °C).[5] In ethylene carbonate, instead of acetonitrile, TCNQ was found to initiate the cationic polymerization of CEVE.

Results of polymerization of TCNQ with CEVE in ethylene carbonate, Me_2SO, and *N*-methylformamide, as well as acetonitrile,[1] are summarized in Table I.

When acetonitrile was employed as solvent, TCNQ and CEVE copolymerized alternatingly and spontaneously.[1]

When ethylene carbonate was employed as solvent, the product obtained was a pale brown, viscous material. The product's molecular weights found by vapor pressure osmometry (benzene) were 5620 and 5310, corresponding to a degree of polymerization of about 50 ($\bar{P}_n = 50$). Figure 1 shows the product's IR spectrum, where an absorption at 1110 cm^{-1} due to an ether linkage can be observed but where absorption at 2240 cm^{-1} due to a nitrile group of the TCNQ unit is absent. Trace 1 in Figure 2 shows the product's NMR spectrum. The peak at 3.7 ppm was assigned to both the methine proton of the main chain and the ethylene protons of the side chain of the CEVE unit.

Table I
Polymerization of TCNQ with CEVE in Various Solvents[a]

run no.	monomer feed, mg		TCNQ, mol %	solvent	ϵ	polymer yield,[c] mg	time, h	elem anal.				copolymer comp		
	TCNQ	CEVE						% C	% H	% N	% Cl	CEVE, mol %	M_n[d]	η_{sp}/c,[e] dL/g
1[b]	103.0	1040.0	4.9	acetonitrile	37.5	46.0	17.7	61.44	4.01	17.26	11.98	52.4		0.449
2	99.5	1012.0	4.9	Me_2SO	46.68	54.2 (I)	23	60.97	4.90	7.10	11.14			
						62.9 (II)		58.72	3.93	12.05	13.86		1220	
						124.4 (III)		57.05	3.22	11.00	17.81		550	
3	98.9	841.4	5.1	ethylene carbonate	89.6	425.7	23	44.91	6.15	0	33.04	100	5620	
	4.2	440.5	0.4	ethylene carbonate	89.6	95.6	15	44.12	6.35	0	33.16	100	5310	
4	99.7	929.8	5.3	*N*-methylformamide	182.4	67.5 (IV)	23	60.34	4.45	17.43	10.21		760	
						100.4 (V)		58.71	4.53	15.85	12.76		530	
						47.2 (VI)		54.68	5.42	10.65	15.55		435	

[a] Solvent, 10 mL. Without initiator. Temperature of polymerization, 60 °C. [b] Temperature of polymerization, 50 °C. [c] Fractions I and IV are insoluble in benzene. Fractions II and V are soluble in benzene and insoluble in petroleum ether. Fractions III and VI are soluble in petroleum ether. [d] Determined by vapor pressure osmometry. Solvent: benzene, chloroform, and acetone. [e] Solvent, acetonitrile. Temperature of measurement, 30 °C.

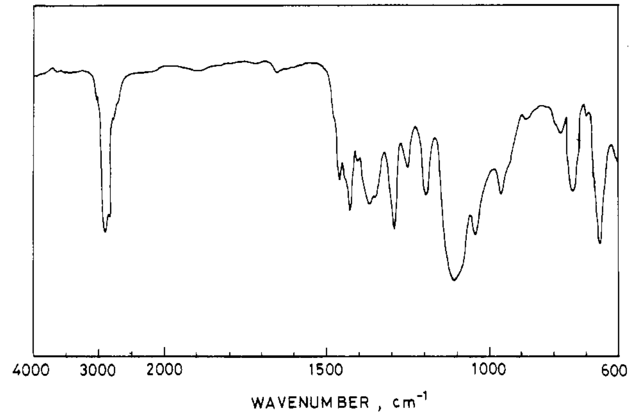


Figure 1. Film IR spectrum of the reaction product obtained in the polymerization of TCNQ with CEVE in ethylene carbonate (film).

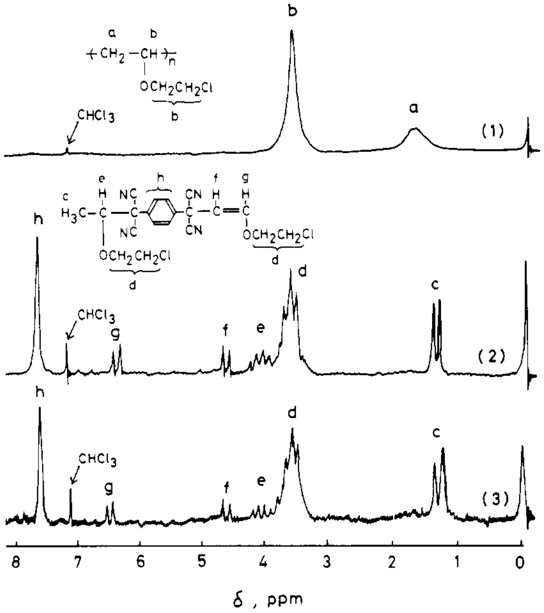
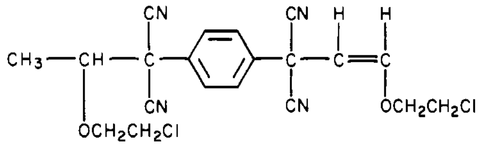


