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Studies in Cyclocopolymerization. X. Cyclocopolymerization of Tetrahydronaphthoquinone and Dimethyl Tetrahydronaphthoquinone with Divinyl Ether

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**Studies in Cyclocopolymerization. X.
Cyclocopolymerization of
Tetrahydronaphthoquinone and
Dimethyl Tetrahydronaphthoquinone
with Divinyl Ether**

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ABSTRACT

Tetrahydronaphthoquinone (THNQ) and dimethyl tetrahydronaphthoquinone (DMTHNQ) were found by UV spectroscopy to form donor-acceptor complexes with divinyl ether (DVE), the latter being the electron donor. Since the participation of such complexed species has been considered in the cyclocopolymerization of a 1,4-diene with a monoolefin such as DVE-maleic anhydride (MA) and DVE-fumaronitrile (FN) systems, radical copolymerization of THNQ and DMTHNQ with DVE was studied. It was found that these copolymers have constant 1:1 composition regardless of the feed composition. The terpolymerization of DVE-THNQ-DMTHNQ confirmed the 1:1 donor-acceptor composition in the polymer. The integration of the NMR spectrum was used in determining the copolymer composition. The spectroscopic data suggest a cyclized repeating unit in which the copolymer

main chain consists of only DVE units. There is a marked difference between these copolymers and the typical cyclo-copolymers, such as DVE-MA and DVE-FN, in which the copolymer main chains consist of DVE and the comonomer alternately, with the overall composition being 1:2. These results are interpreted in terms of the steric effect by the bulky acceptor monomers and the electronic interaction between the comonomers. The competition between an acceptor monomer and the charge-transfer (CT) complex toward the cyclized DVE radical in the propagation step appears to favor the CT complex.

INTRODUCTION

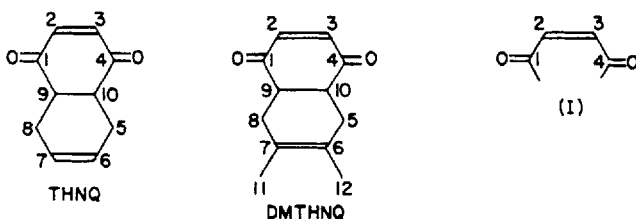
Cyclocopolymerization of 1,4-dienes with certain monoolefins has been shown to undergo an intermolecular-intramolecular mechanism to produce an alternating arrangement of comonomer units in the copolymer with consumption of all the double bonds [1]. The copolymers obtained from radical polymerization of maleic anhydride (MA)-divinyl ether (DVE) [2], MA-1,4-pentadiene [2], and fumaronitrile (FN)-DVE [3] pairs were cyclocopolymers of constant 2:1 (= monoolefin:diene) alternating structure over a wide range of feed composition. Since these combinations of polar comonomers form charge-transfer (CT) complexes, the physical methods of determining the equilibrium constants and the stoichiometry of the complexes have been extensively applied recently in view of the possible participation of the CT complexes in the cyclocopolymerization mechanism [4, 5]. The dilution effects found in the copolymerization of FN-DVE [6] suggest that CT complexes are active in these cyclocopolymerizations.

A steric effect was observed in the copolymerization of tetracyanoethylene (TCNE) with DVE. The large TCNE molecule did not give the usual 2:1 copolymer composition, and the fraction of TCNE in the copolymer changed gradually from 0.4 to 0.6 according to the feed composition, even though TCNE is known to be a strong acceptor in forming CT complexes [3].

It would be expected that a monoolefin which does not homopolymerize easily and has an olefinic group flanked by two strongly electron-withdrawing groups, such as the olefinic double bonds of MA and FN, would be a good acceptor monomer to cyclocopolymerize

with a donor 1,4-diene, such as DVE which is known to homopolymerize very slowly [7]. If the acceptor has large substituents, the steric effect may also play a role.

In this paper, tetrahydronaphthoquinone (THNQ) and dimethyl tetrahydronaphthoquinone (DMTHNQ), which have 1,4-dione-2-ene groups (I) like MA, were studied as the acceptor monoolefins for DVE.



These are particularly interesting monomers because they have two different double bonds, both of which are potentially usable for polymerization. However, these double bonds are oppositely polarized. If the cyclocopolymerization were a random polymerization, both double bonds could conceivably be incorporated in the propagation. Radical copolymerizations and terpolymerizations were studied with DVE in chloroform to compare the results of the MA-DVE system. It was found that both THNQ-DVE and DMTHNQ-DVE systems gave cyclic, noncross-linked copolymers having a 1:1 composition. Both double bonds of DVE and only the double bond of THNQ and DMTHNQ flanked by carbonyl groups were consumed in copolymerization. The backbone chain of the copolymer consisted of only DVE units. These results were interpreted in terms of the CT formation between the comonomers and the steric effect of the acceptor monomers.

