Macromolecules 1983, *16*, 1571-1576 **1571**

Polymerization Behavior of 11,11,12,12-Tetracyanonaphtho-2,6-quinodimethane and 2,5,7,7,8,8-Hexacyanoquinodimethane as Electron-Accepting Monomers

Shouji Iwatsuki,* Takahito Itoh, Hirooki Saito, and Jun Okada

Department of Chemical Research for Resources, Faculty of Engineering, Mie University, Kamihama-cho, Tsu 514, Japan. Received December 22, 1982

ABSTRACT: Because 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TNAP) is intermediate in electron-accepting character between 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF$_4$) and because 2,5,7,7,8,8-hexacyanoquinodimethane (TCNQ(CN)$_2$) is much more electron accepting than TCNQF$_4$, the spontaneous alternating copolymerizations of TNAP and TCNQ(CN)$_2$ with styrene (St) were studied as were the polymerization modes of TNAP and TCNQ(CN)$_2$ with the vinyloxy compounds isobutyl vinyl ether (*i*BVE), *n*-butyl vinyl ether (*n*BVE), 2-chloroethyl vinyl ether (CEVE), phenyl vinyl ether (PhVE), and vinyl acetate (VAc). Rates of the spontaneous copolymerizations of TNAP and TCNQ(CN)$_2$ with St were measured by the time to decrease in half the concentration of their acceptor monomer solution, and the following order, similar to the order of electron-accepting character, was found: TCNQ(CN)$_2$–St (~1/800) > TCNQF$_4$–St (1/250) > TNAP–St (1/6.6) > TCNQ–St (1). It was found that TNAP copolymerizes spontaneously and alternatingly with St in three-halves-order kinetics, similarly to TCNQF$_4$ and TCNQ, whereas TCNQ(CN)$_2$ copolymerizes with a low-order kinetics (first order). It was also found that TNAP is able to initiate the cationic homopolymerizations of *n*BVE, *i*BVE, and CEVE, to copolymerize alternatingly with PhVE, and to react with VAc to give a 1:1 adduct, whereas TCNQ(CN)$_2$ induces the cationic homopolymerizations of *n*BVE, *i*BVE, and CEVE, reacts with PhVE in an ambiguous way, giving an alternating oligomer between PhVE and TCNQ(CN)$_2$ and a cationic oligomer of PhVE, and reacts with VAc to yield a 1:1 adduct. The polymerization modes can be explained consistently in terms of the electron-accepting character of their quinodimethane compounds.

Since 7,7,8,8-tetracyanoquinodimethane (TCNQ) was found to copolymerize spontaneously and alternatingly with styrene (St),[1-4] the electron-accepting quinodimethane compounds 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF$_4$),[5] 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane (TMCQ),[6] 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ),[7] 7,7,8,8-tetrakis(ethylsulfonyl)quinodimethane (TESQ),[8] and 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethane[9] have been studied in their polymerization behaviors as electron-acceptor monomers with respect to their alternating copolymerization with St or donor monomers and the polymerization modes in their reaction with vinyloxy compounds. In those studies it may be pointed out that an electron-accepting character such as electron affinity of the quinodimethane compounds plays an important role in their polymerization behaviors; that is, TCNQF$_4$ copolymerizes alternatingly with St about 190 times as rapidly as TCNQ and, in addition, TCNQF$_4$ can induce the cationic homopolymerization of 2-chloroethyl vinyl ether (CEVE) in acetonitrile whereas TCNQ copolymerizes alternatingly with CEVE. TCNQF$_4$ was reported to be much more electron accepting than TCNQ.[10]

In addition to TCNQ and TCNQF$_4$, 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TNAP)[11,12] and 2,5,7,7,8,8-hexacyanoquinodimethane (TCNQ(CN)$_2$)[13] have been known as cyano group substituted electron-accepting quinodimethane compounds, the former assuming an electron-accepting character intermediate between that of TCNQ and TCNQF$_4$ and the latter being much more electron accepting than TCNQF$_4$.[10] Therefore, both compounds are of interest in investigating the relationship between their electron-accepting character and their polymerization behaviors.

In this work we studied the spontaneous alternating copolymerizations of TNAP or TCNQ(CN)$_2$ with St and the polymerization modes of the reaction in acetonitrile between TNAP or TCNQ(CN)$_2$ and vinyloxy compounds such as isobutyl vinyl ether (*i*BVE), *n*-butyl vinyl ether (*n*BVE), CEVE, phenyl vinyl ether (PhVE), and vinyl acetate (VAc).

Experimental Section

Materials. TNAP was prepared from 2,6-dimethylnaphthalene as a starting material according to the procedures of Diekmann et al.[11] and Sandman and Garito[12] and purified by recrystallization from acetonitrile: mp >300 °C; UV (acetonitrile) 472 (7.0×10^4), 258 (1.23×10^4), 248 (1.65×10^4) nm. Anal. Calcd for $C_{16}H_6N_4$: C, 75.6; H, 2.4; N, 22.0. Found: C, 76.5; H, 1.8; N, 21.7. TCNQ(CN)$_2$ was prepared from 2,5-dichloroterephthalonitrile according to the method of Wheland and Martin[13] and purified by recrystallization from acetonitrile: mp >300 °C; UV (acetonitrile) 395 (5.87×10^4), 373 (2.80×10^4), 354 (1.14×10^4) nm. Anal. Calcd for $C_{14}H_2N_6$: C, 66.1; H, 0.8; N, 33.1. Found: C, 66.2; H, 0.9; N, 32.9. TCNQ was prepared from 1,4-cyclohexanedione according to the procedure of Acker and Hertler[14] and purified by recrystallization from acetonitrile and sublimation (twice) (mp 294–296 °C). St, *i*BVE, *n*BVE, and VAc were purified from commercial products by conventional methods.[15] PhVE was prepared from phenol and dibromoethane according to the procedures of McElvain and Pinzôn[16] and Fueno et al.[17] CEVE was prepared from β,β'-dichloroethyl ether.[18] Acetonitrile was refluxed over phosphorus pentoxide and then distilled at 81.7 °C. Guaranteed reagent grade durene was used without further purification.

