Polymerizations of 7,7,8,8-Tetracyanoquinodimethane with Electron-Rich Olefins

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Introduction

The interesting electron-poor molecule 7,7,8,8-tetracyanoquinodimethane, TCNQ, was originally of interest in connection with electrically conducting salts.[1] Its application to polymer chemistry originated with Stille and co-workers, who showed that TCNQ initiated the cationic homopolymerization of vinyl ethers.[2] This work was greatly extended by Iwatsuki, Itoh, and their colleagues, who confirmed that certain vinyl ethers homopolymerized cationically when exposed to TCNQ, while other less electron-rich vinyl ethers underwent free-radical copolymerization with TCNQ to give 1:1 alternating copolymers.[3,4] Styrenes were also shown to copolymerize alternatingly with TCNQ. These polymerizations and those of a wide variety of other quinodimethane derivatives have recently been reviewed.[3,4] We have also proposed a mechanism for the initiation of these spontaneous polymerizations involving *p*-phenylenetetramethylene intermediates, which can be zwitterionic or diradical depending on the nature of the substituents.[5]

The purpose of this paper is to explore the polymerization of TCNQ with other electron-rich olefins, including 1,3-dienes. Specific questions addressed will be whether polymerization occurs, whether it is cationic homopolymerization or free-radical copolymerization, and whether the reactions occur spontaneously.

Results

Polymerizations. Reactions were carried out by using equimolar concentrations of TCNQ and the electron-rich olefin in acetonitrile at 60 °C. If no spontaneous thermal reaction occurred, AIBN initiator was added. The following olefins were used: α-methylstyrene, 1,1-diphenylethylene, *cis*- and *trans*-stilbene, acenaphthene, phenanthrene, 2,3-dihydrofuran, benzofuran, and *N*-vinylpyrrolidinone. The dienes included isoprene, 2,3-dimethylbutadiene, 1,3-cyclooctadiene, 1-methoxy-1,3-butadiene, 1,3-cyclohexadiene, and 2,5-norbornadiene. Table I lists the donor olefins and dienes, whose reaction with TCNQ resulted in polymer formation, either spontaneous or with initiator.

Electron-Rich Monoolefins. Spontaneous Reactions. α-Methylstyrene (α-MeSt) with TCNQ gave an 88% yield of alternating copolymer (MW 9200), and 1,1-diphenylethylene (DPhE) gave a 32% yield of oligomers (MW 730). Acenaphthene (AcNa) gave a 70% yield of alternating copolymer (η_{inh} 0.58 dL/g).

trans-Stilbene (trSt) and phenanthrene (Phen) gave isolable CT (charge-transfer) complexes in essentially quantitative yields and no polymer. *cis*-Stilbene (cisSt) with TCNQ gave no isolable products. 2,3-Dihydrofuran (DHF) and benzofuran (BF) did not react, while *N*-vinylpyrrolidinone (NVP) gave only a 2.5% yield of alternating copolymer.

Electron-Rich Monoolefins. Free-Radical-Initiated Reactions. Generally, the use of AIBN initiator did not change the outcome significantly but did raise the yield of copolymer of NVP with TCNQ to 8%.

Dienes. Spontaneous Reactions. Isoprene (IP) gave a 78% yield of alternating copolymer (η_{inh} 0.11 dL/g), and 2,3-dimethylbutadiene (DMBD) gave a 60% yield (η_{inh} 0.24 dL/g). 1,3-Cyclooctadiene (COD) gave a 40% yield of alternating copolymer (MW 4600). The more electron-rich 1-methoxy-1,3-butadiene (MeOBD) gives an 80% yield of alternating oligomer (MW 550).

1,3-Cyclohexadiene (CHD) and the formally nonconjugated norbornadiene (NBD) gave no products in the presence of TCNQ.

Dienes. Free-Radical-Initiated Reactions. Again, use of AIBN did not change the results significantly except for NBD. Here the use of AIBN gave a 20% yield of a low MW alternating copolymer (η_{inh} 0.05 dL/g).

Charge-Transfer Complexation. Such complexation was examined by mixing the electron-rich monomers with TCNQ in acetonitrile solution. Crystalline complexes formed in several cases. *trans*-Stilbene and phenanthrene with TCNQ gave the complex as purple needles. Ultraviolet spectra of the acetonitrile solutions were taken to determine the λ_{max} for the CT complexes. The results are collected in Table II with the polymerization results for comparison. The donor olefins and dienes are qualitatively listed in order of decreasing donor ability.

Discussion

We have extended the list of electron-rich vinyl monomers that can copolymerize with TCNQ. In general, it appeared that conjugated monomers with extensive resonance stabilization gave the best results. 1,3-Dienes gave good yields of alternating copolymers, as did α-methylstyrene and 1,1-diphenylethylene. As mentioned, styrene is already known to copolymerize readily in alternating fashion with TCNQ.

Steric problems were encountered as expected with bulky electron-rich monomers. *cis* and *trans*-stilbenes did not copolymerize. Of this group, only acenaphthene copolymerized by virtue of its minimal steric requirements. Polar factors were less important. The highly electron-rich *N*-vinylpyrrolidinone, 2,3-dihydropyran, and 2,3-benzofuran gave no polymers.

