Spontaneous Alternating Copolymerization of Tetracyanoquinodimethane with Styrene

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ABSTRACT: Tetracyanoquinodimethane (TCNQ) was found to copolymerize with styrene (St) alternatingly and spontaneously at room temperature. The kinetic behavior of the copolymerization was studied. The rate of copolymerization was expressed as $R_p = k_p[TCNQ]^1[St]^1$. The apparent rate constant of this copolymerization was estimated to be 2.6×10^{-5} s^{-1} at 15 °C, 4.2×10^{-5} s^{-1} at 25 °C, and 12.9×10^{-5} s^{-1} at 35 °C, and an overall activation energy was given as 14.4 kcal/mol.

Tetracyanoquinodimethane (TCNQ)[1] is well known as a powerful electron acceptor which interacts with various electron donors to form charge-transfer (or electron donor–acceptor) complexes.[2] On the other hand, polymerization concerning TCNQ has not been reported except for the article of Acker et al.[1] describing briefly the polymerizations of TCNQ with 2,3-dimethyl-1,3-butadiene or cyclopentadiene and those of Aoki and Stille[3,4] on cationic polymerizations of vinyl ethers initiated with TCNQ, indicating the powerful electron-accepting property of TCNQ rather than its own polymerizability.

Unsubstituted quinodimethane (QM) is so reactive that it polymerizes spontaneously even at −78 °C.[5] QM derivatives are presumed to become less reactive in connection with the nature and the number of electron-withdrawing substituents as expected from the trend observed in rate of spontaneous homopolymerizations of a series of chlorine-substituted derivatives:[6] QM,[5] $\alpha,\alpha,\alpha',\alpha'$-tetrachloro-*p*-xylylene[7] (TCX), $\alpha,\alpha,\alpha',\alpha'$-2.5-hexachloro-*p*-xylylene:[6] (HCX), and perchloro-*p*-xylylene[8] (PCX). TCNQ is expected, therefore, to be an interesting monomer which carries marginal polymerizability and powerful electron accepting property.

In this work was described an alternating copolymerization of TCNQ with styrene (St) which takes place spontaneously even at room temperature. In addition, some kinetic behavior of the copolymerization was studied.

Experimental Section

Materials. Commercial TCNQ was purified by repeated recrystallizations using acetonitrile as solvent (mp 293.5–295 °C (lit.[1] mp 293.5–296 °C)). St was purified from commercial product by a conventional method. Acetonitrile as solvent was purified by sequential refluxing with phosphorus pentoxide and distilling at 82 °C, which was repeated three times. Other solvents were purified by corresponding conventional methods.

Polymerization Procedure. In copolymerization of TCNQ with St, given amounts of TCNQ and St and 10 mL of acetonitrile were placed in an ampule which was then degassed and sealed. It was set in a bath thermostated at 40 °C for the time of polymerization. It was opened and the reaction mixture was added to an excess amount of acetone to deposite the polymeric product which was collected by filtration, washed well with acetonitrile and acetone, and dried under reduced pressure.

The composition of the polymer was established by its elementary analysis and by NMR measurement in dimethyl-d_6 sulfoxide. Solution viscosity was measured at 30 °C in dimethylformamide containing 0.1 wt % of lithium chloride.

Determination in Association Equilibrium Constant of Charge-Transfer Complex Formation. The solvent for ultraviolet and visible spectrophotometry was acetonitrile. In Figure 1 is shown a spectrum of the mixture of TCNQ and St. Since the spectrum was found to vary with time, absorbance was measured just 2 min after the mixing of TCNQ solution with St solution. Determination of the association constant, K_{CT}, for formation of the charge-transfer complex was carried out according to both the Benesi–Hildebrand equation (eq 1) and the Scott equation (eq 2)

$$[A]_0 l/d = (1/K_{CT}\epsilon_{CT})(1/[D]_0) + (1/\epsilon_{CT}) \quad (1)$$

$$[A]_0[D]_0 l/d = (1/K_{CT}\epsilon_{CT}) + ([D]_0/\epsilon_{CT}) \quad (2)$$

where $[A]_0$ and $[D]_0$ refer to concentration of acceptor and donor solutions, respectively, d is the absorbance, l is the length of the cell, and ϵ_{CT} is the molar extinction coefficient of the complex. The wavelength at which absorbance was measured was 470 nm.