Figure 2. NMR spectra (in chloroform-*d*) of (1) the reaction product obtained in ethylene carbonate, (2) fraction III of that in Me_2SO, and (3) fraction VI of that in *N*-methylformamide.

The peak at 1.8 ppm was assigned to the methylene protons of the main chain of the CEVE unit. The IR and NMR spectra of the product obtained were in good agreement with those of CEVE homopolymer, prepared by the $BF_3 \cdot Et_2O$-initiated polymerization of CEVE in dichloromethane at −78 °C.[1] The product also gave an elemental analysis in good agreement with that of the homopolymer of CEVE. It was therefore concluded that the product was the homopolymer of CEVE. A mixture of CEVE and ethylene carbonate was heated at 60 °C for 24 h but only starting materials were recovered, indicating that ethylene carbonate and a contaminant, if present, cannot initiate the polymerization of CEVE without TCNQ under these experimental conditions. It was therefore concluded that cationic polymerization of CEVE occurs with TCNQ in ethylene carbonate and that ethylene carbonate, with a high dielectric constant, allows an electron transfer reaction of the charge transfer complex between TCNQ and CEVE to take place while acetonitrile, with a lower dielectric constant, does not.

When Me_2SO was employed as solvent, the reaction product obtained was separated into the following three fractions: fraction I, insoluble in benzene; fraction II, soluble in benzene and insoluble in petroleum ether; fraction III, soluble in petroleum ether. Fraction I was obtained as a pale brown powder, while fractions II and III were brown, viscous materials. Fraction I is insoluble in benzene, chloroform, acetone, and ethyl acetate, while fractions II and III are soluble in all of the above-mentioned solvents. Absorptions at 2240 and 1120 cm^{-1} appearing in the IR spectra of fractions I, II, and III, were assigned to a nitrile group and an ether linkage, respectively, indicating incorporation of both TCNQ and CEVE units into the compounds of each fraction. In the IR spectrum of fraction I, absorptions at 3450 and 1720 cm^{-1} were assigned to a carboxylic acid group, probably resulting from the partial hydrolysis of nitrile groups. Trace 2 in Figure 2 shows the ^1H NMR spectrum of fraction III, including assignments of the absorption peaks. Elemental analysis of fraction III gave found values close to the calculated ones for a compound composed of 1 TCNQ unit and 2 CEVE units. It was, therefore, proposed that the compound of fraction III is represented by structural formula A.



A

The ^1H NMR spectrum of fraction II is similar to that of fraction III except that the peaks are broader. The area ratio of the peaks of the phenylene protons in the TCNQ unit to the sum of the peaks of the methine and methylene protons in the CEVE unit in fraction II was estimated to be 1:3.3, corresponding to a TCNQ/CEVE composition ratio of ~1:1.9. In addition, from the molecular weight obtained, the compound of fraction II must contain 3–4 TCNQ units. In view of the above facts, fraction I seems to be similar in chemical structure to fractions II and III except for its much higher degree of polymerization. The difference in nitrogen content between fractions I and II or III can be understood in terms of partial hydrolysis of the nitrile groups. Therefore it is evident that the compounds obtained in Me_2SO contain the TCNQ–CEVE linkage and, furthermore, more than one TCNQ–CEVE linkage is present in the compounds even though they lack the high regularity of unit sequence that alternating copolymers possess. In other words, it is unequivocally shown that a cationic polymerization of CEVE did not take place, as opposed to the reaction in ethylene carbonate.