Charge-Transfer Absorption Band. Absorption spectra of the charge-transfer transition for the TNAP–St, TCNQ(CN)$_2$–durene, and TCNQF$_4$–durene systems were measured in acetonitrile at room temperature. The concentrations of solutions employed were as follows: [TNAP] = 1.0×10^{-4} mol/L and [St] = 2.17 mol/L for the TNAP–St system; [TCNQ(CN)$_2$] = 2.14×10^{-4} mol/L and [durene] = 0.231 mol/L for the TCNQ(CN)$_2$–durene system; [TCNQF$_4$] = 3.17×10^{-4} mol/L and [durene] = 0.231 mol/L for the TCNQF$_4$–durene system.

Determination of the equilibrium constant (K_{CT}) and the molar absorption coefficient (ϵ_{CT}) for the charge-transfer complex of the TNAP–St system was carried out at 15, 25, and 35 °C according to the Benesi–Hildebrand equation. The wavelength at which the absorbance was measured was 532 nm. Since the spectrum was found to vary slowly with time, absorbance was measured just 2 min after the TNAP solution was mixed with the St solution.

Polymerization Procedure. Given amounts of the acceptor

0024-9297/83/2216-1571$01.50/0 © 1983 American Chemical Society

monomer (TNAP or $TCNQ(CN)_2$) and the comonomer and 10 mL of acetonitrile 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 comonomer, the reaction mixture was poured into excess methanol to precipitate the copolymer. For purification, the copolymer obtained was dissolved in *N*,*N*-dimethylformamide (DMF) again, 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, PhVE, or VAc as comonomer except for the $TCNQ(CN)_2$–PhVE system, the reaction mixture was placed under reduced pressure to remove the volatile materials. The viscous residue obtained was dissolved in a small amount of benzene, and the resulting solution was filtrated through a glass filter to remove unreacted acceptor monomer. The filtrate was placed under reduced pressure to remove benzene. The residue was the viscous opaque product. The solvents for the purification were acetone for the TNAP–VAc and $TCNQ(CN)_2$–VAc systems and dichloromethane for the TNAP–PhVE system instead of benzene. In the case of the $TCNQ(CN)_2$–PhVE system, the reaction mixture was placed under reduced pressure to remove the volatile materials. The residue obtained was dissolved in a small amount of acetone, and the resulting solution was filtrated through a glass filter to remove unreacted $TCNQ(CN)_2$. Then the filtrate was placed under reduced pressure to remove acetone. The residue obtained was separated into two fractions soluble and insoluble in chloroform.

Polymer Characterization. Polymer composition was established by elemental analysis. Solution viscosity for the copolymers of TNAP or $TCNQ(CN)_2$ with St was determined in DMF using an Ostwald viscometer at 30 °C. Molecular weight was determined by vapor pressure osmometry, in which the solvents used were benzene for the TNAP- or $TCNQ(CN)_2$-initiated homopolymers of *i*BVE, *n*BVE, and CEVE and acetone (or chloroform) for the alternating copolymers of TNAP or $TCNQ(CN)_2$ with PhVE and VAc. ^1H NMR measurement for the copolymers of TNAP or $TCNQ(CN)_2$ with St was carried out in *N*,*N*-dimethylformamide-d_7 with tetramethylsilane as an internal standard.

Measurement of the Rate of Spontaneous Alternating Copolymerization between TNAP and St or between $TCNQ(CN)_2$ and St. The dependence of the copolymerization rate upon the monomer concentration was determined spectrophotometrically as follows: for the TNAP–St system, 1 mL of a St solution in acetonitrile with a fixed, high St concentration (2.08×10^{-2} mol/L) was mixed with the same volume of a TNAP solution in acetonitrile with a low TNAP concentration (3.84×10^{-5} or 1.88×10^{-5} mol/L) in a UV cell (0.5 cm) kept at 35 °C. Absorbance at 472 nm due to TNAP was measured at 20-min intervals. Decrease in the absorbance was treated separately by first-order, three-halves-order, and second-order kinetics.

For the $TCNQ(CN)_2$–St system, 1 mL of a St solution in acetonitrile with a fixed, high St concentration (3.92×10^{-2} mol/L) was mixed with the same volume of a $TCNQ(CN)_2$ solution in acetonitrile with a low $TCNQ(CN)_2$ concentration (6.30×10^{-5} mol/L) in a UV cell (0.5 cm) kept at 10 °C. Absorbance at 395 nm due to $TCNQ(CN)_2$ was measured at 1-min intervals. Decrease in the absorbance was analyzed.

