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p-Phenylenetetramethylene Diradical and Zwitterion Intermediates in the Spontaneous Copolymerizations of Electrophilic *p*-Quinodimethanes with Electron-Rich Olefins

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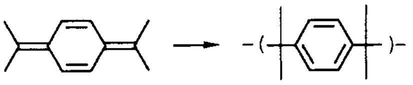
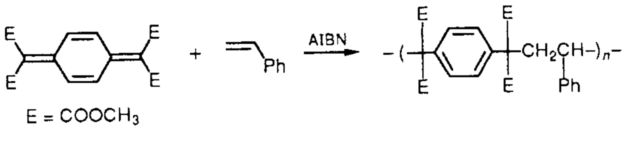
ABSTRACT: Electrophilic *p*-quinodimethanes react spontaneously with electron-rich olefins to form either homopolymers of electron-rich olefins or alternating copolymers. In analogy with the bond-forming initiation theory proposed for the spontaneous reactions observed between electrophilic olefins and electron-rich olefins, a similar mechanism is proposed for the electrophilic *p*-quinodimethane/electron-rich olefin reactions. A bond is formed between the electrophilic *p*-quinodimethane and the electron-rich olefin. The resulting *p*-phenylenetetramethylene intermediate may possess either predominantly zwitterionic or diradical nature, depending on the substituents. Zwitterionic intermediates initiate cationic homopolymerization of the electron-rich olefin, while diradical ones initiate free-radical alternating copolymerization between the two participants. A "periodic table" is constructed to give a rational structure–reactivity correlation. To delineate more clearly the line between diradical and zwitterion mechanisms, additional experimental data are provided using *p*-methoxystyrene and phenyl vinyl ether as the electron-rich olefins.

Introduction

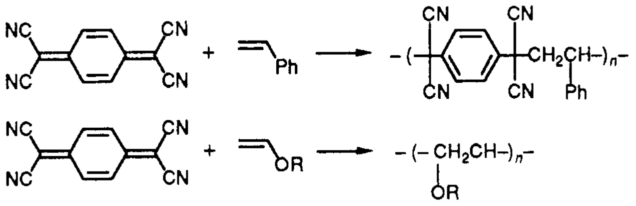
Our two research groups have found independently that electrophilic *p*-quinodimethanes are an interesting new class of monomers.[1–6] Although the best known electrophilic *p*-quinodimethane, tetracyanoquinodimethane (TCNQ), does not homopolymerize, a few other quinodimethanes can be homopolymerized by free-radical or especially anionic initiators. Recovery of the broken aromatic resonance facilitates such polymerizations.



Copolymerization of moderately electrophilic *p*-quinodimethanes with electron-rich olefins can be accomplished by deliberate free-radical initiation. For example



When electron-rich olefins are mixed with more electrophilic *p*-quinodimethanes, charge-transfer complex formation and spontaneous polymerizations are often observed. For example, TCNQ copolymerizes spontaneously and alternatingly with styrene but causes homopolymerization of vinyl ethers.



These observations are highly reminiscent of the electrophilic olefin–electron-rich olefin results, which were successfully explained by our bond-forming initiation theory and correlated by our organic chemist's periodic table.[7,8] Accordingly, in the present work, we extend the bond-forming initiation theory to the spontaneous reactions of electrophilic *p*-quinodimethanes with electron-rich olefins.

Olefin–Olefin Reactions

Spontaneous reactions of electrophilic olefins with electron-rich olefins have long been of interest to organic and

