Alternating Copolymerization Behavior of 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethan as a Very Powerful Acceptor Monomer

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ABSTRACT: Spontaneous alternating copolymerization of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethan ($TCNQF_4$) with styrene (St) in acetonitrile was carried out and compared with that of 7,7,8,8-tetracyanoquinodimethan (TCNQ) with St because $TCNQF_4$ is much more electron accepting and more soluble in organic solvents than TCNQ. The copolymerization of $TCNQF_4$ with St was found to take place about 190 times as rapidly as that of TCNQ with St. The rate of the copolymerization was expressed by $R_p = k_p[\mathrm{St}]^{3/2}\cdot[\mathrm{TCNQF_4}]^{3/2}$. Copolymerizations of $TCNQF_4$ with vinyloxy compounds such as *n*-butyl vinyl ether, isobutyl vinyl ether, 2-chloroethyl vinyl ether, phenyl vinyl ether, and vinyl acetate were studied in acetonitrile. It was found that the first three vinyloxy compounds homopolymerize in the presence of $TCNQF_4$ and the last two compounds copolymerize in an alternating fashion with $TCNQF_4$. In addition, copolymerizations in acetonitrile between $TCNQF_4$ and so-called acceptor monomers with small positive *e* values such as methyl methacrylate (MMA), methyl acrylate (MA), and acrylonitrile (AN) were studied at 60 °C with or without radical initiator. MMA was found to copolymerize alternatingly and spontaneously with $TCNQF_4$, and MA also copolymerized with $TCNQF_4$ alternatingly when radical initiator was used. On the other hand, AN did not react with $TCNQF_4$ in any way. It was pointed out that the great difference in the polar character between $TCNQF_4$ and comonomers (in a relative sense rather than on an absolute scale) is one of the primary factors for their alternating copolymerizations.

The polymerization behavior of some quinodimethan derivatives with electron-accepting character has been studied. 7,7,8,8-Tetracyanoquinodimethan (TCNQ) can copolymerize in an alternating fashion in acetonitrile with donor monomers such as styrene (St),[1] 2-chloroethyl vinyl ether (CEVE),[2] phenyl vinyl ether (PhVE),[2] and vinyl acetate (VAc).[2] TCNQ can initiate the cationic polymerizations of *n*-butyl vinyl ether (nBVE) and isobutyl vinyl ether (iBVE) in acetonitrile.[2,3] TCNQ and CEVE were found to change in their polymerization mode from the alternating copolymerization to the cationic polymerization of CEVE when the polymerization solvent was changed from acetonitrile, a low dielectric constant solvent, to ethylene carbonate, a high dielectric constant solvent.[4] 7,7,8,8-Tetrakis(methoxycarbonyl)quinodimethan[5] (TMCQ) copolymerizes alternatingly in an amphoteric fashion; it can copolymerize in an alternating fashion with donor monomers such as St, VAc, PhVE, CEVE, and iBVE or with strong electron-accepting monomers such as TCNQ. This interesting amphoteric polymerization behavior may allow one to introduce the following scheme: TCNQ is such a powerful electron acceptor that, when TMCQ encounters TCNQ, TMCQ, which behaves as an electron acceptor toward conventional electron donors, changes in its polar character to an electron donor. Thus, the great difference in polar character between TMCQ and TCNQ is responsible for the charge-transfer type interaction between them, even though both of them are generally regarded as electron acceptors.

It is noteworthy that such an interaction between alternatingly copolymerizable monomers cannot be explained in terms of an absolute scale of their polar character such as positive and negative electron charges in Coulomb's law and *e* values in Alfrey-Price's *Q*–*e* scheme. It is conceivable that the great difference in their polar character may be very important for determining their alternatingly copolymerization behavior.

2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethan ($TCNQF_4$) is more soluble[6] in organic solvents and more powerful[7] in electron-accepting character than TCNQ. It is, therefore, expected that the experiment using acceptor monomer with high concentration can be carried out easily to obtain precise information on the kinetics of polymerization and that a monomer with a positive *e* value in the *Q*–*e* scheme, such as methyl methacrylate (MMA), becomes alternatingly copolymerizable with $TCNQF_4$.

In this work we report the copolymerizations of $TCNQF_4$ with St, vinyloxy compounds such as iBVE, nBVE, PhVE, and VAc, and vinyl monomers with positive *e* values such as MMA, methyl acrylate (MA), and acrylonitrile (AN) in acetonitrile. Kinetics on spontaneous alternating copolymerization between $TCNQF_4$ and St was studied in detail.

Experimental Section

Materials. $TCNQF_4$ was prepared according to the method of Wheland et al.[6] (yield 45%; mp 295–300 °C dec (lit.:[6] yield 80%; mp 295–300 °C dec)). Anal. Calcd for $C_{12}F_4N_4$: C, 52.20; N, 20.29; F, 27.51. Found: C, 52.00; N, 20.36; F, 27.64. UV in acetonitrile: 387 ($\epsilon = 5.64 \times 10^4$), 365 ($2.76 \times 10^4$), and 344 nm ($1.29 \times 10^4$). Commercial TCNQ was purified by recrystallization from ethyl acetate and sublimation (twice) (mp 293.5–295 °C). St, iBVE, nBVE, VAc, MMA, MA, and AN were purified from commercial products by conventional methods. PhVE was prepared from phenol and dibromoethane according to the procedure of McElvain et al.[8] and Furukawa et al.[9] CEVE was prepared by the dehydrochlorination reaction of β,β'-dichlorodiethyl ether.[10] Monomer purity was checked by gas chromatography (purity >99.6%). α,α'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Acetonitrile and dichloromethane were refluxed over phosphorus pentoxide and then distilled at 81.7 and 40 °C, respectively.