Instruments for Measurement. ^1H NMR and UV-vis spectral determinations were made on Varian A-60D, Hitachi Perkin-Elmer Model 139, and Shimadzu Model UV-200 instruments. A Knauer vapor pressure osmometer and Yanagimoto CHN Corder Model MT-2 instrument were used for molecular weight determination and elemental analysis, respectively.

Results and Discussion

Charge-Transfer Absorption Band. Addition of St to TNAP in acetonitrile caused the red color of the TNAP solution to deepen as shown in Figure 1, where the difference spectrum between the mixture and TNAP shows a broad absorption band in the range 530–630 nm, corresponding to an absorption of the charge-transfer complex between TNAP and St. St does not absorb any light at wavelengths longer than 400 nm. The difference spectra between TCNQ and St and between $TCNQF_4$ and St show bands in the range 450–580 nm and of 500–750 nm, respectively, as shown additionally in Figure 1. Comparison of the absorption bands among those three complexes permits us to say that TNAP is intermediate in electron-accepting character between TCNQ and $TCNQF_4$, corresponding well to the half-wave reduction potential data of Wheland and Gillson.[10]

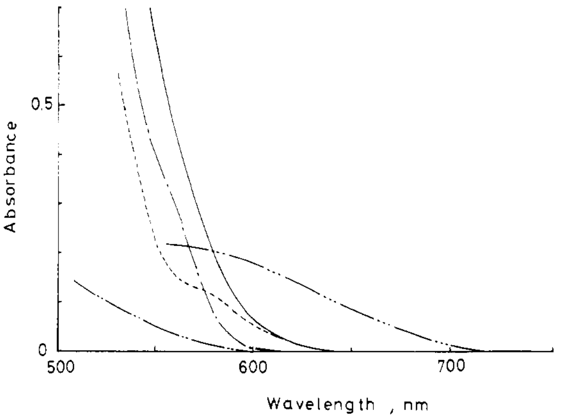

Figure 1. UV–vis spectra of mixtures of TNAP with St in acetonitrile, of TCNQ with St, and of $TCNQF_4$ with St in dichloromethane: (—) spectrum of a mixture of TNAP with St; (–-–) spectrum of TNAP; (---) difference spectrum between the previous two spectra, corresponding to that of the complex; (–--–) difference spectrum between TCNQ and a mixture of TCNQ with St; (–---–) difference spectrum between $TCNQF_4$ and a mixture of $TCNQF_4$ with St. Concentrations of solutions employed are [TNAP] = 1.0×10^{-4} mol/L and [St] = 2.17 mol/L for the TNAP–St system, [TCNQ] = 1.30×10^{-3} mol/L and [St] = 0.218 mol/L for the TCNQ–St system, and [$TCNQF_4$]= 1.3×10^{-3} mol/L and [St] = 0.218 mol/L for the $TCNQF_4$–St system.

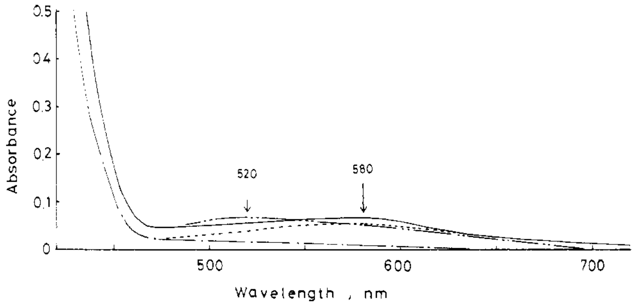

Figure 2. UV–vis spectra of a mixture of $TCNQ(CN)_2$ and durene in acetonitrile: (—) spectrum of a mixture of $TCNQ(CN)_2$ and durene: (–-–) spectrum of $TCNQ(CN)_2$; (---) difference spectrum between a spectrum of the $TCNQ(CN)_2$–durene mixture and that of $TCNQ(CN)_2$, corresponding to that of the complex; (–--–) difference spectrum between a spectrum of a mixture of $TCNQF_4$ with durene and that of $TCNQF_4$. Concentrations of solutions employed are [$TCNQ(CN)_2$] = 2.14×10^{-4} mol/L, [$TCNQF_4$] = 3.17×10^{-4} mol/L, and [durene] = 0.231 mol/L.

The charge-transfer transition band between $TCNQ(CN)_2$ and St could not be measured because the absorbance of the mixture decreased so rapidly that it disappeared completely within a minute, probably due to very rapid polymerization of $TCNQ(CN)_2$ with St. Therefore, measurement of the charge-transfer transition band between $TCNQ(CN)_2$ and durene instead of St was carried out because durene is a donor compound without polymerizability. The UV–vis spectrum is shown in Figure 2. The difference spectrum between the mixture and $TCNQ(CN)_2$ shows an absorption maximum at 580 nm. The complex between $TCNQF_4$ and durene carries an absorption maximum at 520 nm, as shown additionally in Figure 2. It is obvious, therefore, that $TCNQ(CN)_2$ is more

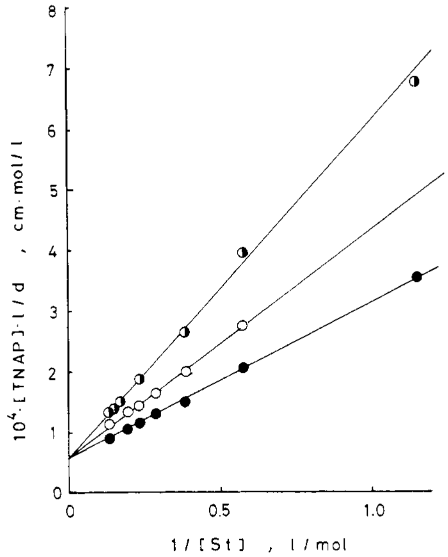

Figure 3. Benesi-Hildebrand plot for the TNAP-St system. Temperatures of measurement are (●) 15 (○) 25, and (◑) 35 °C. l and d are cell length (in cm) and absorbance, respectively.

