whereas in poly(M_2) (see Figure 4d), C^1 is split into three peaks (with upfield intensities in the ratio 1:1.3:1.8), showing the presence of isotactic, heterotactic, and syndiotactic triads in the chain.[20] However, the carbonyl carbon (C^1) is susceptible to tacticity and is distinctly split into two peaks (relative upfield intensities in the ratio of 1:1.6). In copoly(M_1–M_2) (Figure 4c), C^1 of the M_1 units splits into two peaks (with relative upfield intensities of 1.5:1), whereas C^1 of the M_2 units is split into four peaks (with relative intensities, upfield, of 1:1.2:3.3:1.7). Similarly, the carbonyl carbon in the same copolymer is split into three peaks (relative upfield intensities of 10.2:2:2.3:1). The additional splittings in copoly(M_1–M_2) over those observed in the respective homopolymers indicate the presence of unsymmetrical sequence triads in the copolymer chains. A detailed study of the sequence distribution of M_1 and M_2 in the copolymers will be reported in the future.

A set of upfield peaks with low intensity (around 15–35 ppm) and also downfield peaks (at 65.84, 72.54, and 130.77 ppm) in the spectra of poly(M_2) (Figure 4d) and copoly(M_1–M_2) (Figure 4c) seem to be due to the end groups that are attached to the low molecular weight polymer chains. For reasonably high molecular weight polystyrene ($\bar{M}_n \simeq$ 80 000), the ^{13}C spectrum does not show any peaks in these regions. However, it is rather difficult to identify the chemical nature of end groups purely by ^{13}C NMR because of their low concentration.

Acknowledgment. We gratefully acknowledge support for this work both from the Wolfson Foundation (award to Professor W. J. Albery and Dr. M. H. George, Chemistry Department, Imperial College, for the development of chemically modified electrodes) and from the Science and Engineering Research Council, England (Oxford-Imperial Energy Group). Thanks are also due to Dr. S. Holding, RAPRA, Shawbury, Shrewsbury, England, for carrying out the GPC measurements.

Registry No. 2,4,5-Trichlorophenyl acrylate, 40952-23-6; styrene, 100-42-5; 2,4,5-trichlorophenyl acrylate–styrene copolymer, 87555-24-6.

References and Notes

(1) Su, C.-P.; Morawetz, H. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 185.

(2) Batz, H. G.; Franzman, G. F.; Ringsdorf, H. *Makromol. Chem.* **1973**, *172*, 27.

(3) Polak, A.; Blumenfeld, H.; Wax, M.; Baughn, R. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6324.

(4) (a) Arshady, R.; Atherton, E.; Sheppard, R. C. *Tetrahedron Lett.* **1979**, 1521. Arshady, R.; Ugi, I. *Z. Naturforsch., B.* **1981**, *36B*, 1202. (b) Arshady, R.; Holy, N., to be published.

(5) Arshady, R. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 573.

(6) Arshady, R.; Ugi, I. *Angew Chem.* **1982**, *94*, 367. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 374. Arshady, R., to be published.

(7) Kelen, T.; Tudos, F. *J. Macromol. Sci., Chem.* **1975**, *A9* (1), 1.

(8) Ebdon, J. R.; Kandil, S. H.; Morgan, K. J. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2783. Mirabella, F. M.; Barrell, I. I. *J. Appl. Polym. Sci.* **1975**, *19*, 2131.

(9) Natansohn, A. *Br. Polym. J.* **1978**, *10*, 218 and references therein.

(10) Kotaka, T.; White, J. H. *Macromolecules* **1974**, *7*, 106.

(11) Chau, T. C.; Rudin, A. *Polymer* **1974**, *15*, 593. Spatorico, A. L. *J. Appl. Polym. Sci.* **1974**, *18*, 1793.

(12) Bevington, J. C.; Melville, H. W.; Taylor, R. P. *J. Polym. Sci., Polym. Chem. Ed.* **1954**, *12*, 449.

(13) Arshady, R. Research Report, University of Tabriz, 1977.

(14) For general reviews on (i) polymer–monomer and (ii) polymer–polymer interactions see: (i) Shapiro, A. *Pure Appl. Chem.* **1981**, 643. (ii) Challa, G.; Tan, Y. Y. *Ibid.* **1981**, 627.

(15) Teramachi, S.; Hasegawa, A.; Akatsuka, M.; Yamashita, A.; Takemoto, N. *Macromolecules* **1978**, *11* (6), 1206.

(16) Melville, H. W.; Noble, B.; Watson, W. F. *J. Polym. Sci.* **1949**, *4*, 629.

(17) Odian, G. "Principles of Polymerization"; McGraw-Hill: New York, 1970.

(18) North, A. M. "The Kinetics of Free Radical Polymerization"; Pergamon Press: Oxford, 1966.

(19) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience: New York, 1972; p 81.

(20) Inoue, Y.; Nishioka, A.; Chujo, R. *Makromol. Chem.* **1972**, *156*, 207. Shaefer, J. *Macromolecules* **1971**, *4*, 107.

Amphoteric Polymerization Behavior of 7,7,8,8-Tetrakis(ethoxycarbonyl)quinodimethane in Its Alternating Copolymerizations

Shouji Iwatsuki,* Takahito Itoh, and Isao Yokotani

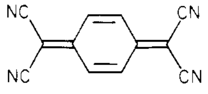
Faculty of Engineering, Department of Chemical Research for Resources, Mie University, Kamihama-cho, Tsu 514, Japan. *Received December 29, 1982*

ABSTRACT: The preparation and polymerization behavior of 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane (TECQ) were studied to confirm an amphoteric behavior in the charge-transfer complex formation and in the radical alternating copolymerization. Both of these amphoteric behaviors could be well explained in terms of the π-electron density scheme. TECQ was found to exhibit very poor homopolymerizability with radical, cationic, and anionic initiators relative to the moderate one for 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane.