When *N*-methylformamide was used as solvent, the reaction product obtained was separated into three fractions in a manner similar to that for Me_2SO: fraction IV, insoluble in benzene; fraction V, soluble in benzene and insoluble in petroleum ether; fraction VI, soluble in petroleum ether. Fraction IV was obtained as a green powder while fractions V and VI were brown, viscous materials. Fraction IV is insoluble in benzene and chloroform but soluble in acetone. Fractions V and VI are soluble in all of the above-mentioned solvents. In the IR spectra, absorptions due to nitrile groups appear at 2150 cm^{-1} for fractions IV and V and at 2240 cm^{-1} for fraction VI, and absorptions due to an ether linkage appear at 1120 cm^{-1} for all three fractions, indicating incorporation of both TCNQ and CEVE units into the compounds of each fraction. Trace 3 in Figure 2 shows the ^1H NMR spectrum of fraction VI, a spectrum similar to that for fraction III obtained in Me_2SO. Elemental analysis of fraction VI gave found values close to the calculated ones for a compound composed of 1 TCNQ unit and 2 CEVE units. It was therefore concluded that the compound of fraction VI is also represented by formula A. The found values of fraction IV were close to the calculated ones for a compound composed of 1 TCNQ unit and 1 CEVE unit. In addition, the value of the molecular weight for fraction IV is consistent with a compound containing at least 2 TCNQ units. The elemental analysis and IR spectrum of fraction V suggest that it has a composition intermediate between that of fraction IV and that of fraction VI. It is likely that the compounds obtained in *N*-methylformamide contain at least two TCNQ–CEVE linkages even though they have very low molecular weights. Therefore, as with Me_2SO, cationic polymerization of CEVE did not take place in *N*-methylformamide.

In summary, the type of product obtained in the polymerization between TCNQ and CEVE depends on the solvent as follows: in acetonitrile, alternating copolymer; in ethylene carbonate, homopolymer of CEVE; in Me_2SO and *N*-methylformamide, low molecular weight compounds composed of both TCNQ and CEVE units.

This difference in polymerization mode may be explained reasonably in terms of the polarity and basicity of the solvent. The dielectric constants of acetonitrile, Me_2SO, ethylene carbonate, and *N*-methylformamide are 37.5, 46.68, 89.6, and 182.4, respectively.[5] Frequency shifts, $\Delta\nu_{OH}$, of phenol with acetonitrile, ethylene carbonate, and Me_2SO are 155, 159, and 350 cm^{-1}, respectively.[6] Frequency shifts, $\Delta\nu_{OH}$, of *p*-fluorophenol with *N*-methylformamide and Me_2SO are 271 and 367 cm^{-1}, respectively.[7] It is, therefore, obvious that the basicity of these solvents increases in the following order: acetonitrile $\leq$ ethylene carbonate < *N*-methylformamide < Me_2SO. It is reasonable from the difference in the dielectric constants that the electron transfer reaction between TCNQ and CEVE takes place more readily in the following order: *N*-methylformamide > ethylene carbonate > Me_2SO > acetonitrile. Since *N*-methylformamide is more basic than ethylene carbonate, the cationic end of the radical cation species formed by the electron transfer reaction can be more tightly solvated by solvent molecules, leading probably to a deactivation of the cationic end. Another free radical end may undergo a reaction to give low molecular weight compounds composed of both monomer units. The formation of low molecular weight compound in Me_2SO also may be attributable to its high basicity. The drastic difference in polymerization mode between acetonitrile and ethylene carbonate conceivably arises primarily from the polarity of the solvents. The more polar ethylene carbonate permits the electron transfer reaction between TCNQ and CEVE to occur, while the less polar acetonitrile does not. Because ethylene carbonate and acetonitrile have low basicities of similar magnitude, the cationic end is considered to be only weakly solvated and not to inhibit the cationic polymerization.

Materials. Commerical TCNQ was purified by recrystallization from ethyl acetate and was sublimed twice (mp 293.5–295.0 °C). CEVE was prepared by the dehydrochlorination β,β'-dichlorodiethyl ether[8] and distilled over calcium hydride under nitrogen at 108 °C. After *N*-methylformamide was shaken with phosphorus pentoxide and filtered through glass wool, it was distilled under reduced pressure at 59 °C (1 mmHg). This treatment was repeated three times, followed by two distillations under nitrogen. Dimethyl sulfoxide and ethylene carbonate were distilled three times under reduced nitrogen pressure at 85 °C (21 mmHg) and 113 °C (11 mmHg), respectively.

Polymerization Procedure. Given amounts of TCNQ and CEVE and 10 mL of the solvent (Me_2SO, ethylene carbonate, or *N*-methylformamide) were placed in an ampule, which was degassed completely by three freeze–thaw cycles and sealed. No initiator was added. The ampule was set in a bath thermostated at 60 °C for the time of the polymerization. The ampule was opened and the solvent and unreacted CEVE were distilled off under reduced pressure. Then, in the case of ethylene carbonate, the product obtained was dissolved in dichloromethane and the resulting solution was poured into excess cooled methanol to precipitate the product, which was dried under reduced pressure. In the case of Me_2SO and *N*-methylformamide, the products were dissolved in benzene and were separated into the two fractions soluble and insoluble in benzene. The fractions soluble in benzene were separated further into the two fractions soluble and insoluble in petroleum ether.

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