The ability to polymerize was related to the feasibility of the propagation steps and not the initiation step. This is shown by the virtual equivalence of the results from spontaneous and free-radical-initiated experiments.

Charge-transfer complexation showed a significant correlation with copolymerization (Table II). If complexation was too weak, copolymerization did not occur. If moderately strong CT complexation occurred, copolymerization was possible. But, if CT complexation was too strong, again no copolymerization occurred. No cationic homopolymerizations of the electron-rich olefins were observed in this series of experiments. The cationic polymerization initiated by TCNQ has only been observed with the most electron-rich olefins, such as *N*-vinylcarbazole and *n*-butyl vinyl ether.[2,4-6]

These results agree with the correlation between CT complexes and polymerization behavior advanced by Iwatsuki and Yamashita for the olefin–olefin case.[7] For that situation, they indicated that strong CT complexation would give rise to ionic homopolymerizations. However, TCNQ cannot homopolymerize anionically, nor can stilbene or phenanthrene homopolymerize cationically. Accordingly, the only possibility is extensive CT complex formation, often with crystallization, as observed. In previously examined cases of strong donor olefins with TCNQ, such as *N*-vinylcarbazole or *n*-butyl vinyl ether, cationic homopolymerization of the donor olefins was

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Table I
Polymerizations of TCNQ with Electron-Rich Olefins[a]

					polymer			
run no.	donor	TCNQ, mol %	AIBN, mol %	time, h	yield, %	composn,[b] % TCNQ	$\bar{M}_n$[c]	η_{inh}, dL/g
1	DPhE	47.8	0	24	31.7	37.5	730	
2	α-MeSt	49.2	0	70	88.4	49.3	9200	
3	AcNa	49.5	0	5	70.2	49.6		0.58[d]
4	NVP	39.6	0	42	2.5	47.2		
5	NVP	34.8	3	42	7.9	49.6		0.20[e]
6	COD	45.3	0	48	39.6	48.0	4600	
7	IP	42.6	0	3	77.7	48.0		0.11[d]
8	DMBD	42.9	0	3	60.2	48.9		0.24[f]
9	MeOBD	45.4	0	24	80.0	45.0	550	
10	NBD	38.8	2	50	19.8	57.0		0.05[e]

[a] Reaction conditions: about 0.5 mmol of each reactant in 12 mL of CH_3CN at 60 °C. Abbreviations: see Results and the Experimental Section. [b] Determined from chemical analysis. [c] Determined by GPC. [d] Solvent: DMF – conc = 0.16 g/dL. [e] Solvent: acetone – conc = 0.16 g/dL. [f] Solvent: concentrated H_2SO_4 – conc = 0.15 g/dL.

Table II
UV Data of CT Complexes[a] and Comparison to Polymerization Behavior

donor olefin	color[b]	λ_{max}, nm	polymn behavior
trSt	green	565 (vbr)	CT complex isolated
Phen	red	500 (br)	
AcNa	red	500 (br)	spontaneous copolymn
DPhE	orange	475	
αMeSt	orange	475	
cisSt	yellow	vbr	no spontaneous polymn
BF	red	sh[d]	
DHF	yellow	vw	
NVP	yellow	sh[d]	

donor diene	color[b]	λ_{max}, nm	polymn behavior
MeOBD	orange	470[c]	spontaneous copolymn
DMBD	orange	470	
IP	orange	470	
COD	yellow	sh[d]	
CHD	yellow		no spontaneous polymn
NBD	yellow		

[a] Concentrations: see the Experimental Section. [b] Color of solution upon mixing. [c] Absorption band for $TCNQ^{\bullet -}$ also visible at 660 nm. [d] sh = shoulder.

observed.[4-6] In the case of 1-methoxybutadiene, the extra double bond compared to butyl vinyl ether favors the radical mechanism over cationic homopolymerization. Weaker CT complexes of TCNQ with the olefins with decreasing donor ability result in, consecutively, radical copolymerization and no spontaneous polymerization, in total analogy with the Iwatsuki/Yamashita scheme.

Experimental Section

Instrumentation. ^1H NMR spectra were taken on a Bruker Model WM-250 multinuclear FT spectrometer. Infrared spectra were obtained with a Perkin-Elmer 983 grating infrared spectrophotometer. UV spectra were recorded on a Perkin-Elmer 552 double-beam spectrophotometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ. All melting points were obtained with a Thomas-Hoover capillary melting point apparatus and were uncorrected. Number-average molecular weights were measured on a Shodex GPC A-804 column, calibrated with polystyrene standards, with chloroform as eluent and a Spectra Physics UV detector at 254 nm.