Charge-Transfer Absorption Band. Absorption spectra of the charge-transfer transition between $TCNQF_4$ and St and between $TCNQF_4$ and MMA were measured in dichloromethane at room temperature. Determinations of an association equilibrium constant, K_{CT}, and a molar absorption coefficient, ϵ_{CT}, for the charge-transfer complex were made at 12.5 and 19.5 °C for the $TCNQF_4$–St system and at 20 and 30 °C for the $TCNQF_4$–MMA system according to the Benesi-Hildebrand equation. The wavelengths at which the absorbance was measured were 570 nm for the $TCNQF_4$–St system and 460 nm for the $TCNQF_4$–MMA system. Since both spectra were found to vary slowly with time, absorbance was measured just 2 min after the $TCNQF_4$ solution was mixed with the St solution or the MMA solution.

Polymerization Procedure. Given amounts of $TCNQF_4$ and the comonomer and 10 mL (or 5 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

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added except for the TCNQF$_4$–MA and TCNQF$_4$–AN systems. The ampule was set in a bath thermostated at 40 °C (or 60 °C) for the time of polymerization and then opened. In the cases of St and MMA as the comonomers, the reaction mixtures were poured into excess methanol to precipitate the copolymer. For purification, the copolymers obtained were dissolved in *N,N*-dimethylformamide (DMF), and the resulting solutions were poured into excess methanol to precipitate again the copolymers, which were dried under reduced pressure. In the cases of PhVE, VAc, and MA as the comonomers, the reaction mixtures were placed under reduced pressure to remove the volatile materials. The solid residues obtained were dissolved in a small amount of ethyl acetate and then the resulting solutions were poured into excess petroleum ether to precipitate the products, which were dried under reduced pressure. In the cases of iBVE, nBVE, and CEVE as the comonomers, the reaction mixtures were placed under reduced pressure to remove the volatile materials. The viscous residues were dissolved in benzene, and the resulting solutions were passed through a silica gel column to remove unreacted TCNQF$_4$. The solutions were placed under reduced pressure to remove benzene and to give the viscous opaque products.

Polymer Characterization. Polymer composition was established by elemental analysis. Solution viscosity for the copolymers of TCNQF$_4$ with St and MMA was determined in DMF containing 0.1 wt % lithium chloride using an Ostwald viscometer at 30 °C. Molecular weights were determined by vapor pressure osmometry, in which the solvents used were acetone for the reaction products of TCNQF$_4$ with VAc, PhVE, and MA and benzene for those of TCNQF$_4$ with CEVE, iBVE, and nBVE. ^{1}H NMR measurement for the copolymers of TCNQF$_4$ with St and MMA was carried out in dimethyl-d_6 sulfoxide with tetramethylsilane as an internal standard. ^{13}C NMR measurement of the copolymer of TCNQF$_4$ with MMA was carried out in *N,N*-dimethylformamide-d_7 (DMF-d_7). ^{1}H NMR measurement of the product of TCNQF$_4$ with MA was carried out in acetone-d_6.

Kinetics for Copolymerization of TCNQF$_4$ with St. The dependence of the copolymerization rate upon the monomer concentration was determined spectrophotometrically as follows: A 1-mL solution of St in acetonitrile with a fixed, high St concentration (2.04×10^{-2} mol/L) was mixed with the same volume of a solution of TCNQF$_4$ in acetonitrile containing a very low concentration of TCNQF$_4$ (2.12×10^{-5} or 5.46×10^{-5} mol/L) in a UV cell kept at 24.8 °C. The absorbance at 387 nm due to TCNQF$_4$ was measured at 5-min intervals. The decrease in the absorbance was analyzed separately by first-order, three-halves-order, and second-order kinetics.

The dependence of the rate upon the St concentration could not be determined spectrophotometrically because absorption of St is masked seriously with the strong broad absorption of TCNQF$_4$ but was determined gravimetrically as follows: a fixed, excess amount of TCNQF$_4$ was reacted with various small amounts of St in acetonitrile (ca. 50 mL) at 40 °C. A relationship of polymer yield vs. polymerization time was determined to obtain the copolymerization rate. A log–log plot of copolymerization rate vs. St concentration was drawn and from its slope the order of the dependence upon St concentration was estimated.

Instruments for Measurement. Varian A-60D, JEOL JNM-FX60, Jasco Model A-100, Hitachi Perkin-Elmer Model 139, and Shimadzu Model UV-200 instruments were used for ^{1}H NMR, ^{13}C NMR, IR, and UV–vis spectral determination, respectively. A Knauer vapor pressure osmometer was used for molecular weight determination.

Results and Discussion

Charge-Transfer Complex Formation between TCNQF$_4$ and St. A red color developed immediately when TCNQF$_4$ was mixed with St in dichloromethane. The UV–vis spectrum of the mixture is shown in Figure 1. The difference spectrum between the mixture and TCNQF$_4$ shows a broad absorption peak in the range 500–750 nm, corresponding to an absorption of the charge-transfer complex between TCNQF$_4$ and St. St does not absorb at wavelengths longer than 400 nm. The difference spectrum for the complex between TCNQ and St carries the peak in the range 450–580 nm, as shown additionally in Figure 1. It is obvious from the comparison in the peak position between those two complexes that TCNQF$_4$ is more electron accepting than TCNQ. This fact is confirmed also by their values for electron affinity calculated from their half-wave reduction potentials by Chen and Wentworth.[7] When the yellow TCNQF$_4$ solution was mixed with the MMA solution, no development in color was observed. However, the difference spectrum between the mixture of the TCNQF$_4$–MMA system and the TCNQF$_4$ solution, as shown in Figure 1, shows a very broad absorption in wavelength range 460–550 nm, probably due to the charge-transfer complex formation between TCNQF$_4$ and MMA. The absorption overlaps, unfortunately, with the absorption of TCNQF$_4$. This overlap may be a reason for no apparent development in color when TCNQF$_4$ is mixed with MMA. It is worth noting that the TCNQF$_4$–MMA system is subject to charge-transfer complex formation even though MMA is a so-called acceptor monomer with a positive *e* value of 0.4.