RESULTS AND DISCUSSION

Charge-Transfer Complex

The spectroscopic determination of stoichiometry and the equilibrium constants of the CT complexes of monoolefins with

1,4-dienes have been thoroughly discussed previously [5]. In all cases studied, a 1:1 complex was found with DVE. The equilibrium constant of complexation can be determined either by NMR using the Hanna-Ashbaugh equation [8] or by UV using the Scott equation [9]. The attempted NMR method failed because one of the quartet absorptions of the α -vinyl proton of DVE covered the peak of the protons at the 2 and 3 positions of the acceptor, whose chemical shift was to be used to determine the equilibrium constant. The UV absorption of the CT complexes appeared below 350 $m\mu$ (Fig. 1).

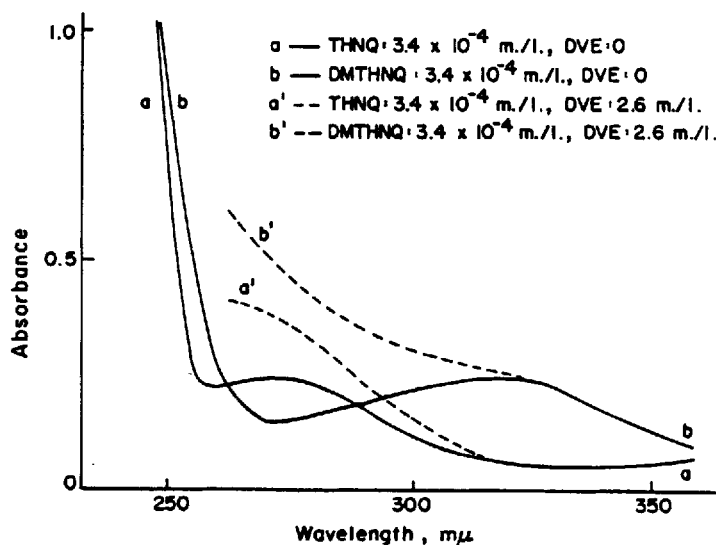


FIG. 1. UV absorption of THNQ and DMTHNQ and their charge-transfer absorption with DVE in CHCl_3 .

The accompanying broken lines show the enhanced absorption due to complexation. The absorption of DVE was cancelled by using the same DVE concentration in the sample cell and in the reference cell. In determining the equilibrium constant of complexation, the small concentration of acceptor (THNQ or DMTHNQ) was kept constant and the concentration of donor (DVE) was changed successively in the sample cell. The same concentration of DVE

was used in the reference cell to cancel the absorption due to DVE. Then the absorption of the acceptor was subtracted numerically from the obtained spectrum to obtain the absorption of only CT complex, which is shown in Fig. 2 for the THNQ-DVE pair taken in CCl_4 and in Fig. 3 for the DMTHNQ-DVE pair taken in CHCl_3 . The equilibrium constant of complexation (K) and the extinction coefficient (ϵ) were determined by the Scott equation as shown in Figs. 4 and 5.

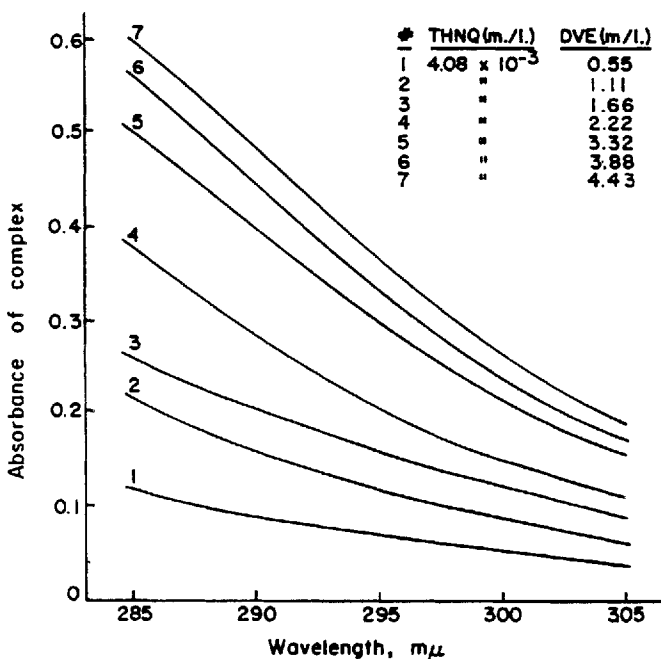


FIG. 2. The charge-transfer absorption of THNQ-DVE complex in CCl_4 at 25°C .