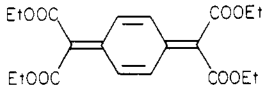
Several electron-accepting quinodimethane compounds, namely, 7,7,8,8-tetracyanoquinodimethane (TCNQ),[1,2] 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$),[3] 7,7,8,8-tetrakis(ethylsulfonyl)quinodimethane,[4] 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane (TMCQ),[5] 2,5,7,7,8,8-hexacyanoquinodimethane,[6] 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TNAP),[6] and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ),[7] have been studied in their alternating copolymerization as acceptor monomers and their initiation ability for the cationic polymerization of vinyl ethers. Especially noticeable is an amphoteric behavior of TMCQ in its alternating copolymerizations; it acts as an acceptor monomer toward a donor monomer such as styrene (St), a vinyl ether, and vinyl acetate, while it is a donor monomer toward the very powerful electron-accepting mo-

0024-9297/83/2216-1817$01.50/0

nomer TCNQ. No other compound has shown such a behavior.



TCNQ



TECQ

In this work were studied the preparation and polymerization behavior of 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane (TECQ) to confirm an amphoteric behavior in the charge-transfer complex formation and in the radical alternating copolymerization. Further, it was surprisingly found that TECQ does not homopolymerize with radical, cationic, and anionic initiators in spite of the moderate homopolymerizability of TMCQ with radical and anionic initiators.

Experimental Section

Preparation of *p*-Phenylenebis(diethyl malonate). *p*-Phenylenedimalononitrile[8] (4.20 g, 20.4 mmol) was refluxed with 250 mL of ethanol containing 1.7 g of water for 5.5 h during which a rapid stream of hydrogen chloride was passed through the solution. The resulting mixture was added to ice water to deposit a granular product, which was filtered, washed with water, and dried to give 6.93 g of the crude *p*-phenylenebis(diethyl malonate) (86.3%), which was then recrystallized from *n*-hexane to yield white needles: mp 68–70 °C; IR (KBr) 1725 (C=O) cm^{-1}; NMR (CDCl$_3$) δ 7.30 (4 H, s), 4.60 (2 H, s), 4.21 (8 H, q), 1.20 (12 H, t). Anal. Calcd for $C_{20}H_{26}O_8$: C, 60.89; H, 6.66. Found: C, 60.65; H, 6.91.

Preparation of TECQ. *p*-Phenylenebis(diethyl malonate) (2.0 g, 5.07 mmol) was added to 160 mL of an ethanol solution containing 1.01 g of potassium ethoxide at room temperature. After it was stirred under nitrogen for 1 h, the resulting mixture was placed under reduced pressure to remove volatile materials. The residue was covered with 80 mL of benzene, and a mixture of 1 mL of benzene and 0.81 g (5.06 mmol) of bromine was added dropwise with stirring under nitrogen. The mixture was filtered, and the filtrate was placed under reduced pressure to remove volatile materials. The yellow residue was recrystallized (twice) from *n*-hexane to give yellow needles of TECQ (1.03 g, 51.7%): mp 73.0–73.5 °C; IR (KBr) 1720 (C=O), 1580 (C=C) cm^{-1}; NMR (CDCl$_3$) δ 7.50 (4 H, s), 4.35 (8 H, q), 1.30 (12 H, t); UV (CHCl$_3$) 371 ($\epsilon = 5.03 \times 10^4$) nm. Anal. Calcd for $C_{20}H_{24}O_8$: C, 61.21; H, 6.18. Found: C, 61.76; H, 6.06.

Other Materials. TCNQ was prepared according to the procedure of Acker and Hertler[8] and purified by recrystallization from ethyl acetate and sublimation (twice) (mp 294–296 °C). Styrene (St), *n*-butyl vinyl ether (*n*BVE), isobutyl vinyl ether (*i*BVE), and vinyl acetate (VAc) were purified from commercial products by conventional methods.[10] Phenyl vinyl ether (PhVE) was prepared from phenol and dibromoethane according to the methods of McElvain and Pinzón[11] and Fueno et al.[12] 2-Chloroethyl vinyl ether (CEVE) was prepared from the dehydrochlorination of β,β'-dichloroethyl ether.[13] Monomer purity was checked by gas chromatography (purity >99.6%). α,α'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Acetonitrile was refluxed over phosphorus pentoxide and then distilled at 81.7 °C. Benzene was washed with concentrated sulfuric acid and water, dried over calcium chloride, refluxed over sodium metal, and distilled at 80.0 °C. Guaranteed reagent grade boron trifluoride etherate was used without further purification. *n*-Butyllithium solution was prepared from the reaction of *n*-butyl bromide and lithium metal in benzene.[10]

Charge-Transfer Complexation of TECQ with St or TCNQ. Absorption spectra of the charge-transfer transition for the TECQ–St and TECQ–TCNQ systems were taken in benzene and acetonitrile, respectively, at room temperature. The concentrations of solutions employed were as follows: [TECQ] = 1.02 × 10^{-2} mol/L and [St] = 0.94 mol/L for the TECQ–St system and [TECQ] = 2.01 × 10^{-2} mol/L and [TCNQ] = 1.85 × 10^{-3} mol/L for the TECQ–TCNQ system.

Determination of the equilibrium constant, K_{CT}, and the molar absorption coefficient, ϵ_{CT}, for the charge-transfer complex of the TECQ–St system in benzene was carried out at 20 and 30 °C according to the Benesi–Hildebrand equation.[14] The wavelength at which the absorbance was measured was 440 nm. Since the spectrum was found to vary slowly with time, absorbance was measured just 2 min after the TECQ and St solutions were mixed.