In Figures 2 and 3 are shown the Benesi–Hildebrand plots at 12.5 and 19.5 °C for the TCNQF$_4$–St system and ones at 20 and 30 °C for the TCNQF$_4$–MMA system, respectively. The linearity of the plots suggests that the

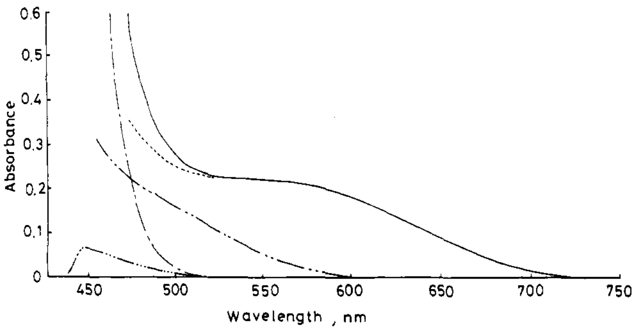

Figure 1. UV–vis spectra of mixtures of TCNQF$_4$ with St, of TCNQ with St, and of TCNQF$_4$ with MMA in dichloromethane: (—) spectrum of a mixture of TCNQF$_4$ with St; (- - -) spectrum of TCNQF$_4$; (···) difference spectrum between the above two spectra, corresponding to that of the complex; (–·–) difference spectrum between TCNQ and a mixture of TCNQ with St; (–··–) difference spectrum between TCNQF$_4$ and a mixture of TCNQF$_4$ with MMA. Concentrations of solutions employed are [TCNQF$_4$] = 1.31×10^{-3} mol/L and [St] = 0.218 mol/L for the TCNQF$_4$–St system, [TCNQ] = 1.30×10^{-3} mol/L and [St] = 0.218 mol/L for the TCNQ–St system, and [TCNQF$_4$] = 1.26×10^{-3} mol/L and [MMA] = 0.5 mol/L for the TCNQF$_4$–MMA system.

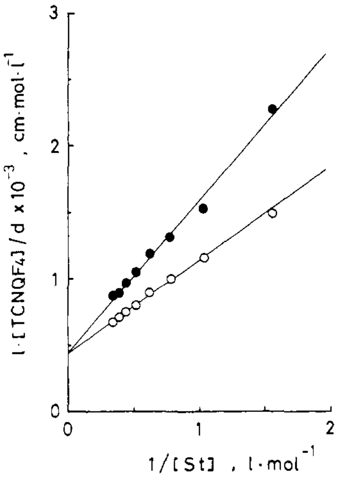

Figure 2. Benesi–Hildebrand plot for the TCNQF$_4$–St system. Temperature of measurement: (○) 12.5 °C; (●) 19.5 °C. *l* and *d* are cell length and absorbance, respectively.

Table I
Association Constants, K_{CT}, and Molar Absorption Coefficient, ϵ_{CT}, of Charge-Transfer Complex Formation for the TCNQF$_4$-St, TCNQF$_4$-MMA, and TCNQ-St Systems

TCNQF$_4$-St			TCNQ-St[1]			TCNQF$_4$-MMA		
temp, °C	K_{CT}	ϵ_{CT}	temp, °C	K_{CT}	ϵ_{CT}	temp, °C	K_{CT}	ϵ_{CT}
12.5	0.64	$\epsilon_{CT}^{570} = 2200$	9	0.43	$\epsilon_{CT}^{470} = 1900$	20	0.40	$\epsilon_{CT}^{460} = 455$
19.5	0.43		15	0.40		30	0.33	
			25	0.36				

Table II
Copolymerization of TCNQF$_4$ with St in Acetonitrile[a] at 40 °C

run no.	monomer feed, mmol TCNQF$_4$	monomer feed, mmol St	amt of TCNQF$_4$, mol %	time, min	polym yield, mg	anal. % C	anal. % H	anal. % N	copolym comp, mol % TCNQF$_4$	η_{sp}/C,[b] dL·g^{-1}
1	0.45	4.91	8.3	60	176	61.34	2.22	13.96	45.5	0.167
2	0.36	1.03	26.0	50	140	60.97	2.42	13.54	43.1	0.337
3	0.36	1.93	15.8	10	137	61.43	2.28	13.82	45.1	0.340
4	0.36	0.47	43.4	15	136	60.59	2.25	14.06	46.0	
5	0.73	0.56	56.5	15	160	60.24	2.57	14.00	45.6	
6	1.31	0.76	63.4	10	253	60.92	2.50	14.18	46.7	
7	1.60	0.41	79.8	11	134	60.72	2.81	13.83	45.1	

[a] 10 mL, without initiator. [b] DMF containing 0.1 wt % LiCl solvent. t = 30 °C, C = 0.25 g/dL.