Structure of the Copolymer

The copolymer of THNQ and DMTHNQ with DVE absorbed in the IR region: 1703 cm^{-1} (s) ($\text{C}=\text{O}$ stretching) and, near 1100 cm^{-1}

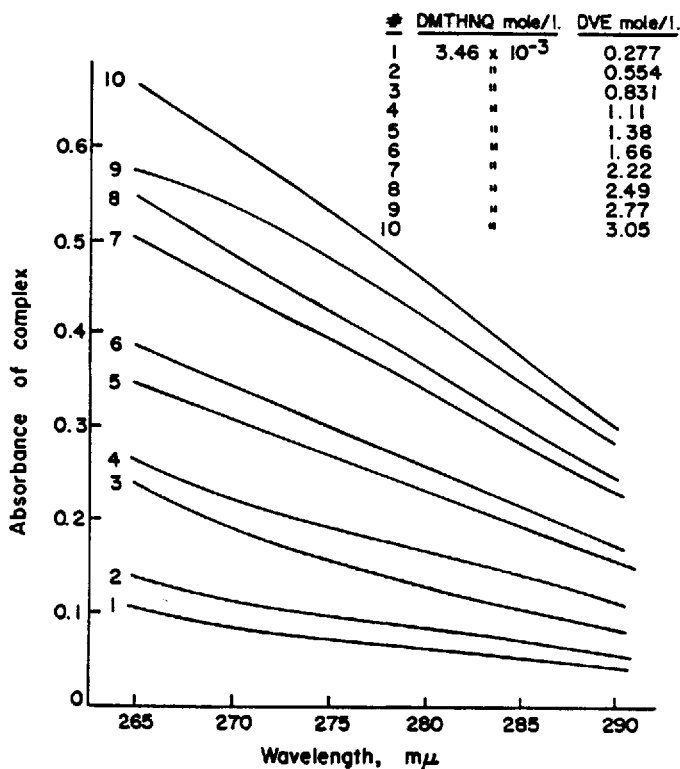


FIG. 3. The charge-transfer absorption of DMTHNQ-DVE in CHCl_3 at 25°C .

(broad) (ether group), showing the existence of the comonomer units. The vinyl C—H absorptions of the 2 and 3 positions of THNQ and DMTHNQ at 1270 and 690 cm^{-1} were absent in the copolymer, indicating that the copolymerization proceeded only through the 1,4-dione-2-ene group; the unsaturated C—H absorption of DMTHNQ at 3040 cm^{-1} was also absent in the copolymer. Therefore a structure such as II does not exist in the copolymer.

The NMR spectra of the polymers are shown in Fig. 6. The complete absence of the proton absorption of the 1,4-dione-2-ene

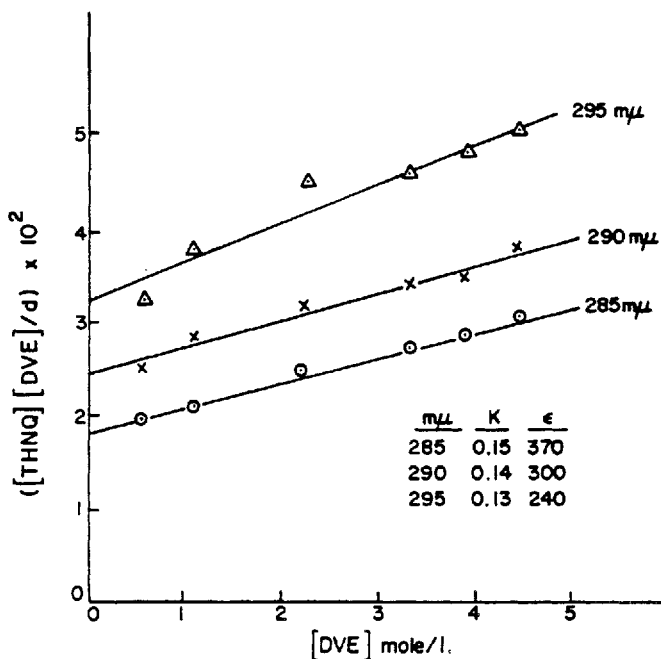
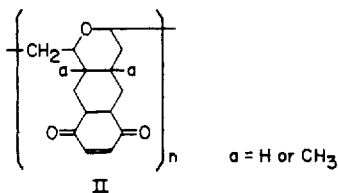


FIG. 4. Determination of the equilibrium constant of complexation between THNQ and DVE in CCl_4 at 25°C by Scott's equation.



group of THNQ and DMTHNQ (6.65δ) explicitly shows consumption of this $\text{C}=\text{C}$ double bond in the copolymerization. The NMR data rule out a Structure III with the pendant vinyl group because the vinyl proton alpha to the oxygen of the ether group was completely absent in the copolymer; ethyl vinyl ether (EVE) shows the absorption of that proton at 6.41δ .