Polymerization Procedure. For homopolymerization using AIBN as an initiator, 50 mg of TECQ, 10 mL of benzene, and 1 mg of AIBN were placed in an ampule, which was degassed completely by the freeze–thaw method (repeatedly three times) and sealed. The ampule was set in a bath thermostated at 60 °C for 48 h. For the case of *n*-butyllithium or boron trifluoride etherate, 50 mg of TECQ and 10 mL of benzene were placed in a flask kept at 5 °C. To the mixture was added three drops of the initiator solution (1 mol/L) in benzene by syringe under nitrogen, and the solution was stirred for half an hour. The reaction mixtures were poured into a large excess of *n*-hexane, and no precipitate was obtained. Then the mixtures were placed under reduced pressure to remove the volatile materials, and the yellow crystalline materials obtained were found to be TECQ.

For copolymerization, given amounts of TECQ and St, 5 mL of benzene, and 1 mg of AIBN were placed in an ampule, which was degassed completely by the freeze–thaw method (repeatedly three times) and sealed. No initiator was added for the TECQ–vinyloxy compound and the TECQ–TCNQ systems. For the TECQ–TCNQ system 10 mL of acetonitrile was used as solvent instead of benzene. The ampule was set in a bath thermostated at 60 °C for the time of polymerization and opened. The reaction mixture was poured into excess methanol to precipitate the copolymer. For purification, the copolymers for the TECQ–St and TECQ–vinyloxy compound systems were dissolved in a small amount of chloroform again, and the resulting solutions were poured into excess methanol to precipitate the copolymers, which were dried under reduced pressure. The copolymer for the TECQ–TCNQ system was washed repeatedly with acetonitrile because it was insoluble in common organic solvents and dried under reduced pressure.

For the terpolymerization of the TECQ–TCNQ–St system, given amounts of the monomers, 50 mL of acetonitrile as a solvent, and 2 mg of AIBN were placed in an ampule. For the case of the TECQ–TMCQ–St system, 5 mL of benzene was used as a solvent instead of acetonitrile. The rest of the procedure was similar to the above-mentioned copolymerization case for the TECQ–St system.

Polymer Characterization. Polymer composition was established by elemental analysis. In the determination of the composition of the terpolymer of TECQ, TCNQ, and St, the TCNQ unit content was calculated from the nitrogen content. The contents of the TECQ and St units were calculated from the remaining carbon and hydrogen contents obtained by subtracting the above TCNQ unit content from the total terpolymer amounts. Because the difference in the carbon content between the TECQ and TMCQ units is as small as 4%, the composition of the terpolymer of TECQ, TMCQ, and St was determined not by elemental analysis but by ^{1}H NMR spectrometry using the ratio of the peak area of the methyl protons due to the TECQ unit to the sum of those of the methylene protons due to the TECQ unit, the methoxy protons due to the TMCQ unit, and the methine and methylene protons due to the St unit, on assumption that the terpolymer should contain 50 mol % of the St unit because both the TECQ–St and TMCQ–St systems are alternatingly copolymerizable.

Solution viscosity was determined at 30 °C in chloroform for the copolymer of TECQ with St and the terpolymer of TECQ, TMCQ, and St and in benzene for the copolymers of TECQ with vinyloxy compounds and at 40 °C in concentrated sulfuric acid for the copolymer of TECQ with TCNQ and the terpolymer of TECQ, TCNQ, and St.

^{1}H NMR measurements was carried out in chloroform-*d* for the copolymer of TECQ with St and the terpolymer of TECQ, TMCQ, and St with tetramethylsilane as an internal standard.

Instruments for Measurement. Instruments for ^{1}H NMR and UV–vis spectral determination were a JEOL JNM-PMX 60 and a Hitachi Perkin-Elmer Model 139 and Shimadzu Model UV-200, respectively. A Yanagimoto CHN Corder Model MT-2 was used for elemental analysis.

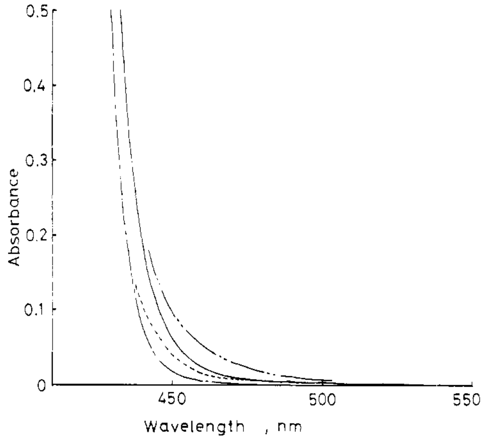


Figure 1. UV–vis spectra of a mixture of TECQ with St in benzene: (—) spectrum of a mixture of TECQ with St; (– – –) spectrum of TECQ; (- - -) difference spectrum between the above two spectra, corresponding to that of the complex. (– - –) Difference spectrum between TMCQ and a mixture of TMCQ with St. Concentrations of solutions employed are [TECQ] = 1.02 × 10^{-2} mol/L and [St] = 0.94 mol/L for the TECQ–St system and [TMCQ] = 8.05 × 10^{-3} mol/L and [St] = 0.90 mol/L for the TMCQ–St system.