Equations 1 and 2 are valid under the condition $[D]_0 \gg [A]_0$. Plots of eq 1 gave straight lines with appreciable positive slope and very small intercepts (see Figure 2), which lead to large errors in the estimation of ϵ_{CT}. On the other hand, plots of eq 2 gave a set of straight and parallel lines with small positive slope and large intercepts (see Figure 3), and the slope enabled one to estimate ϵ_{CT} with much less error than that in the estimation of ϵ_{CT} according to eq 1. Therefore, combined use of both equations was considered to be helpful to obtain values of K_{CT} and ϵ_{CT} with high accuracy.

Results and Discussion

Dark red color developed without delay when TCNQ was mixed with St solution in acetonitrile. Most of the experiments were carried out heterogeneously because of the very low solubility of TCNQ in acetonitrile, which required enormous volumes of solvent to obtain homogeneous solution. TCNQ dissolved slowly but completely to interact with St at the interface and to produce thereby a gelatinous shell of swollen, pink-colored copolymer. After the polymer was separated and dried to a powder, it did not dissolve in common organic solvent such as benzene, chloroform, and acetone. In aprotic polar solvent such as dimethylformamide and dimethyl sulfoxide it swelled only at room temperature and dissolved eventually on prolonged heating at an elevated temperature such as 80 °C. The resulting solution exhibited a polyelectrolyte behavior, that is, it exhibited an increase in viscosity with dilution of the solution, which could be removed by addition of a small amount of neutral salt such as lithium chloride.

The absorption band of the charge-transfer complex between TCNQ and St shows shoulder (an increase in intensity) at the longer wavelength side of the absorption band of TCNQ, as indicated by the dotted curve in Figure 1, rather than definite peak. Absorption maximum of the lowest intermolecular charge-transfer transition, λ_{max}, of the complex could not be determined experimentally. The wavelength for determination of K_{CT} was chosen by taking into account the condition in which the absorbance at a given wavelength may be attributed much more to charge-transfer complex and much less to individual component compounds. The absorption band of the charge-transfer complex decreased in intensity with time even though slowly. The decrease may be attributed to reduction in concentrations of TCNQ and St with copolymerization. Measurement of absorbance for determination of K_{CT} was carried out at a fixed short time after mixing the TCNQ and St solutions in order to reduce the error caused by the decrease in absorption intensity with time. In Figures 2 and 3 are shown plots of Benesi–Hildebrand and Scott equations for the TCNQ–St system, respectively, which dis-

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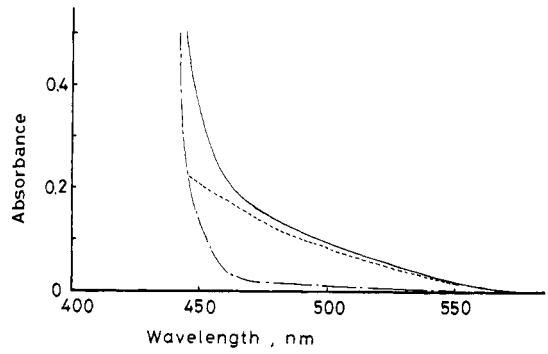

Figure 1. UV–visible spectrum of a mixture of TCNQ and St in acetonitrile: (—) spectrum of mixture of TCNQ and St, (- - -) spectrum of TCNQ, and (- - -) difference spectrum between the above two spectra, corresponding to that of the complex. Concentrations of solutions employed are [St] = 0.144 mol/L and [TCNQ] = 1.61×10^{-3} mol.