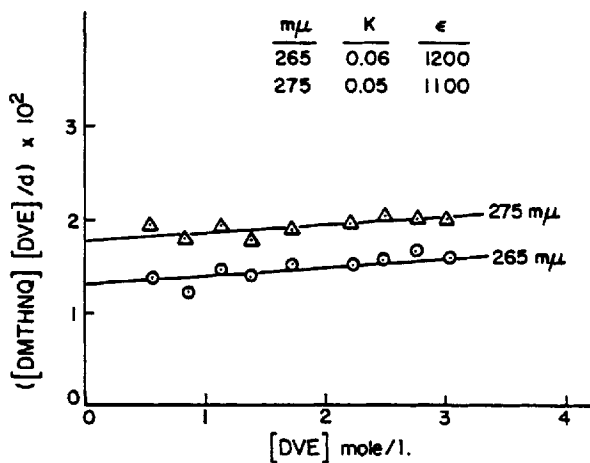
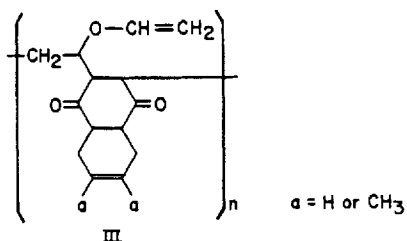
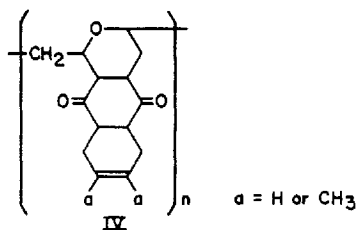
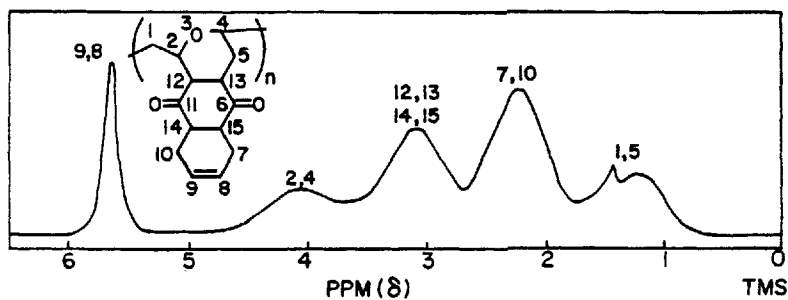


FIG. 5. Determination of the equilibrium constant of complexation between DMTHNQ and DVE in CHCl_3 at 25°C by Scott's equation.

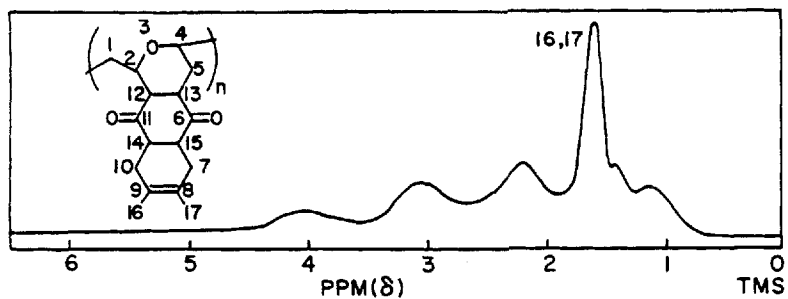


The 1:1 composition of the copolymers, to be discussed later, and the spectroscopic data suggest the cyclized repeating unit is Structure IV.

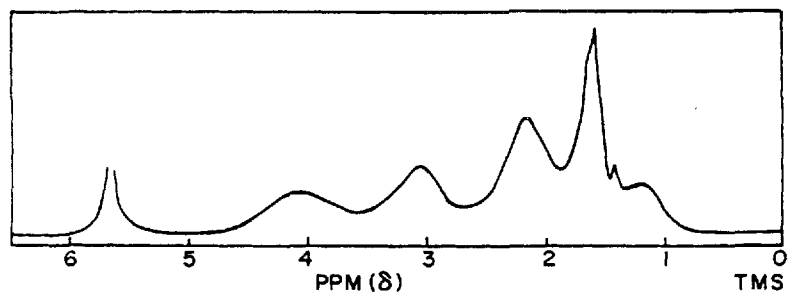




a. THNQ-DVE copolymer



b. DMTHNQ-DVE copolymer

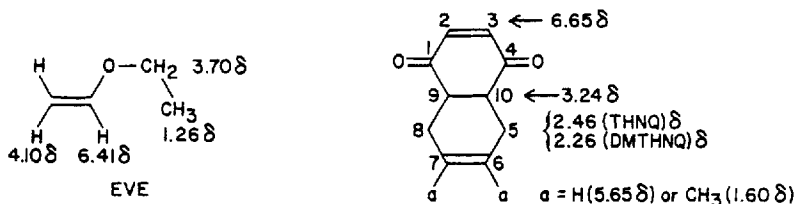


c. THNQ-DMTHNQ-DVE terpolymer

FIG. 6. NMR spectra of copolymers in CDCl_3 .