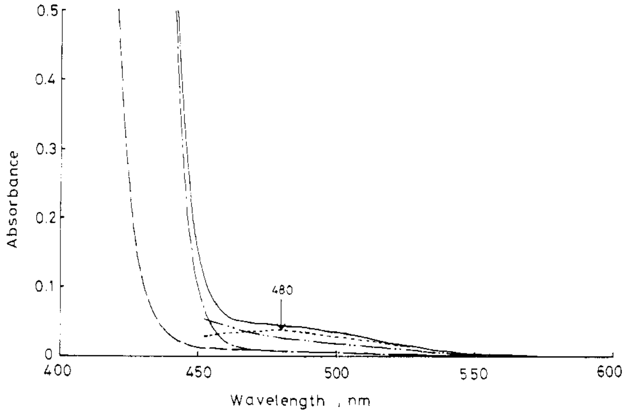


Figure 2. UV–vis spectrum of a mixture of TECQ with TCNQ in acetonitrile: (—) spectrum of a mixture of TECQ with TCNQ; (– – –) spectrum of TCNQ; (— — —) spectrum of TECQ; (- - -) difference spectrum, corresponding to that of the complex. (– - – -) Difference spectrum for the TMCQ–TCNQ system. Concentrations of solutions employed are [TECQ] = 2.01 × 10^{-2} mol/L and [TCNQ] = 1.85 × 10^{-3} mol/L for the TECQ–TCNQ system and [TMCQ] = 2.02 × 10^{-2} mol/L and [TCNQ] = 1.81 × 10^{-3} mol/L for the TMCQ–TCNQ system.

Results and Discussion

Charge-Transfer Absorption Band. Addition of St to TECQ in benzene caused the yellow color of the TECQ solution to deepen as shown in Figure 1, where the difference spectrum between the mixture and TECQ shows a broad absorption band in the range 440–500 nm, corresponding to the charge-transfer transition between TECQ and St. St does not absorb any light at wavelengths longer than 400 nm. The corresponding absorption band between TMCQ and St exists in the range 440–510 nm as shown in Figure 1. From comparison of both absorption bands it may be said that TECQ is a weaker electron acceptor than TMCQ.

The Benesi–Hildebrand plots at 20 °C for the TECQ–St system showed a straight line, indicating that the complex is composed of equimolar amounts of donor and acceptor components. The K_{CT} value at 20 °C for the complex formation of the TECQ–St system was found to be 0.141, and ϵ_{CT} was 88. The K_{CT} value at 20 °C for the TMCQ–St system[5] was reported previously to be 0.121, and ϵ_{CT} was 56. The magnitude of the K_{CT} values for the TECQ–St and TMCQ–St systems are similar and less than unity, corresponding well with the K_{CT} values for many spontaneous alternating copolymerizable quinodimethane compound–St systems, e.g., the TCNQ–St,[1] TCNQF$_4$–St,[3] TNAP–St,[6] DDQ–St,[7] and *p*-chloranil–St systems.[15]

The charge-transfer transition spectrum between TECQ and TCNQ is shown in Figure 2, where the difference spectrum between the mixture and the components reveals a broad absorption band in the range 450–550 nm with a maximum at 480 nm. On the other hand, the corresponding spectrum between TMCQ and TCNQ shows the broad absorption band in the same wavelength range not as a peak form but as an increase in absorption of TCNQ, as shown additionally in Figure 2. It can be presumed therefore that TECQ as well as TMCQ interacts as a donor compound with TCNQ and that TECQ is more electron donating toward TCNQ than TMCQ.

Consequently, it can be pointed out that both TECQ and TMCQ exhibit an amphoteric polar character in their charge-transfer complex formations. Furthermore, their amphoteric polar character may be well explained in terms of the following π-electron density scheme: the highest π-electron density is assigned to St, a medium one to TECQ and TMCQ, for which that for TECQ is a little higher than that for TMCQ, and a much lower one to TCNQ. There should exist a sufficiently great difference in electron density for charge-transfer complexation between St and TECQ or TMCQ as well as between TMCQ or TECQ and TCNQ. Moreover, it is understandable on the basis of the scheme that TECQ is a weaker acceptor compound than TMCQ while TECQ is a stronger donor compound than TMCQ.

Determination of K_{CT} and ϵ_{CT} in the charge-transfer complex formation in acetonitrile for the TMCQ–TCNQ system ([TMCQ] = 2 × 10^{-2} to 7 × 10^{-2} mol/L and [TCNQ] = 1 × 10^{-3} mol/L) and for the TECQ–TCNQ system ([TECQ] = 3 × 10^{-2} to 5 × 10^{-2} mol/L and [TCNQ] = 1 × 10^{-3} mol/L) was attempted at 15.5 °C according to both the Benesi–Hildebrand and Scott equations. However, for the TMCQ–TCNQ system, the solution became turbid immediately, probably due to a rapid homopolymerization of TMCQ at so high a concentration as 2 × 10^{-2} mol/L, and, for the TECQ–TCNQ system, both the Benesi–Hildebrand and Scott plots gave a negative value of $1/\epsilon_{CT}$, implying a contact type of charge-transfer complex. Therefore, K_{CT} and ϵ_{CT} could not be determined for both systems.