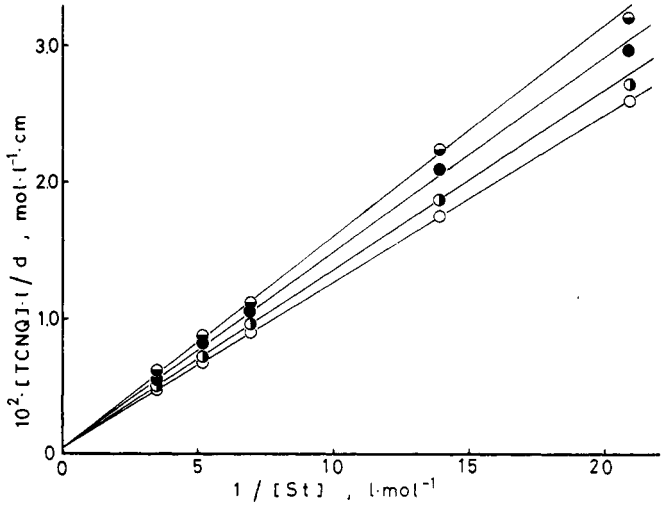

Figure 2. Benesi–Hildebrand plot. Temperatures of measurements are: (○) 9 °C, (◑) 15 °C, (●) 25 °C, and (◒) 35 °C.

play good straight lines, suggesting that the complex is composed of equimolar amounts of donor and acceptor.

K_{CT} and ϵ_{CT} values obtained from these plots are summarized in Table I. The K_{CT} value of the complex is less than unity and corresponds well in magnitude to the K_{CT} values[9] for many alternating copolymerizable donor–acceptor pairs such as vinyl ether–maleic anhydride (MAnh), *p*-dioxene–MAnh, 1,2-dimethoxyethylene–MAnh, and 2-butene–sulfur dioxide systems.

In Table II are summarized results of copolymerization of TCNQ with St, and in Figure 4 is shown an apparent composition diagram of the copolymerization, indicating a typical picture of an alternating copolymerization. The term "apparent" was used here because most experimental runs were carried out in heterogeneous phase. In Figure 5 is shown the IR spectrum of the copolymer. In Figure 6 is shown the NMR spectrum of the copolymer, where only two kinds of peaks are located in the δ 7 to 7.5 ppm region and at the δ 3 to 3.5 ppm region. The former peak can be assigned to protons of the phenyl group of the St unit and the phenylene group of the TCNQ unit. The latter one is assigned to methine and methylene protons of the St unit, which are much more subject to deshielding than corresponding ones in homopolystyrene, because those of homopolystyrene appear generally as absorptions in the δ 1 to 2 ppm region.[10] The deshielding arises primarily from the powerful electron-withdrawing effect of the neighboring dicyanomethylene groups, when the St unit is sandwiched between TCNQ units in the copolymer. It is concluded, therefore, that the copolymer of TCNQ with St is really alternating.

Time–conversion relationships of the copolymerizations under various monomer concentrations are shown in Figure 7 where the formation of the copolymer is suppressed during a fixed time (induction period). The length of the induction period appears to be dependent upon the amount of St and independent upon that of TCNQ in feed. Under the experimental condition, TCNQ dissolves partially in acetonitrile and

Table I
Association Constants, K_{CT}, of Charge-Transfer Complex Formation for the TCNQ–St System

Temp, °C	K_{CT}[a,b]
9	0.426
15	0.400
25	0.361
35	0.333

[a] This temperature dependence of K_{CT} allows the enthalpy, ΔH, and entropy, ΔS, of the complex formation to be calculated: $\Delta H = -0.32$ kcal/mol; $\Delta S = -7.6$ cal/(mol deg). [b] Molar extinction coefficient, ϵ_{CT}, at 470 nm was estimated as 1900.