It is very interesting to note that the backbone of the copolymer consists only of DVE units. This is the striking difference between these copolymers and the typical cyclocopolymers, such as MA-DVE and FN-DVE, whose copolymer backbones are made up of

DVE and the comonomer alternatively. The assignment of the NMR absorption in Fig. 6 was made by comparing the chemical shifts of protons of THNQ, DMTHNQ, and EVE.



Copolymer Composition

The results of the copolymerization studies are shown in Tables 1 and 2.

The copolymer of THNQ-DVE shows the absorption of vinyl protons at the 6 and 7 positions of the THNQ unit at 5.65 δ. Since this peak is separated from absorptions of all other protons, the integration of the absorptions permitted the determination of the copolymer composition. The mechanical integration by the NMR machine and the cut-and-weigh method agreed very well. However, in the case of DMTHNQ-DVE copolymer, the protons of the methyl groups at the 6 and 7 positions of DMTHNQ appear at 1.60 δ, making the integration difficult. Since the tails of the methyl protons and other protons overlap each other, we could not be sure how much of the absorption was due only to the methyl groups. We simply took the inflection points on the integration curve by the NMR machine to calculate the area covered by the methyl groups, assuming that the extent of the overlapping of the tails of the methyl absorption and other proton absorptions are about the same, thus canceling out each other. Therefore this can be the source of the error in the determination of the copolymer composition of DMTHNQ-DVE copolymer. The results are shown in Figs. 7 and 8. Contrary to the MA-DVE, FN-DVE and MA-1,4-pentadiene copolymers, which have constant 2:1 composition, both THNQ and DMTHNQ gave almost perfect 1:1 composition with DVE. Together with the spectroscopic data, this is the basis of assuming the cyclized repeating unit such as IV for these copolymers. This constant 1:1 composition and, hence, the copolymer backbone

TABLE I. Copolymerization of THNQ with DVE at 60°C

Run No.	Mole fraction of THNQ in feed	Reaction time (hr)	Yield of copolymer (wt%)	Mole fraction of THNQ in copolymer	\bar{M}_n	Softening point (°C)
[AIBN] = 5.53×10^{-3} mole/liter, [THNQ + DVE] = 7.30×10^{-1} mole/liter in CHCl ₃						
TH-DV-30	0.30	9.5	4.8	0.51		
TH-DV-48	0.48	3.0	0.8			
TH-DV-70	0.70	9.5	2.0	0.50		
TH-DV-85	0.85	9.5	1.2			
[AIBN] = 2.22×10^{-2} mole/liter, [THNQ + DVE] = 7.30×10^{-1} mole/liter in CHCl ₃						
TH-DV-15	0.15	13.0	15.1	0.373	1100	
TH-DV-35	0.35	13.0	15.7	0.487	1250	
TH-DV-45	0.45	15.5	16.4	0.498	1300	174
TH-DV-65	0.65	15.5	9.7	0.493	1350	177
TH-DV-80	0.80	22.0	5.4	0.512	1250	
[AIBN] = 3.27×10^{-2} mole/liter, [THNQ + DVE] = 1.62 mole/liter in Benzene						
TH-DV-Bz-3	0.272	16.5	14.9	0.45	1400	183

TABLE 2. Copolymerization of DMTHNQ with DVE at 60°C in CHCl₃^a

Run No.	Mole fraction of DMTHNQ in feed	Reaction time (hr)	Yield of copolymer (wt%)	Mole fraction of DMTHNQ in copolymer	Softening point (°C) ^b
DM-DV-15	0.15	21.5	2.5	0.44	172
DM-DV-35	0.35	21.5	7.1	0.47	174
DM-DV-45	0.45	21.5	3.2	0.43	175
DM-DV-65	0.65	21.5	1.6	0.43	181
DM-DV-85	0.85	29.3	0.7		

^a[DMTHNQ + DVE] = 7.30×10^{-1} moles/liter. [AIBN] = 2.22×10^{-1} mole/liter.
^bWith decomposition.