Table I
Equilibrium Constant, K_{CT}, and Molar Absorption Coefficient, ϵ_{CT}, for Charge-Transfer Complex Formation in the TNAP-St, TCNQF$_4$-St, and TCNQ-St Systems at Various Temperatures in Acetonitrile

TNAP-St		TCNQF$_4$-St[a]		TCNQ-St[b]	
temp, °C	K_{CT}	temp, °C	K_{CT}	temp, °C	K_{CT}
15	0.22	12.5	0.64	9	0.43
25	0.15	19.5	0.43	15	0.40
35	0.10			25	0.36
ϵ_{CT}^{532} = 17 000		ϵ_{CT}^{570} = 2200		ϵ_{CT}^{470} = 1900	

[a] Solvent, dichloromethane. Reference 5. [b] Reference 1.

electron-accepting than TCNQF$_4$, corresponding well to the half-wave reduction potential data of Wheland and Gillson.[10]

Figure 3 shows Benesi-Hildebrand plots at 15, 25, and 35 °C for the TNAP-St system. The linearity of the plots suggests that the complex is composed of equimolar amounts of a donor and an acceptor. K_{CT} and ϵ_{CT} values for the complex formation of the TNAP-St system are summarized in Table I, including the corresponding values for the TCNQF$_4$-St and TCNQ-St systems. The magnitude of these K_{CT} values is less than unity and corresponds well with K_{CT} values for many spontaneous alternating copolymerizable donor-acceptor pairs reported previously.[1,5-7,19]

Copolymerization of TNAP or TCNQ(CN)$_2$ with St. Table II summarizes the results of copolymerization of TNAP or TCNQ(CN)$_2$ with St. The copolymers were obtained as pale brown powders. The copolymer compositions were found to be the same by elemental analysis regardless of monomer feed ratio. The found values are in good agreement with the calculated values for the copolymer composed of equimolar amounts of a donor and an acceptor monomer. In the ^1H NMR spectra of the copolymers of TNAP and TCNQ(CN)$_2$ with St, the methine and methylene protons of the St monomer unit of the copolymers appear in the δ 3–4 region, being more subject to deshielding than the corresponding protons of homopolystyrene, appearing in the δ 1–2 region.[20] It is conceivable that the deshielding arises from powerful electron withdrawal by the neighboring dicyanomethylene group when the St monomer unit is sandwiched between acceptor monomer units in the copolymers. It can be concluded, therefore, that TNAP and TCNQ(CN)$_2$ copolymerize with St alternatingly and spontaneously as well as TCNQ,[1] TCNQF$_4$,[5] TMCQ,[6] DDQ,[7] and TESQ.[8]

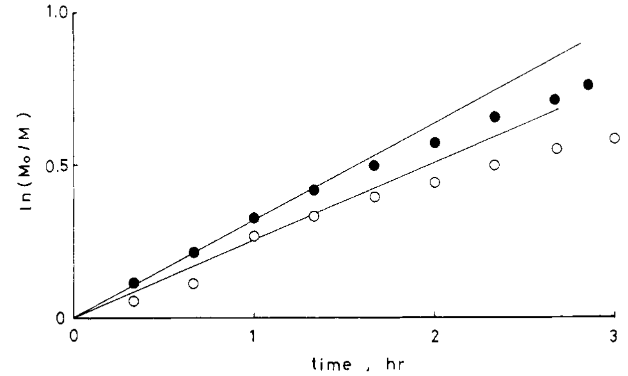

Figure 4. First-order kinetics plots for the rate of copolymerization in acetonitrile at 35 °C. TNAP concentrations employed are [TNAP] = 1.92 × 10^{-5} mol/L (●) and [TNAP] = 0.94 × 10^{-5} mol/L (○). [St] = 1.04 × 10^{-2} mol/L.

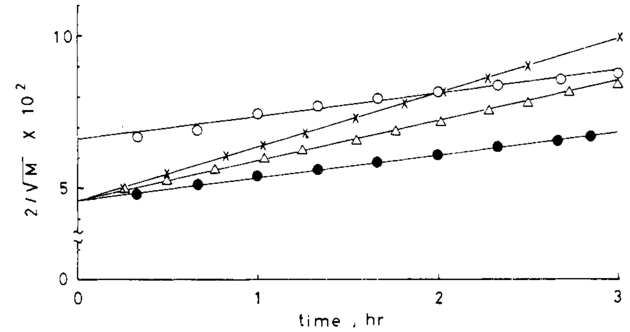

Figure 5. Three-halves-order kinetics plots for the rate of the copolymerization in acetonitrile at 35 (● and ○), 40 (△), and 45 °C (×). Monomer concentrations employed are cited in Figure 4.