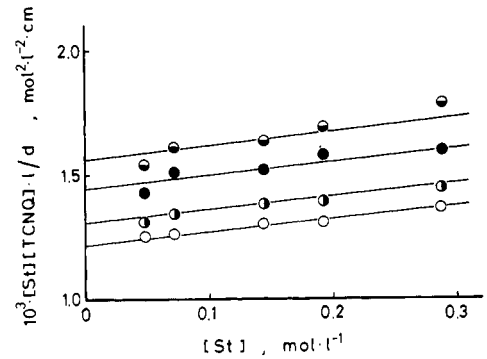

Figure 3. Scott plot. Temperatures of measurements are the same of those in the Figure 2.

Table II
Copolymerizations of TCNQ with St[a]

Run no.	Feed, mg TCNQ	Feed, mg St	TCNQ, mol %	Time of polymn, h	Polymer yield, %	Conversion, %	Copolymer[c] % C	% H	% N	TCNQ, mol %
1	197.4	45.7	68.8	2.25	49.1	20.2	76.86	4.22	17.19	46.1
2	195.4	108.2	46.9	5.25	95.7	31.5	77.06	4.29	17.48	47.2
3	193.9	229.9	30.1	5.0	106.1	25.0	76.82	4.32	17.22	46.2
4	198.4	578.9	14.9	21.0	238.8	30.7	77.00	4.28	17.58	47.6
5[b]	197.4	1895.3	5.0	21.5	276.0	13.2	77.12	4.29	17.10	45.8

[a] No initiator; 10 mL of acetonitrile as polymerization solvent; 40 °C polymerization in the heterogeneous state. [b] $[\eta] = 0.407$ (dL/g) DMF containing 0.1 wt % LiCl as solvent, and at 30 °C. [c] Calcd for $C_{20}H_{12}N_4$, TCNQ, plus St units: C, 77.91; H, 3.92; N, 18.7.

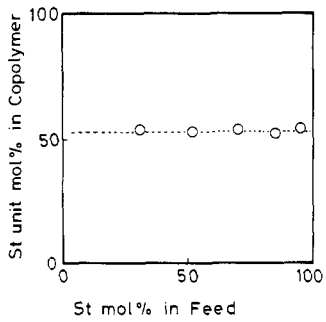

Figure 4. Apparent composition diagram of the copolymerization of TCNQ with St.

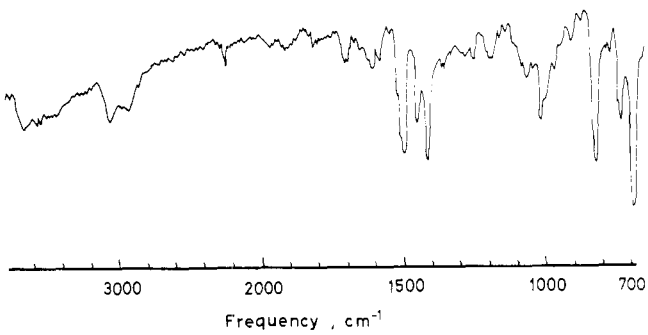

Figure 5. IR spectrum of the copolymer (KBr disk method).

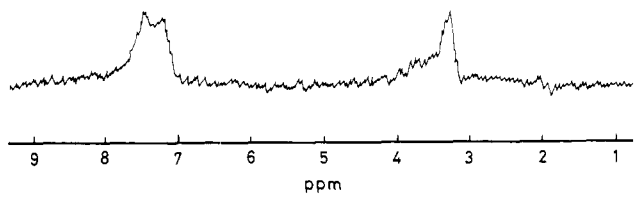

Figure 6. NMR spectrum of the copolymer.

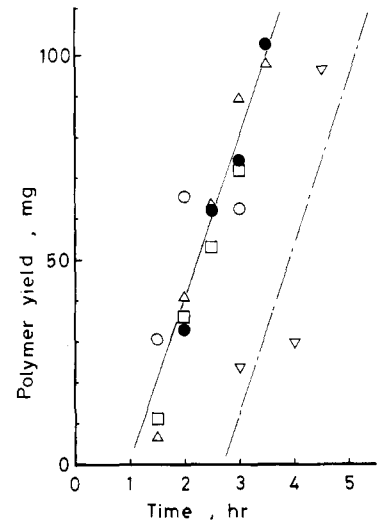

Figure 7. Time–conversion curves of the copolymerization. Monomer concentrations of TCNQ ($\times 10^4$ mol/L) and St ($\times 10^4$ mol/L) are: (○) 9.79, 5.76; (▽) 9.79, 2.88; (△) 4.90, 5.76; (◑) 4.90, 4.80; (□) 2.45, 5.76.