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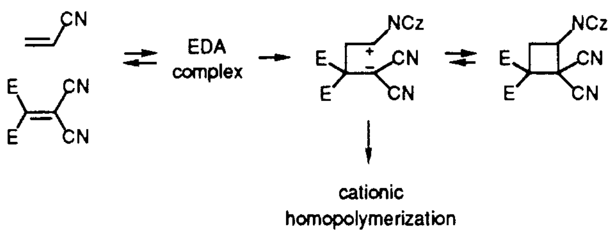
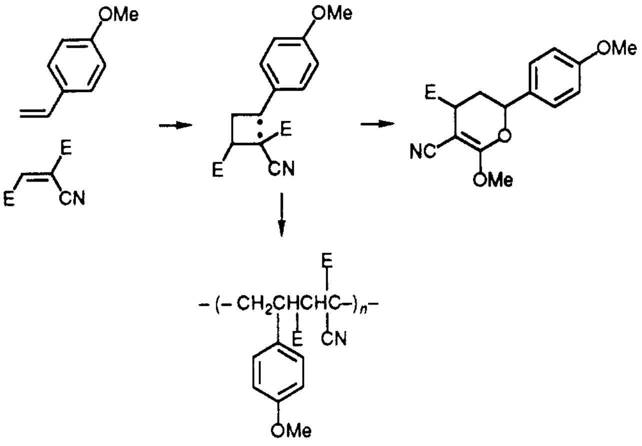
polymer chemists. Such thermal reactions lead, depending on structures and conditions, to small molecules, such as cyclobutanes, 1-butenes, etc., and also to homopolymers or copolymers. For example, if the electron-rich olefin *N*-vinylcarbazole is mixed with dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate, a cyclobutane adduct and/or the homopolymer of *N*-vinylcarbazole are formed, depending on the reaction conditions.[9]



E = COOMe, NCz = *N*-carbazolyl

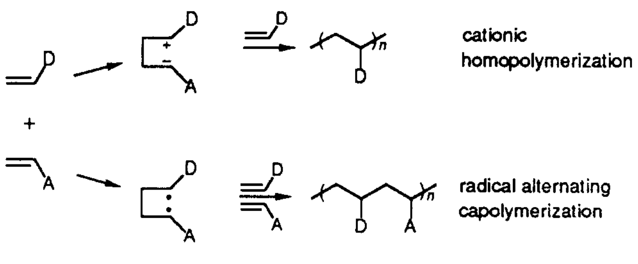
On the other hand, a mixture of *p*-methoxystyrene and dimethyl cyanofumarate yields a perfectly alternating copolymer in concentrated solutions or a cycloadduct in high dilution.[10]



E = $COOCH_3$

Charge-transfer complexes in reactions such as these are visible as brightly colored solutions, which fade as the reactions proceed. In consequence, such spontaneous polymerizations between donor and acceptor monomers have come to be known as "charge-transfer polymerizations". The attributes of such polymerizations are listed in the first column of Table I.

We have proposed the "bond-forming initiation" theory to explain spontaneous "charge-transfer" initiation between electrophilic and electron-rich olefins.[7,8] This theory postulates bond formation between the β-carbons to form a tetramethylene intermediate.



The unused valences may be +,− in zwitterionic form or ↑,↓ in a (singlet) diradical form, depending on the electron-donating and electron-accepting substituents. The zwitterionic tetramethylenes initiate cationic or anionic homopolymerization of the electron-rich or electrophilic olefins, respectively, while diradical ones initiate their copolymerizations.

Table I
Comparison of the Reactions of Electron-Rich Olefins with Electrophilic Olefins and with Electrophilic *p*-Quinodimethanes (QDM's)

	olefins	QDM's
General Reactions		
charge-transfer complexes seen	yes	yes
occurrence of spontaneous reactions	yes	yes
polymers formed	yes	yes
induced by room light, air trace impurities	no	no
small organic molecules, especially cyclobutanes found	yes	no
small molecule and polymer products formed by partitioning of a highly reactive intermediate	yes	
Homopolymerization		
homopolymers of electron-rich olefin formed in certain cases	yes	yes
basic inhibitors effective	yes	yes
vinyl ethers homopolymerize	no[a]	yes[a]
kinetics of homopolymerization agree with a zwitterion tetramethylene	yes	
high solvent polarity effect on rate for a zwitterion tetramethylene	yes	yes
bond formation between donor and acceptor demonstrated	yes	yes
zwitterionic tetramethylene trapped	yes	yes
Copolymerization		
copolymers formed in certain cases	yes	yes
copolymer forms by conventional free-radical propagation, established by controls	yes	yes
kinetics of copolymerization agree with a diradical tetramethylene	yes	yes
small solvent polarity effect on rate for a diradical tetramethylene	yes	
diradical tetramethylene trapped	yes	
bond formation demonstrated	yes	
Mechanism		
rational structure–reactivity relationship (periodic table)	yes	yes
SET not involved:		
reaction not instantaneous	yes	yes
cyclodimers of donor monomer	no	no
mechanism changes with solvent polarity	yes	yes

[a] In the olefin reactions, the centers are too close and the cyclobutane adduct forms preferentially. In the QDM case, the centers are separated and the polymerization proceeds.