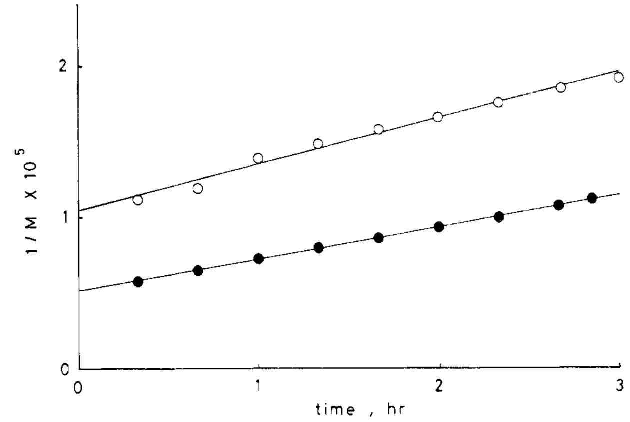

Figure 6. Second-order kinetics plot for the rate of the copolymerization in acetonitrile at 35 °C. Monomer concentrations employed are cited in Figure 4.

Kinetics for Copolymerization of TNAP or TCNQ(CN)$_2$ with St. For the TNAP-St system, under experimental conditions using a St solution with a fixed, high concentration and TNAP solutions with multiple, low concentrations, the rate of consumption of TNAP was determined spectrophotometrically at 35 °C and treated separately by first-order (Figure 4), three-halves-order (Figure 5), and second-order (Figure 6) kinetics with respect to the TNAP concentration. The experimental results were found not to follow first-order kinetics but gave

Table II
Polymerization[a] of TNAP or $TCNQ(CN)_2$ with St in Acetonitrile at 60 °C

run no.	monomer feed, mg		amt of acceptor, mol %	time, h	yield, mg	conv, %	anal.			copolym comp, mol % acceptor	η_{sp}/C,[b] $dL \cdot g^{-1}$
	acceptor	St					% H	% C	% N		
						TNAP					
1	50.2	193.0	9.6	1.5	18.9	7.8	3.43	80.78	15.79	50.8	0.41
2	50.2	155.1	11.7	3.5	31.6	15.4	4.38	79.98	15.83	51.0	0.21
3	49.8	109.0	15.8	4.0	33.8	21.3	4.24	80.17	15.59	49.7	0.18
4	70.4	71.4	28.8	6.1	34.8	24.5	3.90	80.17	15.93	51.6	0.27
5	49.5	30.7	39.8	18.0	17.8	22.0	4.00	80.55	15.45	49.0	
						$TCNQ(CN)_2$					
6	50.5	299.1	6.5	0.25	33.9	9.7	3.35	73.67	22.97	48.9	0.18
7	50.5	204.8	9.2	0.25	27.2	10.7	3.24	73.77	22.99	49.4	0.20
8	50.5	100.9	17.1	0.25	31.8	21.0	3.48	73.26	23.03	50.0	

[a] 10 mL, no initiator. [b] DMF solvent, temp 30 °C. $C = 0.1\text{-}0.2$ g/dL.

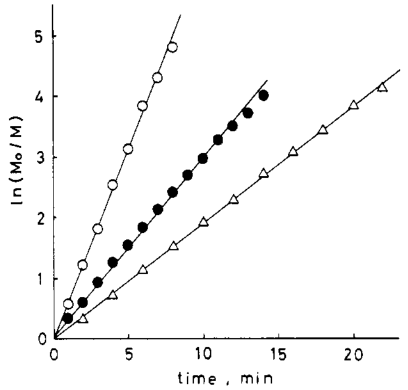

Figure 7. First-order kinetics plots for the rate of the copolymerization in acetonitrile at 5 (△), 10 (●), and 15 °C (○). Monomer concentrations employed are $[TCNQ(CN)_2] = 3.15 \times 10^{-5}$ mol/L and $[St] = 1.96 \times 10^{-2}$ mol/L.

straight lines in both three-halves-order and second-order kinetics treatments. However, in the second-order kinetics treatment the rate constants depend upon the initial monomer concentration while in the three-halves-order kinetics treatment the dependence was not found. Therefore, it is probable that the copolymerization rate obeys three-halves-order kinetics with respect to the TNAP concentration, similarly to the copolymerizations of the $TCNQF_4$–St and TCNQ–St systems.[5] However, the dependence of the rate upon the St concentration could not be determined spectrophotometrically or gravimetrically because the absorbance of St overlaps seriously with the strong broad absorption of TNAP and because the solubility of TNAP in acetonitrile is low, respectively.

Apparent three-halves-order rate constants of the copolymerization of TNAP with St were determined as 2.14×10^{-2} $L^{1/2} \cdot mol^{-1/2} \cdot s^{-1}$ at 35 °C, 3.72×10^{-2} $L^{1/2} \cdot mol^{-1/2} \cdot s^{-1}$ at 40 °C, and 5.00×10^{-2} $L^{1/2} \cdot mol^{-1/2} \cdot s^{-1}$ at 45 °C (see Figure 5). The Arrhenius plot of the rate constants gave a good straight line from the slope of which an overall activation energy of copolymerization was estimated as 68.0 kJ/mol, being similar to corresponding ones for the $TCNQF_4$–St (69.2 kJ/mol)[5] and TCNQ–St (72.3 kJ/mol)[5] systems. It can be proposed, therefore, that the TNAP–St system copolymerizes spontaneously and alternatingly in a reaction scheme similar to that of the $TCNQF_4$–St and TCNQ–St systems.