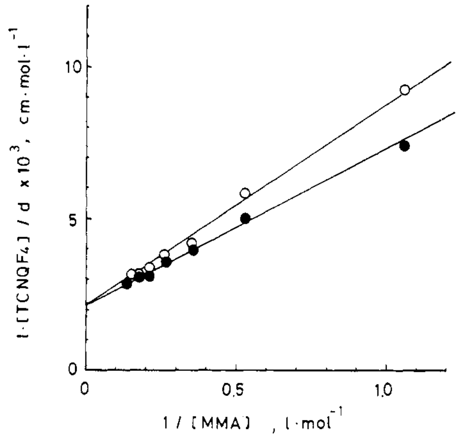

Figure 3. Benesi–Hildebrand plot for the TCNQF$_4$-MMA system. Temperature of measurement: (●) 20 °C; (○) 30 °C. l and d are cell length and absorbance, respectively.

complexes of both systems are composed of equimolar amounts of a donor and an acceptor. K_{CT} and ϵ_{CT} values for the complex formation of the TCNQF$_4$-St and TCNQF$_4$-MMA systems are summarized in Table I, including the corresponding values for the TCNQ-St system.[1] K_{CT} values at 30 °C for the TCNQF$_4$-St system and at 40 °C for the TCNQF$_4$-MMA system in dichloromethane could not be measured because the absorbance of the mixtures of TCNQF$_4$ with St and MMA decreased rapidly with time, probably due to rapid reactions, (polymerization) of TCNQF$_4$ with St and MMA. The magnitude of K_{CT} for the TCNQF$_4$-St and TCNQF$_4$-MMA systems is less than unity and corresponds well with K_{CT} values for many alternating copolymerizable donor–acceptor pairs, e.g., 1,2-dimethoxyethylene (DME)–maleic anhydride (MAnh),[11] *p*-dioxene (PD)–MAnh,[11] and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)–St.[12]

Copolymerization of TCNQF$_4$ with St. Table II summarizes the results of copolymerization of TCNQF$_4$ with St and Figure 4 shows the composition diagram of this copolymerization, indicating a typical picture of an alternating copolymerization. The products were obtained as pale brown powders. In Figure 5 is shown the ^{1}H NMR spectrum of the copolymer obtained. Absorption bands in the 6.5–7.5-ppm region and in the 3–4-ppm region were assigned to the phenyl protons and to the methine and methylene protons of the St unit, respectively. The methine and methylene protons of the St unit of the copolymer are much more subject to deshielding than those of homopolystyrene, which appear generally as absorptions in the 1–2-ppm region.[13] The deshielding conceivably arises from a powerful electron withdrawal by the neighboring dicyanomethylene groups when the St unit is sandwiched between TCNQF$_4$ units in the copolymer. It can be concluded, therefore, that TCNQF$_4$ copolymerizes with St alternatingly and spontaneously as well as TCNQ,[1] TMCQ,[5] and DDQ.[12]

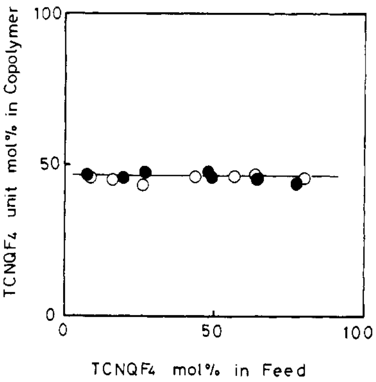

Figure 4. Composition diagram of the copolymerizations of TCNQF$_4$ with St (○) and with MMA (●).

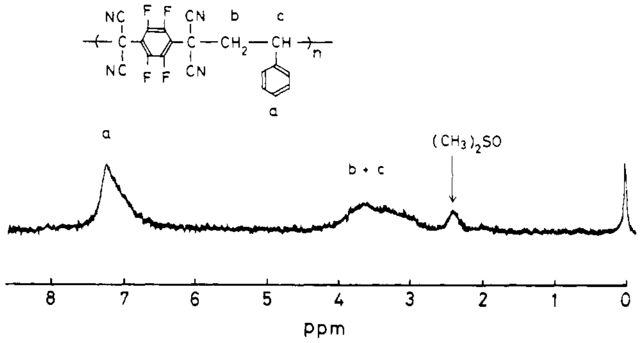

Figure 5. ^{1}H NMR spectrum of the TCNQF$_4$–St copolymer in dimethyl-d_6 sulfoxide.

Kinetics for Copolymerization of TCNQF$_4$ with St. In a set of experiments between St solution with a given high concentration and TCNQF$_4$ solution with multiple,

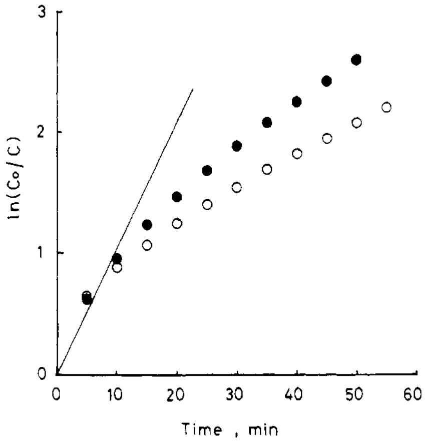

Figure 6. First-order kinetics plots for the rate of the copolymerization of the $TCNQF_4$–St system in acetonitrile at 24.8 °C. Monomer concentrations employed are as follows: $[TCNQF_4] = 1.06 \times 10^{-5}$ mol/L (○) and 2.73×10^{-5} mol/L (●); $[St] = 1.02 \times 10^{-2}$ mol/L.

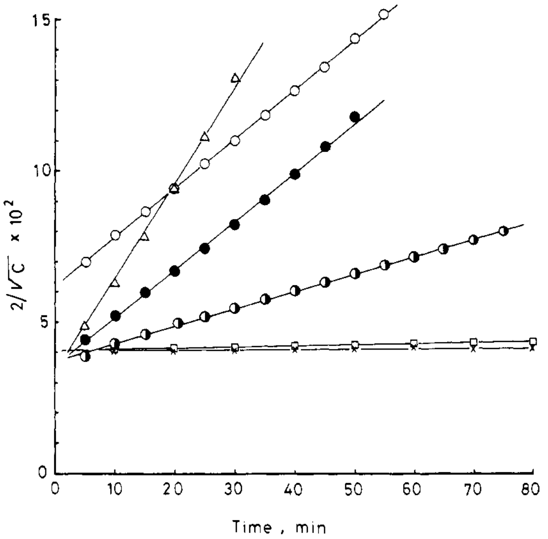

Figure 7. Three-halves-order kinetics plots for the rate of the copolymerization of the $TCNQF_4$–St and TCNQ–St systems in acetonitrile at various temperatures. Monomer concentrations employed are $[TCNQF_4] = 2.73 \times 10^{-5}$ mol/L and $[St] = 1.02 \times 10^{-2}$ mol/L at (◑) 15, (●) 24.8, and (△) 34.5 °C and $[TCNQF_4] = 1.06 \times 10^{-5}$ mol/L and $[St] = 1.02 \times 10^{-2}$ mol/L at (○) 24.8 °C for the $TCNQF_4$–St system and $[TCNQ] = 2.52 \times 10^{-5}$ mol/L and $[St] = 1.05 \times 10^{-2}$ mol/L at (×) 34.5 and (□) 43.8 °C for the TCNQ–St system.