Homopolymerization of TECQ. Homopolymerization of TECQ was attempted in benzene with an initiator such as AIBN, *n*-butyllithium, and boron trifluoride etherate. The reaction was carried out for 48 h at 60 °C in the case of AIBN and for 0.5 h at 5 °C in the cases of *n*-butyllithium and boron trifluoride etherate. In all cases unreacted TECQ was recovered in an almost quantitative amount, indicating that TECQ is not homopolymerizable under these experimental conditions. However, when TECQ was kept in the crystal state for 1 month at room temperature, a small amount of white powder product insoluble in benzene was formed. Its molecular weight was determined by vapor pressure osmometry in chloroform to be 2600 ($\overline{DP}$ = 6.6). This fact implies that TECQ is almost not homopolymerizable but somewhat oligomerizable in its crystal state. On the other hand, it was reported by Acker and Hertler[8] and Hall and Bentley[9] that TMCQ homopolymerizes easily on heating and in the presence of light, AIBN, and *n*-butyllithium. The great difference in the homopolymerizability between TECQ and TMCQ is particularly surprising in view of the steric effect of the ethyl

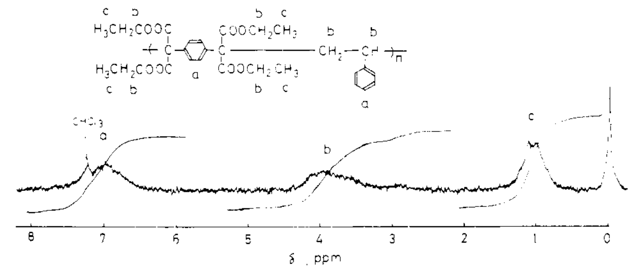


Figure 3. ^{1}H NMR spectrum of the copolymer between TECQ and St in chloroform-*d*.

and methyl groups because of the small difference in the steric effect parameters of the methyl (Taft's steric substituent constant, $E_s = 0.00$)[16] and the ethyl ($E_s = -0.07$)[16] groups, presumably arising from the specific structure of the tetrakis(alkoxycarbonyl)quinodimethane compound.

Copolymerization of TECQ with St or TCNQ. Table I summarizes the results of the copolymerization of TECQ with St or TCNQ. The copolymer of the TECQ–St system was obtained as a white powder soluble in chloroform, acetone, and benzene and insoluble in methanol and *n*-hexane. The copolymer of the TECQ–TCNQ system was obtained as pale pink powder, insoluble in common organic solvents and only soluble in concentrated sulfuric acid. The copolymers for both systems were found to have fixed values in elemental analysis regardless of monomer feed ratio, respectively. The found values are in good agreement with the calculated ones for the copolymers composed of equimolar amounts of both component monomers. The ^{1}H NMR spectrum of the copolymer of TECQ with St is shown in Figure 3, where absorption bands in the 7-ppm region were assigned to the phenyl protons of the St monomer unit and the phenylene protons of the TECQ monomer unit, ones in the 4-ppm region to the methine and methylene protons of the St monomer unit and the methylene protons of the ethyl group of the TECQ monomer unit, and ones in the 1-ppm region to the methyl protons of the ethyl group of the TECQ monomer unit. The methine and methylene protons of the St monomer unit of the copolymer appear in the 4-ppm region, being much more subject to deshielding than the corresponding ones of homopolystyrene, generally appearing in the 1–2-ppm region.[17] It is conceivable that the deshielding arises from a powerful electron withdrawal by the neighboring bis(ethoxycarbonyl)methylene group when the St monomer unit is sandwiched between TECQ monomer units in the copolymer. It can be concluded, therefore, that the copolymer of TECQ with St is really alternating and that TECQ copolymerizes with St alternatingly and spontaneously as well as electron-accepting quinodimethane and quinone compounds as reported previously.[1,3-7]

In the IR spectrum of the copolymer of TECQ and TCNQ, absorptions at 2240 and 1740 cm^{-1} were assigned to the nitrile group and the ester-carbonyl group, respectively, indicating the incorporation of both TCNQ and TECQ monomer units into the copolymer. In the elemental analysis of the copolymers, fixed found values were obtained regardless of the monomer feed ratio, corresponding well with the calculated values for the copolymer composed of equimolar amounts of TECQ and TCNQ. Moreover, although neither TECQ nor TCNQ is homopolymerizable under the experimental conditions, the copolymer with solution viscosity 0.1–0.4 dL/g could be obtained without any initiator. It can be concluded, therefore, that TECQ is alternatingly and spontaneously copolymerizable with TCNQ and that TECQ reacts as a

Table I

Copolymerization of TECQ with St in Benzene at 60 °C[a] and Copolymerization of TECQ with TCNQ in Acetonitrile at 60 °C[b]

run no.	monomer feed, mg		amt of TECQ, mol %	time, h	polym yield, mg	convrsn, %	anal.			copolym comp, mol % of TECQ	η_{sp}/C, dL·g^{-1}
	TECQ	comonomer (St or TCNQ)					% H	% C	% N		
					Copolymerization with St						
1	51.0	51.1	21.0	20	33.2	32.6	5.04	68.90		44.6	0.25[c]
2	92.2	240.8	9.2	4.75	92.2	27.7	6.39	67.22		52.5	0.60[c]
3	98.4	51.0	33.9	6	26.7	17.9	6.34	68.90		44.6	0.38[c]
4	197.8	52.8	49.9	10	39.5	15.8	6.42	67.39		51.7	0.23[c]
5	251.1	44.9	59.8	11.1	42.0	14.2	6.51	67.80		49.6	0.25[c]
6	400.2	34.2	75.7	12.5	68.2	15.7	6.43	66.80		54.7	0.12[c]
7	85.6	97.4	18.9	5	55.4	30.3	6.22	67.55		50.2	
					Copolymerization with TCNQ						
8	100.4	150.7	25.8	0.4	13.7	5.5	4.31	65.13	9.38	50.0	0.46[d]
9	149.6	77.8	50.0	0.5	29.9	13.2	4.75	64.57	9.26	50.5	0.12[d]
10	251.3	41.7	75.8	0.4	34.6	11.8	4.51	65.09	9.14	50.9	0.47[d]

[a] Solvent, 5 mL; AIBN, 1 mg. [b] Solvent, 10 mL; without initiator. [c] Chloroform solvent; $t = 30$ °C, $C = 0.1$–0.2 g/dL. [d] Concentrated H_2SO_4 solvent. $t = 40$ °C, $C = 0.1$–0.2 g/dL.