For the $TCNQ(CN)_2$–St system, under experimental conditions using St solution with a fixed, high concentration and $TCNQ(CN)_2$ solution with multiple, low concentrations, the rate of consumption of $TCNQ(CN)_2$ was determined spectrophotometrically at 10 °C and analyzed separately by first-order (Figure 7), three-halves- order (Figure 8), and second-order (Figure 9) kinetics with respect to the $TCNQ(CN)_2$ concentration. Comparison among the above three analyses allows one to say that the copolymerization rate obeys first-order kinetics with respect to the $TCNQ(CN)_2$ concentration. The dependence of the rate upon the St concentration could not be determined spectrophotometrically or gravimetrically owing to the same reasons stated for the TNAP–St system.

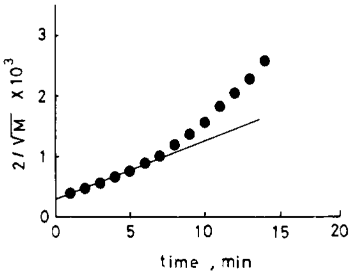

Figure 8. Three-halves-order kinetics plot for the rate of the copolymerization in acetonitrile at 10 °C. Monomer concentrations employed are cited in Figure 7.

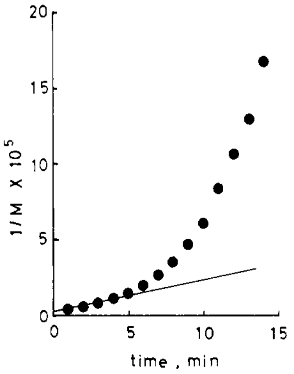

Figure 9. Second-order kinetics plot for the rate of the copolymerization in acetonitrile at 10 °C. Monomer concentrations employed are cited in Figure 7.

Apparent first-order rate constants of the copolymerization of $TCNQ(CN)_2$ with St were obtained as 3.20×10^{-3} s^{-1} at 5 °C, 5.05×10^{-3} s^{-1} at 10 °C, and 1.05×10^{-2} s^{-1} at 15 °C. The overall activation energy of this copolymerization was estimated from the Arrhenius plot of the rate constants as 69.7 kJ/mol, being in the same range of corresponding ones for the copolymerization of the TCNQ–St, $TCNQF_4$–St, and TNAP–St systems.

It should be noted that the acceptor monomer concentration dependence of the copolymerization rate for the $TCNQ(CN)_2$–St system is different from those for the TCNQ–St, $TCNQF_4$–St, and TNAP–St systems. Meanwhile spontaneous alternating copolymerization of TCNQ

Table III
Rate Constant, Overall Activation Energy, and Half-life Time for the TCNQ-St, TNAP-St, TCNQF$_4$-St, and TCNQ(CN)$_2$-St Systems

system	order	rate constant,[a] $L^{1/2} \cdot mol^{-1/2} \cdot s^{-1}$	overall act. energy, kJ/mol	half-life time, min
TCNQ-St	1.5	2.75×10^{-3}	72.3	1000[b]
TNAP-St	1.5	2.14×10^{-2}	68.0	151
TCNQF$_4$-St	1.5	5.29×10^{-1}	69.2	4.0
TCNQ(CN)$_2$-St	1.0	5.05×10^{-3}[c]	69.7	1.2

[a] Values at 34.5 °C for the TCNQ-St, TNAP-St, and TCNQF$_4$-St systems and at 10 °C for the TCNQ(CN)$_2$-St system, respectively. [b] Calculated from the rate constant. [c] In s^{-1}.

Table IV
Reactions[a] of TNAP or TCNQ(CN)$_2$ with Vinyloxy Compounds in Acetonitrile at 60 °C

monomer feed, mg			time, h	polym yield, mg	anal.				copolym comp, mol % comonomer	$\overline{M}_n$
acceptor	comonomer				% H	% C	% N	% Cl		
				TNAP						
15.2	*n*BVE	557.8	48.4	203.3	8.77	70.08	0		100	610[c]
18.1	*i*BVE	541.0	86.4	208.0	10.13	70.56	0		100	750[c]
19.5	CEVE	829.0	86.4	170.6	6.33	45.65	1.41	32.15	~100	860[c]
19.0	PhVE	633.3	77.2	33.7	4.37	75.51	11.29		66.1	890[d]
18.7	VAc	587.0	115.0	9.1	4.05	70.62	14.34		52.0	300[d]
				TCNQ(CN)$_2$						
1.64	*n*BVE	473.6	12.0	399.3	12.81	71.02	0		100	730[c]
1.77	*i*BVE	415.2	12.0	363.4	10.43	71.40	0		100	870[c]
1.58	CEVE	406.7	72.0	303.1	6.71	46.25	0	33.06	100	850[c]
1.96	PhVE	475.7	52.0	trace						
1.06	VAc	196.1	120.0	trace						
57.3	PhVE	275.5	24.0	I[b] 98.2	4.80	73.23	14.09		74.0	640[d]
				II[b] 31.3	3.25	70.11	22.36		50.3	840[e]
48.1	VAc	232.8	72.0	43.3	3.07	62.81	23.53		54.7	310[e]

[a] 10 mL, no initiator. [b] Fractions I and II are soluble and insoluble in chloroform, respectively. [c] Determined by vapor pressure osmometry; benzene solvent. [d] Determined by vapor pressure osmometry; chloroform solvent. [e] Determined by vapor pressure osmometry; acetone solvent.

with methyl methacrylate (MMA) was found to obey as low as half-order kinetics with respect to the TCNQ concentration.[4] In comparison of the difference in the polar character between the donor and acceptor monomers, the TCNQ-MMA system seems the smallest among the other alternating copolymerizable systems containing electron-accepting quinodimethane compounds, whereas the TCNQ(CN)$_2$-St system should be the largest. It can be pointed out, therefore, that both extreme cases with regard to the difference in polar character between donor and acceptor monomers interestingly obey low-order kinetics, whereas the other cases with a medium difference obey three-halves-order kinetics. However, a reaction mechanism relevant to this low-order kinetics cannot be proposed at the moment.