low concentrations, the rate of consumption of $TCNQF_4$ determined spectrophotometrically was analyzed separately by first-order (Figure 6), three-halves-order (Figure 7), and second-order (Figure 8) kinetics with respect to the $TCNQF_4$ concentration. It is probable in comparison with the above three analyses that the copolymerization rate obeys the three-halves-order kinetics with respect to the $TCNQF_4$ concentration.

From another set of experiments between $TCNQF_4$ solution with a given high concentration and St solutions with multiple, low concentrations, a log–log plot of copolymerization rate vs. St concentration was obtained as shown in Figure 9. It was found from the slope of the plot that the copolymerization rate is of the 1.6th order with respect to the St concentration. When both of the above dependences of the copolymerization rate upon monomer concentration were combined, the rate of copolymerization was expressed as

$$R_p = k_p[St]^{1.6}[TCNQF_4]^{1.5}$$

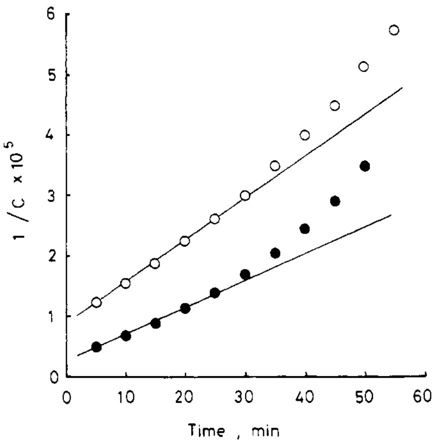

Figure 8. Second-order kinetics plots for the rate of the copolymerization in acetonitrile at 24.8 °C. Monomer concentrations employed are cited in Figure 6.

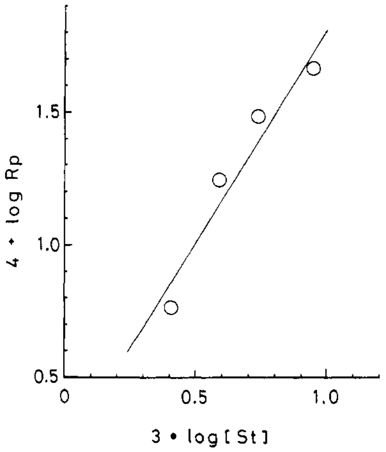

Figure 9. log–log plot of the rate of the copolymerization vs. the concentration of St; 0.138 g of $TCNQF_4$ and 50 mL of acetonitrile are used. The temperature of polymerization is 40 °C.

The 1.6th order of the copolymerization rate with respect to the St concentration may be regarded to be the three-halves order. This equation for monomer concentration dependence of the copolymerization rate is in good agreement with those for the following spontaneous alternating copolymerizations of the PD–MAnh and DME–MAnh systems:[14] $R_p = k_p[\text{donor}]^{3/2}[\text{MAnh}]^{3/2}$. It is thought, therefore, that the $TCNQF_4$–St system may be similar in the polymerization reaction scheme to the PD–MAnh and DME–MAnh systems.

Apparent three-halves-order rate constants of the copolymerization of $TCNQF_4$ with St were obtained as 0.094 $L^{1/2}$ $mol^{-1/2}$ s^{-1} at 15 °C, 0.269 $L^{1/2}$ $mol^{-1/2}$ s^{-1} at 24.8 °C, and 0.529 $L^{1/2}$ $mol^{-1/2}$ s^{-1} at 34.5 °C (see Figure 7). The Arrhenius plot of the rate constants gave a good straight line from the slope of which an overall activation energy of the copolymerization was estimated as 69.2 kJ/mol. In a previous paper[1] the copolymerization rate for the TCNQ–St system was reported to be of the first order with respect to each of the monomer concentrations and an overall activation energy of the copolymerization was estimated as 60.2 kJ/mol. The monomer concentration dependence of the copolymerization rate is different between the $TCNQF_4$–St and TCNQ–St systems. The apparent copolymerization rate for the TCNQ–St system was found to be much slower than that of the $TCNQF_4$–St system, so the TCNQ–St system was reinvestigated under the same conditions of the kinetics measurement for the $TCNQF_4$–St system. The experimental points were found

Table III
Polymerization of $TCNQF_4$ with Vinyloxy Compounds in Acetonitrile[a] at 60 °C

	monomer feed, mg					anal.					
donor	co-monomer	$TCNQF_4$	time, h	polym yield, mg	conversn, %	% H	% C	% Cl	% N	copolym comp, mol % comonomer	M_n
iBVE	202.8	1	7.3	174.4	86	11.75	71.65		0	100	610[b]
nBVE	201.1	1	6.4	140.6	70	12.87	71.20		0	100	570[b]
CEVE	408.5	1	17.3	183.8	45	6.55	45.00	33.82	0	100	850[b]
PhVE	179.0	1	2.5	trace							
VAc	207.4	1	3.5	trace							
PhVE	210.5	50.5	4.3	29.0	11	1.76	56.80		12.17	60.0	1970[c]
VAc	205.6	50.5	18.0	63.4	25	1.35	52.40		14.30	57.3	1290[c]