The nature of the tetramethylene intermediate depends on the electron-donating and electron-accepting substituents at the terminal carbons in a rational way. Strong electron-donating substituents such as alkoxy or amino groups and strong electron-accepting substituents such as a cyano group favor the zwitterionic tetramethylene intermediates. Resonance-stabilizing substituents such as phenyl, vinyl, and ester groups favor diradical tetramethylene intermediates. We were able to portray the nature of the tetramethylene as a function of electron-donating and electron-accepting ability of the terminal substituents as an organic chemist's periodic table.[7] In this way, a rational structure–reactivity correlation with predictive power was shown to exist.

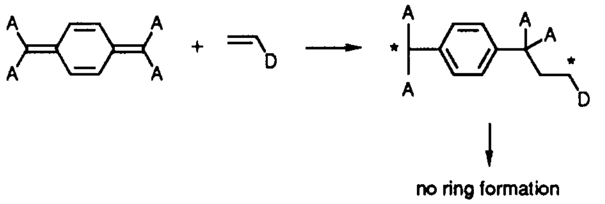
The bond-forming initiation theory has demonstrated great ability to interpret a vast amount of data from both organic and polymer chemistry.

Electrophilic *p*-Quinodimethane. Electron-Rich Olefin Reactions

We have surveyed the available literature on the spontaneous reactions of electrophilic *p*-quinodimethanes with electron-rich olefins. The results are summarized in the second column of Table I. The impressive correspondence with the olefin–olefin case in every aspect leaves no doubt that the same phenomena are at work in these two cases of charge-transfer polymerizations.

General Reactions. Spontaneous thermal reactions between electron-rich olefin and electrophilic *p*-quinodimethanes, leading to polymers, are widely observed. Charge-transfer complexes are visible as brightly colored solutions, which fade as the reactions proceed. The reactions are reproducible and do not depend on trace impurities or light. They are chain-growth reactions as shown by the independence of molecular weight on time.

Unlike the olefin–olefin case, small molecule formation does not accompany polymerization. Joining the active centers of a *p*-phenylenetetramethylene intermediate would cause the formation of a very highly strained 4-paracyclophane.

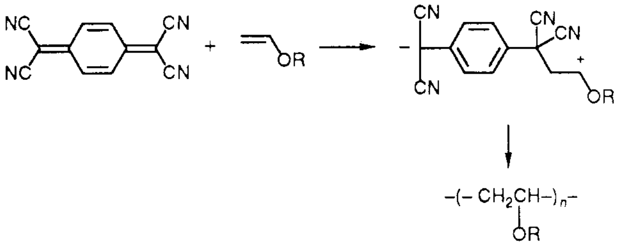


D = donor substituent such as –OR or *N*-carbazolyl;

A = acceptor substituent such as CN or COOMe;

$\star, \ast$ = +, – or ↑,↓.

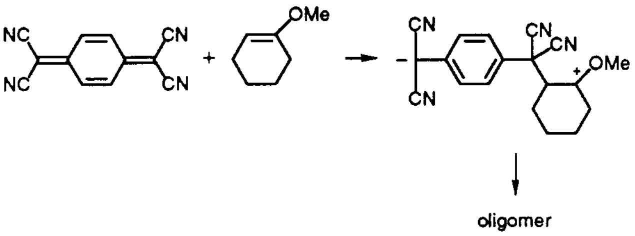
Cationic Homopolymerization. Vinyl ether reactions exemplify this case: TCNQ induces homopolymerization of alkyl vinyl ethers.[1,2,11]



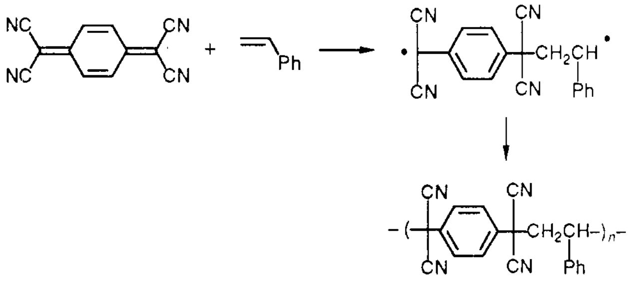
Stille and co-workers were able to isolate oligomers containing a TCNQ unit.[11]