Owing to different order kinetics, comparison of the rates of those spontaneous alternating copolymerizations was carried out not with their rate constant values, but with the time (the so-called half-life time) to decrease in half the concentration of their acceptor monomer solution under a given similar monomer concentration. Table III summarizes the rate constant, overall activation energy of the spontaneous alternating copolymerization, and the half-life time for the TCNQ(CN)$_2$-St, TCNQF$_4$-St, TNAP-St, and TCNQ-St systems. It was found that the TCNQF$_4$-St system reacts about 250 times as fast as the TCNQ-St system and the TNAP-St system reacts about 6.6 times as rapidly as the TCNQ-St systems. The rate data for the TCNQ(CN)$_2$-St system were barely obtained at low temperature as 10 °C because the rate at 35 °C is too fast to be measured accurately. The half-life time for the TCNQ(CN)$_2$-St system at 35 °C should be much shorter than 1 min. It can be said, therefore, that the TCNQ(CN)$_2$-St system copolymerizes more than 4 times as rapidly as the TCNQF$_4$-St system. The order of the copolymerization rates for those systems was obtained as TCNQ(CN)$_2$-St > TCNQF$_4$-St > TNAP-St > TCNQ-St. Half-wave reduction potential values of TCNQ(CN)$_2$, TCNQF$_4$, TNAP, and TCNQ were reported by Wheland and Gillson[10] to be 0.65, 0.53, 0.20, and 0.17 V, respectively, being related intimately with their electron affinity. It can be concluded, therefore, that the copolymerization rate for those electron-accepting quinodimethane compound-St systems is correlated closely with the electron affinity of the acceptor monomers.

Polymerization Modes of TNAP or TCNQ(CN)$_2$ with Vinyloxy Compounds. Results of the reactions of TNAP or TCNQ(CN)$_2$ with *i*BVE, *n*BVE, CEVE, PhVE, and VAc in acetonitrile at 60 °C are summarized in Table IV. The reaction products for the TNAP-*i*BVE, TNAP-*n*BVE, TNAP-CEVE, TCNQ(CN)$_2$-*i*BVE, TCNQ(CN)$_2$-*n*BVE, and TCNQ(CN)$_2$-CEVE systems were pale yellow, viscous materials. The molecular weights of the products for the TNAP-*i*BVE, TNAP-*n*BVE, TNAP-CEVE, TCNQ(CN)$_2$-*i*BVE, TCNQ(CN)$_2$-*n*BVE, and TCNQ(CN)$_2$-CEVE systems were measured by vapor pressure osmometry in benzene to be 610, 750, 860, 730, 870, and 850, respectively. IR spectra of the products showed absorptions at 1110 cm^{-1} due to the ether linkage of the vinyl ether unit but no absorption due to the nitrile group of the TNAP or TCNQ(CN)$_2$ units. The products for the TNAP-*i*BVE, TNAP-*n*BVE, TNAP-CEVE, TCNQ(CN)$_2$-*i*-BVE, TCNQ(CN)$_2$-*n*BVE, and TCNQ(CN)$_2$-CEVE systems were in good agreement in their elemental analyses and IR and ^{1}H NMR spectra with the homopolymers of *i*BVE, *n*BVE, and CEVE, respectively, indicating that they are each homopolymers of *i*BVE, *n*BVE, and CEVE and that cationic polymerizations of

Table V
Polymerization Modes of TCNQ, TNAP, $TCNQF_4$, or $TCNQ(CN)_2$ with Vinyloxy Compounds in Acetonitrile

vinyloxy compd	Taft's constant	TCNQ (0.17 V)[a]	TNAP (0.20 V)[a]	$TCNQF_4$ (0.53 V)[a]	$TCNQ(CN)_2$ (0.65 V)[a]
VAc	+1.65	alternating copolymer	adduct	alternating copolymer	adduct
PhVE	+0.60	alternating copolymer	alternating copolymer	alternating copolymer	alternating copolymer and cationic homopolymer
CEVE	+0.385	alternating copolymer	cationic homopolymer	cationic homopolymer	cationic homopolymer
*i*BVE	−0.125	cationic homopolymer	cationic homopolymer	cationic homopolymer	cationic homopolymer
*n*BVE	−0.130	cationic homopolymer	cationic homopolymer	cationic homopolymer	cationic homopolymer

[a] Reference 10.

*i*BVE, *n*BVE, and CEVE can be induced with TNAP or $TCNQ(CN)_2$ in acetonitrile.