[a] 5 mL, without initiator. [b] Determined by vapor pressure osmometry. Benzene solvent. [c] Determined by vapor pressure osmometry. Acetone solvent.

to obey three-halves-order kinetics as shown in Figure 7. Apparent three-halves-order rate constants of copolymerization between TCNQ and St at 34.5 and 43.0 °C were found to be 2.75×10^{-3} and 6.00×10^{-3} $L^{1/2}$ $mol^{-1/2}$ s^{-1}, respectively, and an overall activation energy of the copolymerization was established as 72.3 kJ/mol. Since the apparent three-halves-order constants at 34.5 °C were found to be 0.529 $L^{1/2}$ $mol^{-1/2}$ s^{-1} for the $TCNQF_4$-St system and 2.75×10^{-3} $L^{1/2}$ $mol^{-1/2}$ s^{-1} for the TCNQ-St system, the $TCNQF_4$-St system copolymerizes about 190 times as rapidly as the TCNQ-St system. Electron affinities of $TCNQF_4$ and TCNQ are reported to be 3.22 and 2.88 eV, respectively.[7] It is, therefore, conceivable that the large difference in the copolymerization rate between the $TCNQF_4$-St system and the TCNQ-St system is attributed to that of the electron affinities between $TCNQF_4$ and TCNQ.

Copolymerizations of $TCNQF_4$ with Vinyloxy Compounds. The results of the copolymerizations of $TCNQF_4$ with iBVE, nBVE, CEVE, PhVE, and VAc in acetonitrile at 60 °C are summarized in Table III. The reaction products for the $TCNQF_4$-iBVE, $TCNQF_4$-nBVE, and $TCNQF_4$-CEVE systems were pale brown, viscous materials. The molecular weights of the products obtained for the $TCNQF_4$-iBVE, $TCNQF_4$-nBVE, and $TCNQF_4$-CEVE systems were measured by vapor pressure osmometry in benzene to be 850, 570, and 610, respectively. The IR spectra of all three products show 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 $TCNQF_4$ unit. The products for the $TCNQF_4$-iBVE, $TCNQF_4$-nBVE, and $TCNQF_4$-CEVE systems were in good agreement in their elemental analyses and IR and ^1H NMR respectively, indicating that these products are each homopolymers of iBVE, nBVE, and CEVE. It is, therefore, concluded that cationic polymerizations of iBVE, nBVE, and CEVE take place and that $TCNQF_4$ allows these vinyl ethers to give cationic species by electron-transfer reactions between them.

On the other hand, reactions of $TCNQF_4$ with PhVE and VAc gave only trace reaction products when a small amount of $TCNQF_4$ was used as a catalyst. When more than 50 mg of $TCNQF_4$ was used, complete conversion to the reaction products occurred. Both reaction products obtained were pale brown powders which were soluble in acetone, DMF, dimethyl sulfoxide, and ethyl acetate and insoluble in benzene, chloroform, and dichloromethane.

The molecular weights of the products for the $TCNQF_4$-PhVE and $TCNQF_4$-VAc systems were measured by vapor pressure osmometry in acetone to be 1970 and 1290, respectively. Their elemental analyses suggest that the products for the $TCNQF_4$-PhVE and $TCNQF_4$-VAc systems are composed of equimolar amounts of $TCNQF_4$ and donor monomers PhVE and VAc. Therefore, the $TCNQF_4$-PhVE and $TCNQF_4$-VAc systems were considered to copolymerize alternatingly just as the TCNQ-PhVE[2] and TCNQ-VAc systems.[2] When TCNQ was replaced with $TCNQF_4$ as the acceptor monomer, a change in polymerization mode toward CEVE in acetonitrile was observed as follows: cationic polymerization took place for the $TCNQF_4$-CEVE system while alternating copolymerization occurred for the TCNQ-CEVE system. It is probable that this difference is attributable to the electron affinity (EA) between $TCNQF_4$ (EA = 3.22 eV[7]) and TCNQ (EA = 2.88 eV[7]). Since $TCNQF_4$ is a better electron acceptor than TCNQ, one-electron-transfer reaction through a charge-transfer complex between $TCNQF_4$ and CEVE in acetonitrile takes place readily to yield a radical anion of $TCNQF_4$ and a radical cation of CEVE, the latter of which is able to initiate the polymerization of CEVE. On the other hand, since TCNQ is weaker in electron-accepting character than $TCNQF_4$, one-electron-transfer reaction between TCNQ and CEVE hardly takes place. In the TCNQ-CEVE system, when acetonitrile was replaced with the higher dielectric constant solvent ethylene carbonate, TCNQ and CEVE were found to be subject to an electron-transfer reaction through their charge-transfer complex to yield a homopolymer of CEVE.[4] In addtion, DDQ, with a stronger electron-accepting character (EA = 3.00 eV[7]) than TCNQ, was also found to be able to initiate a cationic polymerization of CEVE in bulk to yield the homopolymer of CEVE.[12] From these facts, we point out that an electron-transfer reaction between donor and acceptor monomers should play an important role in the determination of the polymerization mode.