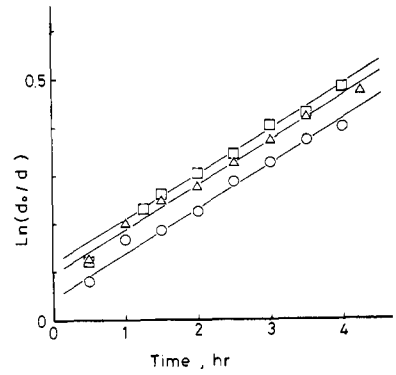

Figure 8. First-order kinetic plots for the rate of the copolymerization at 15 °C. Monomer concentrations employed are as follows: [TCNQ] = (△) 2.69×10^{-3}, (○) 1.34×10^{-3}, and (□) 0.76×10^{-3} mol/L and [St] = 0.289 mol/L.

the concentration of TCNQ dissolved in the polymerization medium is apparently constant at the saturated concentration regardless of various amounts of TCNQ charged to the system. The larger amount of St leads to the higher concentration of the complex, resulting in the shorter induction period. It is suggested that TCNQ and St are probably involved in interactions during the induction period, which consume inhibiting contaminants via free-radical intermediates, or that a critical concentration of the TCNQ–St complex must accumulate in solution before polymerization can occur. The initiation could not be explained in a definite reaction mechanism, however, because zeroth-order kinetics of the initiation was derived from monomer order kinetics of the copolymerization as described later.

Under the condition of constant concentration of St with varying but very low concentration of TCNQ (phase being homogeneous), a rate of the copolymerization was determined spectrophotometrically by using absorbance at 470 nm. The rate was found to obey the first-order kinetics with respect to concentration of TCNQ (see Figure 8) rather than the second-order kinetics (see Figure 9) and apparent first-order rate constants at three different temperatures were obtained as 2.6×10^{-5} s^{-1} at 15 °C, 4.2×10^{-5} s^{-1} at 25 °C, and 12.9×10^{-5} s^{-1} at 35 °C. 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 14.4 kcal/mol.

In another set of experiments, a fixed amount (0.1 g in 10 mL of acetonitrile) of TCNQ was caused to react with a varying concentration of St (phase being heterogeneous), and the rate of the copolymerization was determined gravimetrically. In the log–log plot of the rate of the copolymerization vs. the concentration of St (see Figure 10) the rate was found to be of the first order with respect to concentration of St.

When both these results that show the dependence of the copolymerization rate upon monomer concentration are combined, the rate of the copolymerization can be expressed in the following equation

$$R_p = k_p[\mathrm{St}]^{1.0}[\mathrm{TCNQ}]^{1.0} \quad (3)$$

This rate expression for the copolymerization, which is first order with respect to each monomer, is obviously different from those for other spontaneous alternating copolymerizations: $R_p = k_p[\mathrm{MCP}]^3[\mathrm{SO_2}]^2$ in copolymerization of 1-methylcyclopropene (MCP) with sulfur dioxide (SO_2),[11] $R_p = k_p[\mathrm{CPT}]^3[\mathrm{SO_2}]^2$ in copolymerization of cyclopentene (CPT) and SO_2,[12] and $R_p = k_p[\mathrm{donor}]^{3/2}[\mathrm{MAnh}]^{3/2}$ in copolymerizations of 1,2-dimethoxyethylene of *p*-dioxene and MAnh.[13] Moreover, no regularity was found among this set of rate expressions, which required that a different reaction scheme should be postulated for each copolymerization. The monomer order of this copolymerization allows one to propose the zeroth-order kinetics with respect to monomer concentration for the initiation, leading unlikely to a reasonable reaction scheme