Table II
Copolymerization of TECQ with Vinyloxy Compounds in Benzene at 60 °C[a]

monomer feed, mg		amt of TECQ, mol %	time, h	polym yield, mg	convrsn, %	anal.		copolym comp, mol % of TECQ	η_{sp}/C,[b] dL·g^{-1}
TECQ	comonomer					% H	% C		
100.7	*i*BVE, 409.9	5.9	65.5	69.4	13.6	6.92	63.15	53.5	0.11
100.2	*n*BVE, 418.0	5.8	65.5	54.8	10.6	7.44	63.45	49.0	0.07
103.9	CEVE, 418.0	6.3	62.1	60.1	11.5	6.39	57.34	46.3	0.18
102.7	PhVE, 405.4	7.2	48.2	78.7	15.5	6.50	65.52	50.6	0.24
101.6	VAc, 406.6	5.2	64.5	32.0	6.3	6.30	59.97	42.6	0.03

[a] Solvent, 2 mL; without initiator. [b] Benzene solvent. t = 30 °C, C = 0.11-0.37 g/dL.

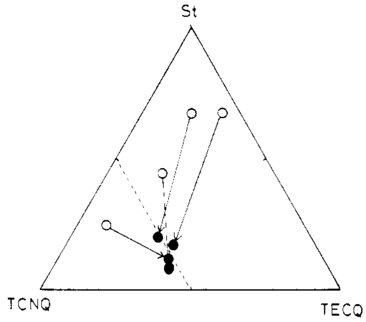


Figure 4. Triangular composition diagram of the terpolymerization of TECQ, TCNQ, and St: (○) feed composition; (●) terpolymer composition. Arrows show change in composition from the feed to the terpolymer obtained.

donor monomer toward TCNQ. Accordingly, it was well confirmed that TECQ can copolymerize in an amphoteric fashion in its alternating copolymerizations as well as TMCQ.

Copolymerization of TECQ with Vinyloxy Compounds. Table II summarizes the results of the copolymerizations of TECQ with *i*BVE, *n*BVE, CEVE, PhVE, and VAc. The products were obtained as white powders soluble in benzene and chloroform and insoluble in methanol and *n*-hexane. It is evident from their copolymer composition data that the copolymers are composed of equimolar amounts of TECQ and donor comonomers, indicating alternating copolymers of TECQ with vinyloxy compounds and that TECQ could not initiate cationic polymerization of the vinyloxy compounds in benzene, similarly to TMCQ.

Terpolymerizations of the TECQ–TCNQ–St and TECQ–TMCQ–St Systems. Table III summarizes the results of the terpolymerization of the TECQ–TCNQ–St system. Compositions of the monomer feed and the terpolymer obtained are shown as open and closed circles, respectively, in the triangular composition diagram of Figure 4. All terpolymers obtained always contain about 50 mol % of the TCNQ monomer unit regardless of the monomer feed ratio, and the sum of the TECQ and St monomer unit contents is 50 mol %, indicating that both TECQ and St copolymerize as donor monomers with TCNQ as a strong acceptor monomer. This terpolymerization behavior is similar to that of the TMCQ–TCNQ–St system reported previously.[5] The terpolymerization composition relationship is illustrated as a binary copolymerization between TECQ and St in Figure 5, containing additionally the corresponding composition diagram between TMCQ and St for the terpolymerization of the TMCQ–TCNQ–St system. According to the complex mechanism treatment,[18] the apparent monomer re-

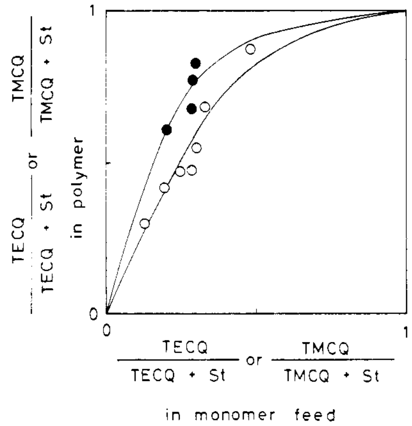


Figure 5. Composition diagrams of the terpolymerizations of TECQ, TCNQ, and St as the binary copolymerization between TECQ and St and of TMCQ, TCNQ, and St as the binary copolymerization between TMCQ and St. The line is calculated by using $r_1(K_1/K_2)$ = 15 ± 10 and $r_2(K_2/K_1)$ = 0.5 ± 0.3 for the terpolymerization of the TECQ–TCNQ–St system (●) and is calculated by using $r_1(K_1/K_2)$ = 7 ± 3 and $r_2(K_2/K_1)$ = 0.7 ± 0.3 for the terpolymerization of the TMCQ–TCNQ–St system (○).

activity ratios of the complexes were calculated to be $r_1(K_1/K_2)$(TECQ–TCNQ complex) = 15 ± 10 and $r_2(K_2/K_1)$(St–TCNQ complex) = 0.5 ± 0.3 for the TECQ–TCNQ–St system and to be $r_1(K_1/K_2)$(TMCQ–TCNQ complex) = 7 ± 3 and $r_2(K_2/K_1)$(St–TCNQ complex) = 0.7 ± 0.3 for the TMCQ–TCNQ–St system.[19] The relative reactivity of the complexes can be compared on the basis of the reciprocal of the monomer reactivity toward the polymer radical with a given terminal complex unit. The relative reactivity of the TMCQ–TCNQ and TECQ–TCNQ complexes toward the polymer radical with the St–TCNQ complex unit was obtained as St–TCNQ complex (1) < TMCQ–TCNQ complex (1.4) < TECQ–TCNQ complex (2.0). Thus, it can be pointed out that the TECQ–TCNQ complex is more reactive than the TMCQ–TCNQ complex and that this reactivity order as donor monomers between TECQ and TMCQ coincides with their electron-donating character order toward TCNQ.