Copolymerizations of $TCNQF_4$ with Monomers with Positive e Values. Table IV summarizes the results of copolymerization of $TCNQF_4$ with MMA ($e = 0.4^{15}$) and Figure 4 shows a composition diagram of this copolymerization, indicating a typical picture of an alternating copolymerization. The products were obtained as a pale yellow powder. The IR spectrum of the product obtained shows absorptions at 2250 and 1740 cm^{-1}, assignable to the nitrile group and to the carbonyl group in the ester linkage, respectively, indicating an incorporation of both $TCNQF_4$ and MMA units into the copolymer. The ^1H NMR and ^{13}C NMR spectra of the copolymer obtained are shown in Figures 10a and 11, respectively. The ^1H NMR spectrum of the homopolymer of MMA, prepared by its polymerization with AIBN in benzene at 60 °C, is shown in Figure 10b, where absorptions at 3.8, 3.3, and 1.9 ppm were assigned to the methoxy, the methylene, and the α-methyl protons of the MMA unit, respectively. The methylene and α-methyl protons of the MMA unit of the copolymer were found to be much more subject to deshielding than the corresponding ones for the homopolymer of MMA. In Figure 11, absorption bands at 65.8,

Table IV
Copolymerization of $TCNQF_4$ with MMA in Acetonitrile[a] at 60 °C

run no.	monomer feed, mg TCNQF$_4$	monomer feed, mg MMA	amt of TCNQF$_4$, mol %	time, h	polym yield, mg	conversn, %	anal. % H	anal. % C	anal. % N	copolym comp, mol % TCNQF$_4$	η_{sp}/C,[b] dL·g^{-1}
1	118.4	513.0	7.7	1.9	64.3	10.2	2.02	53.54	14.35	46.7	
2	112.4	167.9	19.5	4.8	49.6	17.7	2.21	53.71	14.11	45.3	0.161
3	142.9	141.2	26.9	5.5	32.1	11.3	1.03	54.54	14.51	47.6	
4	275.7	108.0	48.1	17.5	182.6	47.6	2.50	53.59	14.45	47.3	0.242
5	278.6	102.7	49.5	3.5	17.4	4.6	2.32	54.63	13.98	44.6	
6	360.0	71.6	64.6	13.7	65.9	15.3	2.05	53.93	14.04	44.9	0.183
7	444.6	47.4	77.3	13.7	21.3	4.3	2.88	52.86	13.79	43.5	

[a] 10 mL, without initiator. [b] DMF containing 0.1 wt % LiCl solvent. t = 30 °C, C = 0.25 g/dL.

Table V
Copolymerization of $TCNQF_4$ with MA in Acetonitrile at 60 °C[a]

run. no.	monomer feed, mg TCNQF$_4$	monomer feed, mg MA	amt of TCNQF$_4$, mol %	time, h	polym yield, mg	conversn, %	anal. % H	anal. % C	anal. % N	copolym comp, mol % TCNQF$_4$	M_n[b]
1	100.2	200.1	13.5	135.3	102.2	34.0	1.13	53.90	15.08	47.4	2395
2	97.7	101.6	23.1	119.8	49.3	24.7	2.20	54.85	15.40	49.5	2140
3	103.4	52.5	38.0	120.2	46.8	30.0	1.73	53.68	15.58	50.8	2355
4	195.6	37.4	62.0	119.0	47.1	20.2	1.25	52.97	15.24	48.5	

[a] 10 mL, 5 mg of AIBN. [b] Determined by vapor pressure osmometry. Acetone solvent.

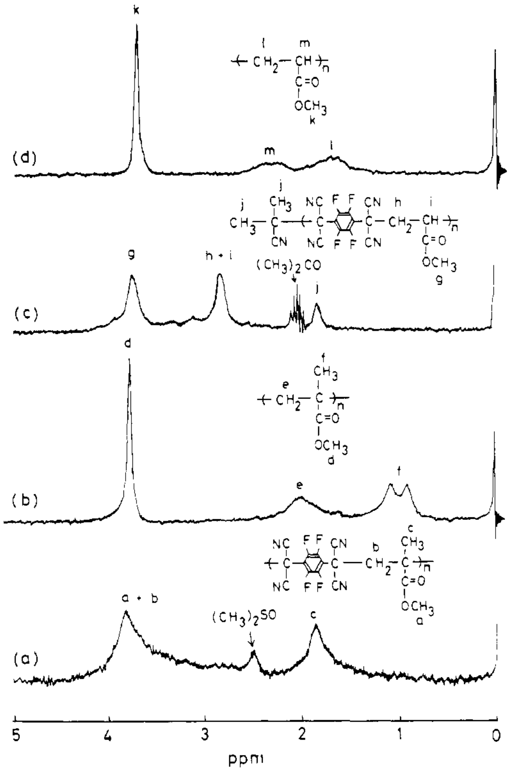

Figure 10. ^1H NMR spectra of (a) copolymer of $TCNQF_4$ with MMA in dimethyl-d_6 sulfoxide, (b) homopolymer of MMA in chloroform-d, (c) copolymer of $TCNQF_4$ with MA in acetone-d_6, and (d) homopolymer of MA in chloroform-d.

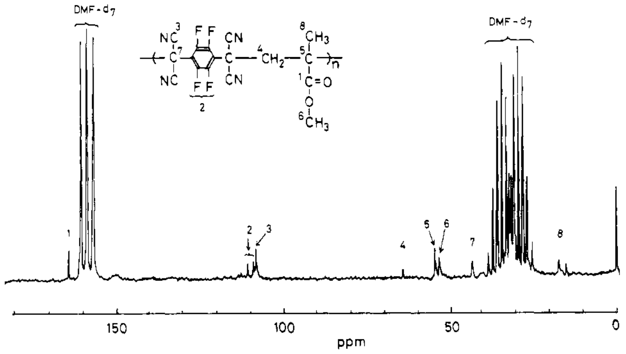

Figure 11. ^{13}C NMR spectrum of the copolymer of $TCNQF_4$ with MMA in DMF-d_7.