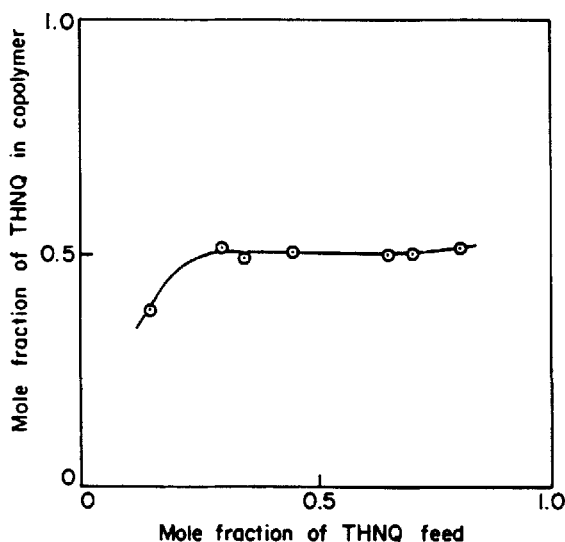


FIG. 7. Composition of THNQ-DVE copolymer.

consisting of only DVE units can be a good indication of similar effects which may be operative in the copolymerization of MA-p-dioxene [10] in which the homopolymerization of a 1:1 CT complex was considered.

Terpolymerization Studies

To confirm the 1:1 composition of the binary systems, the terpolymerization of these three components was carried out. It was expected that if the acceptor-donor pairs are the polymerizing species in each binary system and form copolymers of 1:1 composition, the mole ratio of the acceptors to the donor (DVE) should be 1:1 in the terpolymer, the mole fraction of DVE unit being always 0.5. The results of the terpolymerization studies are summarized in Table 3.

The 1:1 composition of binary systems was confirmed; the mole fraction of DVE in the terpolymer was always close to 0.5 regardless of the feed composition. Since the terpolymer showed no absorptions due to the vinyl group of DVE and 1,4-dione-2-ene

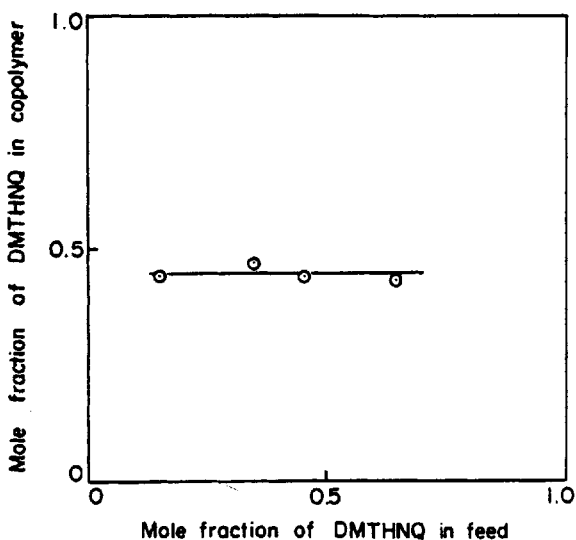
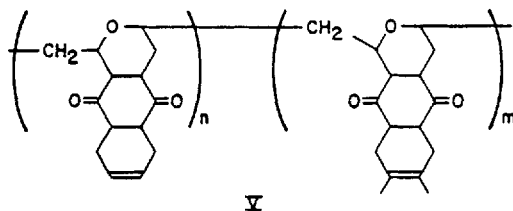


FIG. 8. Composition of DMTHNQ-DVE copolymer.

group of the acceptors in NMR (Fig. 6c) and IR, the intermolecular propagation was concluded to be between the cyclized DVE radical and DVE monomer to produce a terpolymer of Structure V.



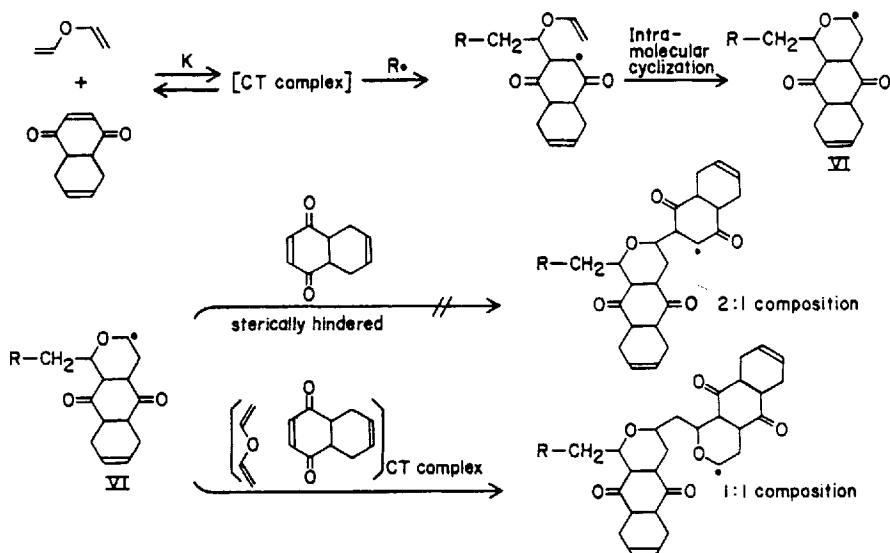
In both copolymerization and terpolymerization, the cyclized DVE radical (VI) attacked DVE monomer to produce polymers of Structures IV and V, respectively. This cannot be explained by the polarity of the radical and the monomer, because negatively polarized radical (VI) would attack the positively polarized C=C double bond of an