On the other hand, the $TCNQ(CN)_2$–PhVE and $TCNQ(CN)_2$–VAc systems gave only a trace amount of reaction products when a small amount of $TCNQ(CN)_2$ was used as a catalyst, and the reaction products could be obtained in sufficient amount to be characterized when about 50 mg of $TCNQ(CN)_2$ was used. The reaction product obtained for the $TCNQ(CN)_2$–PhVE system could be separated into two fractions: fraction I, soluble in chloroform, and fraction II, insoluble in chloroform and soluble in acetone. Fraction I was a pale brown, viscous material while fraction II was a pale brown powder. Molecular weights of fractions I and II were measured by vapor pressure osmometry to be 640 and 840, respectively. Absorption at 2220 cm^{-1} appearing in the IR spectra of fractions I and II was assigned to the nitrile group, indicating an incorporation of the $TCNQ(CN)_2$ unit into the compounds of both fractions. Furthermore, from their elemental analysis and molecular weight data, it was proposed that fraction I is composed of one $TCNQ(CN)_2$ unit and three to four PhVE units, suggesting a cationic oligomer of PhVE with a terminal $TCNQ(CN)_2$ unit and that fraction II is composed of two $TCNQ(CN)_2$ and two to three PhVE units, indicating the alternating copolymerization oligomer product. Thus, it can be presumed that $TCNQ(CN)_2$–PhVE system is a borderline case, with additions such as their alternating copolymerization addition and cationic addition of PhVE taking place simultaneously. The reaction product for the TNAP–PhVE system was obtained as a pale brown powder. Its elemental analysis permitted us to suppose the product to be composed of two TNAP units and three PhVE units, implying the alternating copolymerization oligomer and no cationic polymer of PhVE. The products for the TNAP–VAc and $TCNQ(CN)_2$–VAc systems were found from their elemental analyses and molecular weights to be the 1:1 adduct between donor and acceptor compounds.

Table V summarizes the polymerization modes between electron-accepting quinodimethane compounds and vinyloxy compounds, such as alternating copolymerization, adduct formation, and homopolymerization. When TCNQ was replaced with TNAP or $TCNQ(CN)_2$, the polymerization mode with CEVE in acetonitrile was found to change from the alternating copolymerization of CEVE with TCNQ to the cationic homopolymerization of CEVE. Moreover, when the strongest electron-accepting monomer, $TCNQ(CN)_2$, was used, the cationic homopolymerization of PhVE in acetonitrile could be observed even partially, whereas for other weaker electron-accepting quinodimethane compounds, their alternating copolymerizations with PhVE always took place. Therefore, it is obvious that these changes in the polymerization modes are related closely with difference in polar character between the quinodimethane compounds and vinyloxy compounds.

From the experimental results of the polymerization behaviors of TNAP and $TCNQ(CN)_2$ such as their spontaneous alternating copolymerizations with St (see Table III) and their polymerization modes in their reaction with vinyloxy compounds (see Table V), it can be confirmed at least in the range of the cyano group substituted electron-accepting quinodimethane compounds such as $TCNQ(CN)_2$, $TCNQF_4$, TNAP, and TCNQ that their polymerization behaviors are related closely with their electron-accepting character. On the other hand, there remains an interesting but unresolved problem about the polymerization mechanism of the spontaneous alternating copolymerizations between $TCNQ(CN)_2$ and St and between TCNQ and MMA,[4] from the lower monomer concentration dependence of their alternating copolymerization rate in the extreme cases with regard to the difference in polar character between donor and acceptor monomers.

References and Notes

(1) Iwatsuki, S.; Itoh, T.; Horiuchi, K. *Macromolecules* **1978**, *11*, 497.
(2) Iwatsuki, S.; Itoh, T. *Macromolecules* **1979**, *12*, 208.
(3) Iwatsuki, S.; Itoh, T.; Sadaike, S. *Macromolecules* **1981**, *14*, 1608.
(4) Iwatsuki, S.; Itoh, T. *Macromolecules* **1983**, *16*, 332.
(5) Iwatsuki, S.; Itoh, T. *Macromolecules* **1982**, *15*, 347.
(6) Iwatsuki, S.; Itoh, T. *Macromolecules* **1980**, *13*, 983.
(7) Iwatsuki, S.; Itoh, T. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2971.
(8) Iwatsuki, S.; Itoh, T.; Shimizu, Y. *Macromolecules* **1983**, *16*, 532.
(9) Iwatsuki, S.; Itoh, T.; Nishihara, K.; Furuhashi, H. *Chem. Lett.* **1982**, 517.
(10) Wheland, R. C.; Gillson, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3916.
(11) Diekmann, J.; Hertler, W. R.; Benson, R. E. *J. Org. Chem.* **1963**, *28*, 2719.
(12) Sandman, D. J.; Garito, A. F. *J. Org. Chem.* **1974**, *39*, 1165.
(13) Wheland, R. C.; Martin, E. L. *J. Org. Chem.* **1975**, *40*, 3101.
(14) Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370.
(15) Otsu, T.; Kinoshita, M. "Experimental Methods of Polymer Synthesis"; Kagakudojin: Kyoto, 1972; p 69–91.
(16) McElvain, M.; Pinzōn, B. F. *J. Am. Chem. Soc.* **1945**, *67*, 650.
(17) Fueno, T.; Matsumura, I.; Okuyama, T.; Furukawa, J. *J. Bull. Chem. Soc. Jpn.* **1968**, *41*, 818.
(18) Cretcher, L. H.; Koch, J. A.; Pittenger, W. H. *J. Am. Chem. Soc.* **1925**, *47*, 1173.
(19) Kokubo, T.; Iwatsuki, S.; Yamashita, Y. *Macromolecules* **1968**, *1*, 482 and references therein.
(20) Bovey, F. A.; Tiers, G. V. D.; Filipovich, G. *J. Polym. Sci.* **1959**, *38*, 73.