Because of the electron-withdrawing chlorine, β-chloroethyl vinyl ether is less prone than alkyl vinyl ethers to undergo cationic homopolymerization and does not do so with TCNQ. However, if more cyano groups are present in the quinodimethane, as in hexacyanoquinodimethane, cationic homopolymerization of β-chloroethyl vinyl ether does take place. Alternatively, carrying out the reactions in the highly polar solvent propylene carbonate also allows cationic homopolymerization of β-chloroethyl vinyl ether in the presence of TCNQ.[1]

The zwitterionic intermediate postulated in such reactions has not yet been trapped, but bond formation has been demonstrated for the oligomerizable 1-methoxycyclohexane.[12]

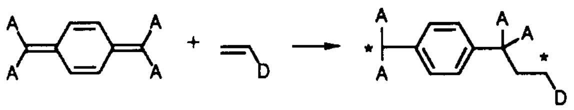


Free-Radical Copolymerization. When the electron-donating substituent prefers to delocalize an odd electron by resonance as in styrene, alternating copolymers are formed spontaneously in the presence of an electrophilic *p*-quinodimethane:[1,2]



The normal free-radical chain propagation is observed. The reactions follow free-radical kinetics.[13] No diradical *p*-phenylenetetramethylene has been trapped as yet.

Proposed Initiation Mechanism. We propose that, analogous to the olefin–olefin case, bond formation to form a *p*-phenylenetetramethylene intermediate is the key initiation step:



$\star, \ast$ = +,– or ↑,↓

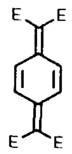
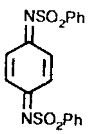
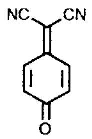
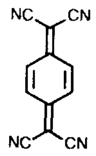
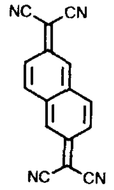
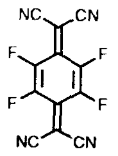
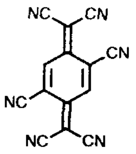
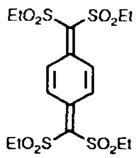
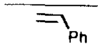
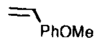
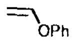
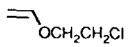
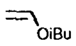
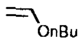
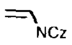
As for the all-olefin cases, the terminal substituents determine the nature of the *p*-phenylenetetramethylene intermediate.

From our survey of the existing literature, we conclude that the electron-donating and electron-accepting substituents influence the nature of the *p*-phenylenetetramethylene intermediate exactly as they do in the tetramethylene case. That is, combination of an electron-rich olefin carrying an alkoxy group with a *p*-quinodimethane carrying cyano groups favors zwitterions, while combination of an electron-rich olefin carrying an aryl group with a *p*-quinodimethane carrying ester groups favors diradicals. As before, we express these trends in a periodic table format (Table II).

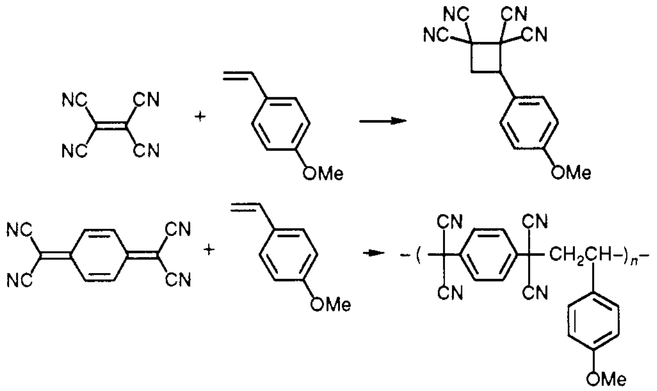
All the available data can be fitted into this scheme. The reactivity of the reported pairs must increase diagonally downward and to the right. As for the olefin–olefin case, a clean division between zwitterions and diradicals is found. The nature of the intermediate is identified by the type of the observed polymerization: zwitterions initiate ionic homopolymerization, while diradicals initiate radical copolymerization.