TABLE 3. Terpolymerization of THNQ-DMTHNQ-DVE System at 60° in CHCl₃^a

Run No.	Feed mole fraction THNQ/DMTHNQ/DVE	Reaction time (hr)	Yield (wt%)	Terpolymer composition mole fraction THNQ/DMTHNQ/DVE
TH-DM-DV-135	0.15/0.35/0.50	15.0	12.7	0.19/0.32/0.49
TH-DM-DV-225	0.25/0.25/0.50	15.0	16.2	0.26/0.25/0.49
TH-DM-DV-424	0.38/0.24/0.38	15.0	11.4	0.33/0.17/0.50
TH-DM-DV-117	0.15/0.10/0.75	20.0	18.0	0.25/0.19/0.56
TH-DM-DV-514	0.50/0.10/0.40	16.5	15.3	0.41/0.11/0.48
TH-DM-DV-217	0.20/0.10/0.70	16.5	22.9	0.26/0.17/0.57
TH-DM-DV-154	0.10/0.50/0.40	16.5	11.9	0.07/0.33/0.60

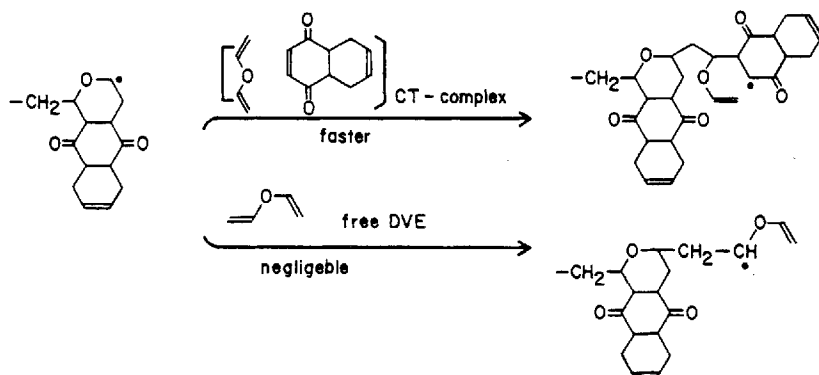
^a[THNQ + DMTHNQ + DVE] = 8.72×10^{-1} mole/liter. [AIBN] = 2.77×10^{-2} mole/liter.

acceptor monomer since polymerization of DVE under the same reaction conditions is negligible. The propagation of the copolymerization can be interpreted as a competition between the acceptor monomer (THNQ or DMTHNQ) and the charge-transfer complex toward the cyclized DVE radical (VI).



Although the cyclized radical of DVE (VI) could react preferably with the acceptor because the reaction of a radical and a monomer of opposite polarities would stabilize the transition state [11], the huge acceptor monomer may not be able to react in that way because of the steric interaction between the acceptor units in the polymer and the reacting monomer. Thus the steric effect reduces the reactivity of the acceptor monomers toward the cyclized DVE radical (VI). As a result, the donor-acceptor complex was added through the DVE component to give a 1:1 composition of successively cyclic structure instead of the more common alternating 2:1 composition. As is usual with 1,2-disubstituted monomers, the steric hindrance is evident from the fact that neither THNQ nor DMTHNQ homopolymerized under the same conditions used for the copolymerization after 3 days at 60°C, even though each of them has donor and acceptor C=C double bonds in the same molecule potentially

capable of polymerization. It is most plausible that steric hindrance favors the cyclized DVE radical (VI) attacking the positively polarized side of the CT complex. Thus the more positively polarized DVE, being the donor, adds to VI, and successively the complexed acceptor will be combined. Thus these co- and terpolymerizations could be regarded as homo- and copolymerization of the acceptor-donor complexes, respectively.