55.8, and 17.7 ppm were assigned to the methylene, quaternary, and α-methyl carbons of the MMA unit, respectively. The former two carbons are much more subject to deshielding, by about 10 ppm, than the corresponding ones for the homopolymer of MMA, appearing at 55.0 and 46.0 ppm,[16] respectively. On the other hand, the absorption due to the α-methyl carbon of the MMA unit of the copolymer was observed at higher field than that (at 20.0 ppm) of the homopolymer of MMA. This was considered probably to be a steric compression shift.[17] It is conceivable that the deshielding in the ^1H NMR and ^{13}C NMR spectra arises from a neighboring powerful electron-withdrawing dicyanomethylene group when the MMA unit is sandwiched between $TCNQF_4$ units in the copolymer. Similar behavior was observed in alternating copolymers between $TCNQF_4$ and St, TCNQ and St,[1] and TMCQ and St.[5] It can be concluded, therefore, that the copolymer between $TCNQF_4$ and MMA is indeed alternating.

Copolymerization between $TCNQF_4$ and MA, with a higher positive e value (e = 0.6[15]) than that of MMA, was carried out. A mixture of $TCNQF_4$ and MA in acetonitrile was heated at 60 °C for 70 h without any initiator, and only starting materials were recovered. The copolymerization took place successfully when AIBN was used as an initiator. In Table V are summarized the results of the copolymerization of $TCNQF_4$ with MA. The copolymer was obtained as a pale yellow powder. Its molecular weight was measured by vapor pressure osmometry in acetone to be ca. 2000, indicating that the copolymer is oligomeric (DP = 6). The copolymer composition was established by elemental analysis to be composed of equimolar amounts of $TCNQF_4$ and MA units. Absorptions at 2250 and 1740 cm^{-1} in the IR spectrum of the copolymer obtained were assigned to the nitrile group and to the carbonyl group of the ester linkage, respectively, indicating an incorporation of both $TCNQF_4$ and MA units into the copolymer. In Figures 10c and 10d are shown the ^1H NMR spectra of the copolymer in acetone-d_6 and the homopolymer of MA in chloroform-d, prepared by its polymerization with AIBN in benzene at 60 °C. In Figure 10c, absorptions at 3.8 and

2.8 ppm were assigned to the methoxy protons and methine and methylene protons of the MA unit, respectively. The methine and methylene protons of the MA unit of the copolymer were found to be much more subject to deshielding than those of the homopolymer of MA. Similar behavior was observed for protons of the donor monomer unit in many alternating copolymers containing $TCNQF_4$ or TCNQ.[1] The deshielding arises conceivably from a neighboring powerful electron-withdrawing dicyanomethylene group when the MA unit is sandwiched between the $TCNQF_4$ units in the copolymer. Additional absorption at 1.8 ppm was assigned reasonably to methyl protons of the isobutyronitrile group, the radical initiator AIBN fragment. When the product obtained is considered as an oligomer composed of six $TCNQF_4$–MA units with a radical initiator AIBN fragment at an end, the ratio of protons of the isobutyronitrile group to methine and methylene protons of the MA units is calculated as 1:3, consistent with the found area ratio of the peaks at 1.8 ppm to the ones at 2.8 ppm in Figure 10c. The elemental analysis data and molecular weight of the product obtained are also compatible with the proposed oligomer. It can be concluded, therefore, that the copolymer obtained is indeed alternating even though oligomeric.

Copolymerization of $TCNQF_4$ with AN ($e = 1.2$[15]), with a much higher positive e value, was attempted in acetonitrile with and without AIBN. Neither copolymer of $TCNQF_4$ with AN nor homopolymer of AN was obtained, and the starting materials were recovered.

St ($e = -0.8$), MMA ($e = 0.4$), and MA ($e = 0.6$) were found to be alternatingly copolymerizable with $TCNQF_4$. While St and MMA copolymerize with $TCNQF_4$ spontaneously and rapidly, MA, which has the lowest electron density among them, does not copolymerize spontaneously at an appreciable rate and it can copolymerize alternatingly when radical initiator was added. Finally, AN ($e = 1.2$), with less electron density, is no longer copolymerizable with $TCNQF_4$ in any fashion. These copolymerization behaviors with $TCNQF_4$ were found to be related intimately to the polar character of the comonomers. Moreover, it should be emphasized that MMA and MA, with positive e values, are alternatingly copolymerizable with $TCNQF_4$ as donor monomers. This alternating tendency between MMA or MA and $TCNQF_4$ cannot be explained in terms of polar effects in Alfrey–Price's Q–e scheme because all of them carry positive e values and repulsive forces would be expected instead of attractive ones. It is proposed, therefore, that the great difference in polar character between $TCNQF_4$ and alternatingly copolymerizable comonomers (in a relative sense rather than on an absolute scale) may be one of the primary factors for their alternating tendency as proposed previously in the study of the amphoteric behavior of TMCQ[5] in its alternating copolymerizations.

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Ethylene–1-Butene Copolymers. 1. Comonomer Sequence Distribution

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ABSTRACT: A carbon-13 NMR method is presented for a quantitative determination of the comonomer distribution, the triad and tetrad sequence distributions, average sequence lengths, and run numbers in ethylene–1-butene copolymers. A series of hydrogenated polybutadienes and a poly(1-butene) served as reference systems for establishing chemical shift assignments and for determining optimum conditions for a quantitative development. A dependence of relative spectral areas upon concentrations was noted at polymer sample weight percents of 30 and higher. The method presented should be free of errors associated with differences in spectral line widths, peak overlap, difficulties in detailed assignments, and complexities introduced through a configurational sensitivity.

Introduction

1-Butene and 1-hexene are frequently used in ethylene polymerizations to control polymer density. By varying the amount of comonomer incorporated, it is possible to produce copolymers with densities in a range of 0.90–0.94 g/cm^3, a result which has led to a line of commercial polyethylenes known as linear low-density polyethylenes (LLDPE). Superior film and processing properties coupled with recent manufacturing developments have created a renewed interest in this area.

Commercial ethylene–1-butene copolymers contain principally isolated ethyl branches; however, dependent

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