In comparison to the olefin–olefin case, the presence of the phenyl ring in the *p*-phenylenetetramethylene intermediate shifts the transition state of diradical to zwitterionic character farther downward and to the right than in the olefin–olefin periodic table. In other words, a combination of substituents, which would lead to a zwitterionic intermediate in the olefin–olefin reactions, shows up as a diradical in the quinodimethane–olefin reaction. For example, the reaction of *p*-methoxystyrene and tetracyanoethylene, leading to a cyclobutane adduct, clearly proceeds through a zwitterionic tetramethylene,[14] while the reaction of TCNQ with *p*-methoxystyrene yields an alternating copolymer, initiated by the diradical *p*-phenylenetetramethylene. This is due to the preference of the phenyl group in the acceptor portion to stabilize a diradical intermediate.

Table II
Quinodimethane Periodic Table[a]

donor ability	acceptor ability[b,c]							
								
	copol	copol[e]	copol[e]	copol	copol	copol	copol	copol
	copol[d]	copol[e]	copol[e]	copol[d]	copol[d]	copol[d]	copol[d]	copol[d]
	copol[d]	copol[e]		copol	copol	copol	copol + homop	homop
	copol	copol[e]		copol	homop	homop	homop	homop
	copol	copol[e]		homop	homop	homop	homop	homop
	copol	copol[e]		homop	homop	homop	homop	homop
	copol			homop				

[a] All data except as noted from refs 1–3. E = $COOCH_3$, copol = alternating copolymer, homop = homopolymer of the electron-rich olefin. [b] Electron affinity (eV): *p*-quinone bis(benzenesulfonimide), 2.17; 7,7-dicyanoquinone methide, 2.36; TCNQ, 2.88; F_4TCNQ, 3.22.[1,2] [c] *First reduction potentials* (V): tetracarbomethoxyquinodimethane, −0.83;[21] TCNQ, 0.127;[19] 0.1,[20] −0.2;[21] tetracyanonaphthoquinodimethane, 0.21;[20] F_4TCNQ, 0.53;[20] hexacyanoquinodimethane, 0.65;[20] tetra(ethylsulfonyl)quinodimethane, 0.092.[19] [d] New results: the spontaneous polymerizations were carried out in acetonitrile at 60 °C. Feed ratios of electron-rich olefin to electrophilic quinodimethanes were 1 to 1. Methanol was used as precipitant. [e] The spontaneous polymerization were carried out in benzene at 60 °C.



The division between zwitterions and diradicals is logical in terms of increasing electron-donating and electron-accepting ability of the substituents and represents a structure–reactivity relationship with correlative and interpretative power.

We provide some new data involving *p*-methoxystyrene and phenyl vinyl ether as electron-rich olefins in order to more sharply delineate the line of mechanism change.

Three *p*-quinodimethanes were omitted from our periodic table, because they can homopolymerize due to their high ceiling temperatures.[15–17] For reasons unknown, their behavior differs from those of the other *p*-quinodimethanes and from the electrophilic tri- and tetrasubstituted ethylenes, which do not homopolymerize.

We defer trying to correlate the position of a compound with fundamental properties, such as electron affinity or reduction potential, because steric effects will influence such correlations.

Exclusion of Single-Electron Transfer. Electron transfer should be instantaneous, but those polymerizations are moderate or slow in rate.

Also, no cyclodimer of electron-rich olefin has ever been observed in these reactions. Such cyclodimers would be characteristic products of reactions of the radical cations from the electron-rich olefins.[18]

Conclusion

Due to the obvious large similarity between the spontaneous reactions of electrophilic *p*-quinodimethanes and electrophilic olefins with electron-rich olefins, we have proposed a parallel mechanism to the bond-forming initiation theory. In this scheme, a bond is formed between the electron-rich olefin and *p*-quinodimethane. The resulting *p*-phenylenetetramethylene intermediate can be predominantly zwitterionic or diradical in nature. This intermediate is the proposed initiating species for the observed spontaneous polymerizations.

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Registry No. TCNQ, 1518-16-7; F_4-TCNQ, 29261-33-4; $(CN)_2$TCNQ, 29097-90-3; *p*-methoxystyrene, 637-69-4; phenyl vinyl ether, 766-94-9; tetracarbomethoxyquinodimethanol, 65649-20-9; 1,6-(dinitrilemethylene)naphthalene, 6251-01-0; tetraethylquinodimethane tetrasulfonate, 84928-90-5.