Materials. TCNQ was recrystallized from acetonitrile. *trans*-Stilbene, acenaphthene, and phenanthrene were recrystallized from a mixture of benzene with hexane (1:1 by volume), chloroform, methanol containing active carbon, and ethanol, respectively. 1,1-Diphenylethylene [bp 80 °C (0.1 mmHg)], α-methylstyrene [bp 65 °C (20 mmHg)], 1,3-cyclooctadiene [bp 55 °C (34 mmHg)], isoprene (bp 34 °C), 2,3-dimethyl-1,3-butadiene (bp 68 °C), 2,5-norbornadiene (bp 87 °C), and 1-methoxy-1,3-butadiene (bp 91 °C) were washed with 2% aqueous sodium hydroxide solution and water, dried over anhydrous magnesium sulfate, stirred with calcium hydride at room temperature for 24 h, and then distilled under nitrogen. *N*-Vinyl-2-pyrrolidinone [bp 76 °C (20 mmHg)], *cis*-stilbene [bp 83 °C (10.4 mmHg)], 2,3-benzofuran [bp 90 °C (30 mmHg)], 2,3-dihydropyran (bp 83 °C), 1,3-cyclohexadiene (bp 80 °C), and acetonitrile (bp 81 °C) were stirred over calcium hydride at room temperature for 2 days and then distilled under nitrogen. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol.

Polymerization Procedure. Given amounts of TCNQ, donor monomer, and 12 mL of acetonitrile (in some cases AIBN) were placed in an ampule, which was degassed by the freeze–thaw method (repeated three times), and then nitrogen gas was introduced. The ampule was placed in a bath thermostated at 60 °C for a given time. The reaction mixture was poured into excess methanol. When 1,1-diphenylethylene and 1-methoxy-1,3-butadiene were used as donor monomers, hexane was used as precipitant instead of methanol. The product was filtered and washed and the precipitating solvent dried under reduced pressure.

Charge-Transfer Absorption Band. Absorption spectra of the charge-transfer transition for the TCNQ–electron-rich olefin and TCNQ–conjugated diene systems were recorded in acetonitrile at room temperature. The concentrations of solutions employed were as follows: [TCNQ] = 5×10^{-3} mol/L, [*trans*-stilbene, trSt] = 1.2×10^{-2} mol/L, [*cis*-stilbene, cisSt] = 2.5×10^{-2} mol/L, [1,1-diphenylethylene, DPhE] = 1.2×10^{-2} mol/L, [α-methylstyrene, α-MeSt] = 1.4×10^{-2} mol/L, [phenanthrene, Phen] = 5.9×10^{-3} mol/L, [acenaphthene, AcNa] = 6.9×10^{-3} mol/L, [*N*-vinyl-2-pyrrolidinone, NVP] = 4.5×10^{-2} mol/L, [2,3-dihydropyran, DHP] = 5.9×10^{-2} mol/L, [2,3-benzofuran, BF] = 1.7×10^{-2} mol/L, [1,3-cyclooctadiene, COD] = 4×10^{-2} mol/L, [1,3-cyclohexadiene, CHD] = 5×10^{-2} mol/L, [2,5-norbornadiene, NBD] = 4.9×10^{-2} mol/L, [isoprene, IP] = 6×10^{-2} mol/L, [2,3-dimethyl-1,3-butadiene, DMBD] = 6×10^{-2} mol/L, and [1-methoxy-1,3-butadiene, MeOBD] = 5×10^{-2} mol/L. The results are given in Table II.

Characterization. Copolymer composition was established by elemental analysis and was shown to be close to 50/50 in most cases with always slightly less TCNQ. The NMR spectra confirm that these polymers are alternating within the detection limits of the NMR.

The molecular weight (M_n) of the product was determined by gel permeation chromatography by using standard polystyrene as reference and chloroform as eluent and a Shodex 804 A column.

^1H NMR measurement for the copolymers was carried out in chloroform-*d* or dimethyl-d_6 sulfoxide with tetramethylsilane as internal standard. Solution viscosity was determined at 30 °C by using the Ostwald viscometer in dimethylformamide (DMF) for the copolymers of TCNQ with acenaphthene and with isoprene, in concentrated sulfuric acid for the copolymer of TCNQ with 2,3-dimethyl-1,3-butadiene, and in acetone for the copolymers of TCNQ with *N*-vinyl-2-pyrrolidinone and with 2,5-norbornadiene.

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References and Notes

(1) Melby, L. R. In *The Chemistry of the Cyano Group*; Rappoport, Z., Ed.; Interscience Publishers: London, 1970; p 639.

(2) Tarvin, R. F.; Aoki, S.; Stille, J. K. *Macromolecules* **1972**, *3*, 663.

(3) Mulvaney, J. E. In *New Monomers and Polymers*; Culbertson, B. M., Pittman, C. V., Jr., Eds.; Plenum: New York, 1984.

(4) Iwatsuki, S. In *The Chemistry of Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1988; Vol. II, p 1068.

(5) Hall, H. K., Jr.; Itoh, T.; Iwatsuki, S.; Padias, A. B.; Mulvaney, J. G. *Macromolecules* **1990**, *23*, 913.

(6) Iwatsuki, S. *Adv. Polym. Sci.* **1984**, *58*, 94.

(7) Iwatsuki, S.; Yamashita Y. *Progr. Polym. Sci. Jpn.* **1971**, *2*, 31.