Two terpolymerization experiments of the TECQ–TMCQ–St system with monomer feed ratios (mol) of TECQ/TMCQ/St = 14.2/14.9/70.9 and 11.2/36.4/52.4 were carried out at 60 °C for 3 and 2.5 h, respectively. The former yielded 29.0 mg of terpolymer (conversion 11.5% and η_{sp}/C = 0.30 dL/g) with composition ratio (mol) TECQ/TMCQ/St = 22.6/27.4/50.0 and the latter yielded 24.0 mg of terpolymer (conversion 7.6% and η_{sp}/C = 0.38 dL/g) with composition ratio (mol) TECQ/TMCQ/St = 10.2/39.8/50.0; in both cases the St unit content were held constant at 50%. The terpolymers obtained were white

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

run no.	monomer feed, mg			mol % of monomer			time, min	polym yield, mg	convrsn, %	anal.			terpolymer comp, mol %			η_{sp}/C,[b] dL·g^{-1}
	TECQ	St	TCNQ	TECQ	St	TCNQ				% H	% C	% N	TECQ	St	TCNQ	
1	314.0	210.1	40.7	26.5	66.9	6.6	45	31.6	5.6	4.49	66.81	10.03	17.2	36.9	45.9	
2	194.5	205.8	101.4	16.7	66.6	16.7	80	113.0	22.5	4.50	67.85	11.95	29.6	19.1	51.3	
3	227.4	141.5	237.4	18.7	43.8	37.5	45	78.0	13.0	4.77	65.92	10.90	29.3	8.2	52.5	0.21
4	115.2	75.2	403.0	9.8	24.1	66.0	55	47.2	8.0	4.72	66.29	10.98	37.4	10.9	51.7	0.12

[a] 50 mL, 2 mg of AIBN. [b] Concentrated H_2SO_4 solvent. t = 40 °C, C = 0.1–0.2 g/dL.

powders soluble in benzene, chloroform, and acetone and insoluble in methanol and *n*-hexane. Comparison of the ratios (TECQ/TMCQ = 0.49/0.51 and 0.24/0.76) of the TECQ and TMCQ contents in the monomer feeds with those (TECQ/TMCQ = 0.45/0.55 and 0.20/0.80) of the TECQ and TMCQ unit contents in the terpolymers allowed us to suppose that TMCQ is somewhat more reactive than TECQ in its alternating copolymerization with St. In other words, the TMCQ–St complex is more reactive than the TECQ–St complex in the complex mechanism treatment of alternating copolymerization. In any case, it can be pointed out that this reactivity order, TMCQ > TECQ, as acceptor monomer in the alternating copolymerizations with St is in good agreement with the electron-accepting character order of TMCQ and TECQ toward St.

Although TECQ is just a homologue of TMCQ, it is certain that TECQ is the second monomer with amphoteric behavior in alternating copolymerization as well as in the charge-transfer complex formation. Furthermore, slight but definite differences are found to exist in the amphoteric behaviors of these homologues. These differences can be explained consistently in terms of a π-electron density scheme. Gaps in π-electron density between the homologues and donor monomer such as St or acceptor monomer such as TCNQ are considered to be great enough to give rise to charge-transfer complex formation and alternating copolymerization. When the magnitudes of the gaps are determined in detail by means of the π-electron density scheme, it can be pointed out that the magnitudes are in good agreement with the absorption wavelength of the charge-transfer transition and the reactivity in the alternating copolymerization, indicating a significant effect of the gap in the π-electron density between donor and acceptor monomers on their charge-transfer complex formation as well as their alternating copolymerization. Moreover, it is noteworthy that there is found to be a sharp contrast in homopolymerization behavior between TECQ and TMCQ.

As substitutents, the ethyl and methyl groups are regarded as almost the same in their inductive and steric influences on the basis of their values of Hammett and Taft substituent constants. Therefore, it is presumable that the specific strcture of tetrakis(alkoxycarbonyl)quinodimethane or quinodimethane compounds would amplify the slight difference between ethyl and methyl groups to cause those observed differences.

Registry No. TECQ, 87532-18-1; TMCQ, 65649-20-9; TCNQ, 1518-16-7; styrene, 100-42-5; isobutyl vinyl ether, 109-53-5; butyl vinyl ether, 111-34-2; 2-chloroethyl vinyl ether, 110-75-8; phenyl vinyl ether, 766-94-9; vinyl acetate, 108-05-4; tetraethyl *p*-phenylenedimalonate, 79815-73-9.

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. *Macromolecules* **1982**, *15*, 347.
(4) Iwatsuki, S.; Itoh, T.; Shimizu, Y. *Macromolecules* **1983**, *16*, 532.
(5) Iwatsuki, S.; Itoh, T. *Macromolecules* **1980**, *13*, 983.
(6) Iwatsuki, S.; Itoh, T.; Saito, H.; Okada, J. *Macromolecules* **1983**, *16*, 1571.
(7) Iwatsuki, S.; Itoh, T. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2971.
(8) Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370.
(9) Hall, H. K., Jr.; Bentley J. H. *Polym. Bull.* **1980**, *3*, 203.
(10) Otsu, T.; Kinoshita, M. "Experimental Methods of Polymer Synthesis"; Kagakudojin: Kyoto, 1972; Chapter 3.
(11) McElvain, M.; Pinzōn, B. F. *J. Am. Chem. Soc.* **1945**, *67*, 650.
(12) Fueno, T.; Matsumura, I.; Okuyama, T.; Furukawa, J. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 818.