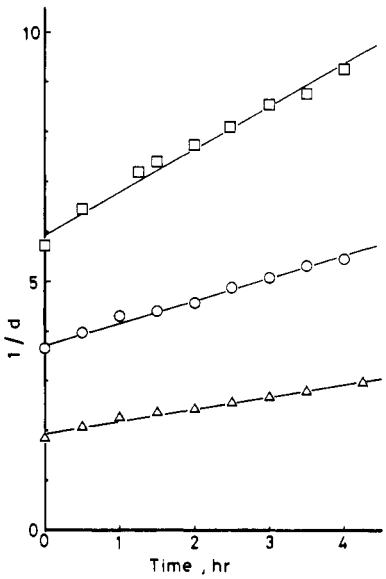

Figure 9. Second-order kinetic plots for the rate of the copolymerization at 15 °C. Monomer concentrations employed are cited in Figure 8.

for the initiation. In ESR measurement at liquid nitrogen temperature the mixture of TCNQ and St, which was placed in an ESR sample tube at room temperature and then degassed well at −78 °C, manifested a single peak at $g = 2.0005 \pm 0.0005$, which was approximately 10 G wide at half-maximum absorption. This suggests that this spontaneous alternating copolymerization occurs via a free-radical mechanism.

The polymerization behavior of TCNQ is similar to those of MAnh, SO_2, and especially *p*-chloranil,[14] which copolymerize alternatingly and sometimes spontaneously with a donor monomer such as St, but do not undergo homopolymerization. Interestingly TCNQ and *p*-chloranil have isostructures, polymerize via 1,6-polymerization, and have a powerful electron-accepting property similar in electron affinity (E_A = 1.37 and 1.7 eV for *p*-chloranil and TCNQ, respectively[15]).

Copolymerization behaviors of QM derivatives with chlorine substituents and St were summarized as follows: In the mixture of QM and St, QM polymerizes spontaneously to result in its homopolymer only.[5] Copolymerization of TCX can give copolymers containing both monomer units, but the St unit content of the copolymers obtained is much smaller than the conjugate TCX unit even if the St monomer feed is very high.[7] Copolymerization of HCX can give copolymers and the copolymer obtained in the high St monomer feed such as 92 mol % was found to be an alternating copolymer.[6] Finally when a mixture of PCX and St was heated at 60 °C with azobis(isobutyronitrile) as initiator, homopolymer of St was obtained.[16] An increase in the number of chlorine substituents of QM derivatives results in a decrease in reactivity, as mentioned in the introduction, and also an increase in cross propagation in their copolymerization of St except for PCX. This exception was considered to arise probably because PCX is extremely stable as reported by Ballester et al.[7] It should be noted, however, that TCNQ is much different from PCX with respect to their copolymerization behaviors with St. PCX was observed to be a weaker acceptor than TCNQ since the yellow color of PCX did not vary when PCX was mixed with St.[16] The difference in electron affinity between PCX and TCNQ was expected to be an important factor that affects their copolymerization behavior. It is suggested that the charge-transfer complex between TCNQ and St probably plays an important role in their alternating copolymerization.

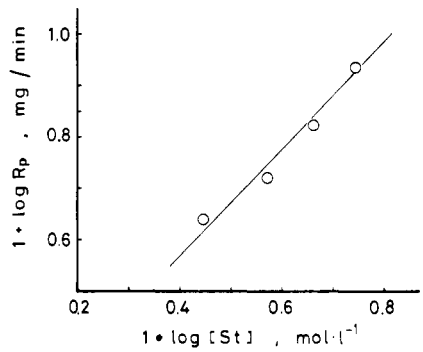

Figure 10. Log–log plot of the rate of the copolymerization vs. the concentration of styrene in the feed; 0.10 g of TCNQ and 10 mL of acetonitrile are used. The temperature of polymerization is 40 °C.

References and Notes

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