(13) Cretcher, L. H.; Koch, J. A.; Pittenger, W. H. *J. Am. Chem. Soc.* **1926**, *47*, 1173.
(14) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.
(15) Iwatsuki, S.; Itoh, T.; Hiraiwa, A. *Makromol. Chem.* **1981**, *182*, 2161.
(16) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; p 153.
(17) Bovey, F. A.; Tiers, G. V. D.; Filipovich, G. *J. Polym. Sci.* **1959**, *38*, 73.
(18) Iwatsuki, S.; Yamashita, Y. *Makromol. Chem.* **1967**, *104*, 263.
(19) Calculated on the data in ref 5.

Desolvation Effects in the Esterolysis Catalyzed by Imidazole-Containing Polymers

Hiromi Kitano, Zong-Hua Sun,† and Norio Ise*

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.
Received November 19, 1982

ABSTRACT: Catalytic effects of poly(acrylic acid-*co*-*N*-acryloylhistamine) (His-AA) or a terpolymer of acrylic acid, *N*-acryloylhistamine, and *N*-acryloyl-*n*-hexylamine (C_6-His-AA) on the hydrolyses of *p*-nitrophenyl acetate (PNPA) or *N*-carbobenzoxy-L-phenylalanine *p*-nitrophenyl ester (Z-Phe-ONP) are examined at various temperatures and pressures. In the hydrolysis of PNPA, all catalysts accelerate the reaction linearly with their concentration, whereas in the hydrolysis of Z-Phe-ONP catalyzed by C_6-His-AA, a saturation phenomenon is observed because of a complexation process like enzyme catalysis due to the hydrophobic interaction between the substrate and the catalyst. By double-reciprocal plots, both the reaction rate and dissociation constant of the substrate–catalyst complex are determined. Comparison of thermodynamic parameters such as $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta V^{\ddagger}$, ΔH, ΔS, and ΔV of these polymeric reaction systems with those of imidazole-catalyzed ones shows an increase in $\Delta V^{\ddagger}$ and a decrease in $\Delta S^{\ddagger}$, which suggest the important role of the desolvation effect and the restricted conformation effect of the ionic polymer catalyst, respectively.

Introduction

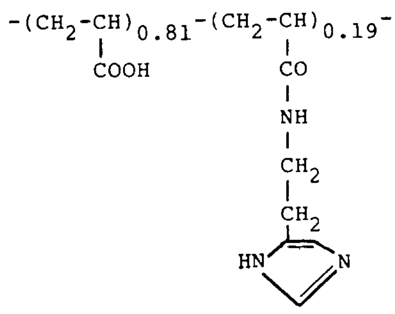
Polyelectrolytes have been paid keen attention as effective catalysts like enzymes.[1,2] Among the many factors that contribute to enzyme catalyses, solvation and/or desolvation effects of substrate and/or transition state have been pointed out to be quite important.[3,4] In various kinds of polyelectrolyte-catalyzed reactions such as cyanoethylation of an amino acid,[5] induced aquation of metal-ion complexes,[6] and alkaline hydrolyses of phenyl esters,[7] we have also pointed out the importance of the solvation–desolvation effect.[8] The polyelectrolytes we examined are so-called "domain catalysts", which carry out catalyses by providing reaction sites in the vicinity of their molecules with the help of hydrophobic and/or electrostatic interactions between substrates and catalysts. However, there have been very few studies concerning the solvation–desolvation effect in the catalyses by polyelectrolytes that have catalytically active sites in their molecules.[9]

In this paper, we examine desolvation effects in the ester hydrolysis catalyzed by imidazole-containing polymers, the catalytic activities of which have been extensively studied by many researchers.[1,2]

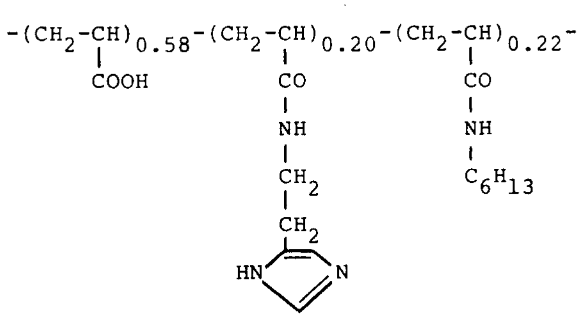
Experimental Section

Chart I
Chemical Structures of Catalysts

His-AA



C_6-His-AA



Materials. *p*-Nitrophenyl acetate (PNPA) (Tokyo Kasei Co., Tokyo) is recrystallized twice from chloroform. *N*-Carbobenzoxy-L-phenylalanine *p*-nitrophenyl ester (Z-Phe-ONP) from Sigma is used without further purification. A water-soluble carbodiimide, 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide hydrochloride (EDC), is obtained from Nakarai Chemicals, Kyoto, Japan. Poly(acrylic acid) solution (25%, 8000–12000 cP at 30 °C, Wako Pure Chemicals, Osaka, Japan) is dialyzed for a week against water, which is purified by deionization and distillation. The other reagents are commercially available and are used without further purification.

Polymer Catalysts. His-AA. To 40 mL of poly(acrylic acid) solution (0.23 equiv·L^{-1}) are added 2.0 g (10.4 mmol) of EDC and 0.20 g (1.8 mmol) of histamine, and the pH of the solution is kept at 4.5 for 1 h at room temperature.[10] The mixed solution is continuously stirred for 2 days. Then the pH of the solution is raised to 12 by addition of 1 N NaOH solution in order to hydrolyze the acylated imidazole ring of histamine,[11] and the solution

---

† Present address: Chengdu Institute of Organic Chemistry, Chinese Academy of Science, Chengdu, China.

0024-9297/83/2216-1823$01.50/0