The yield of the copolymer showed a maximum instead of a minimum with respect to the feed composition (Figs. 9 and 10). This is not expected in the case of a random copolymerization [12] which shows a minimum in the rate profile. Also the number-average molecular weight seems to have a maximum (see Table 2). These results can be explained by the fact that the concentration of the complex, which may be acting as a monomer, is maximum at 1:1 feed composition since the concentration of the complex is expressed as

$$[\text{complex}] \simeq k[A][D]$$

Treatment of the Terpolymerization by the Complex Mechanism

If this terpolymerization is regarded as a copolymerization of two kinds of complexes, C_1 and C_2 , formed by THNQ-DVE and DMTHNQ-DVE, respectively, the derivation of the copolymer

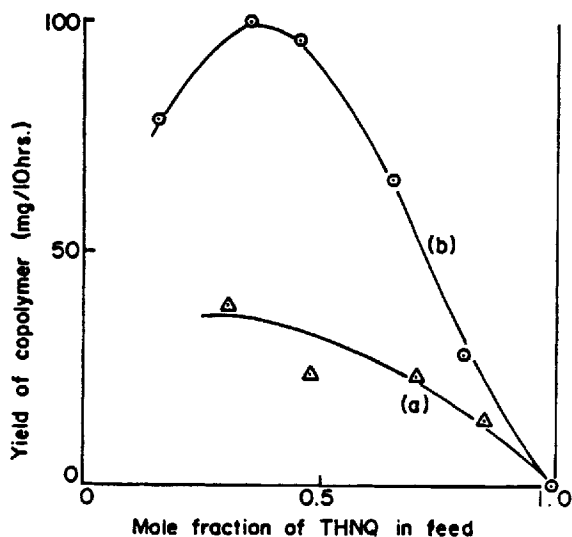


FIG. 9. Rate of copolymerization of THNQ-DVE. $[\text{THNQ} + \text{DVE}] = 7.30 \times 10^{-1}$ mole/liter at 60°C in CHCl_3 . (a) $[\text{AIBN}] = 0.553 \times 10^{-2}$ mole/liter. (b) $[\text{AIBN}] = 2.22 \times 10^{-2}$ mole/liter.

composition equation for random copolymerization [13] can be followed in terms of the concentrations of the complexes to obtain a "copolymer composition equation" for the terpolymerization [14]. Since the stoichiometry of complexation of all the previously investigated donor-acceptor combinations of DVE-monoolefin pairs were shown to be 1:1 [4, 5], it is assumed that the stoichiometry of the complexation of these systems is 1:1.

$M_1 = \text{DVE (donor)}$, $M_2 = \text{THNQ (acceptor)}$, $M_3 = \text{DMTHNQ (acceptor)}$



$$\frac{d[M_2]}{d[M_3]} = \frac{[C_1]}{[C_2]} \frac{R_1[C_1] + [C_2]}{[C_1] + R_2[C_2]} = \frac{[M_2]}{[M_3]} \frac{R_1(K_1/K_2)[M_2] + [M_3]}{[M_2] + R_2(K_2/K_1)[M_3]}$$

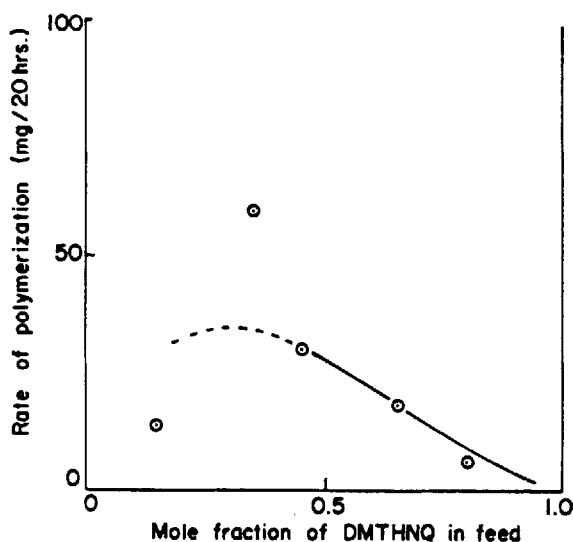


FIG. 10. Rate of copolymerization of DMTHNQ-DVE, $[M_1 + M_2] = 7.30 \times 10^{-1}$ mole/liter, $[AIBN] = 2.22 \times 10^{-2}$ mole/liter at 60°C in CHCl_3 .

where R_1 and R_2 are the "monomer reactivity ratios" of the complexes C_1 and C_2 , respectively. From the data of the terpolymerizations in Table 3, the values of $R_1(K_1/K_2)$ and $R_2(K_2/K_1)$ were calculated by two methods and are shown in Table 4.

Figure 11 shows the "copolymer composition curve" of this "copolymerization" of the two CT complexes. The figure shows that the "copolymerization" is fairly random with slight alternating tendency, which can also be observed from the R_1R_2 value of about 0.2 in Table 4.

TABLE 4. "Monomer Reactivity Ratios" of the Complexes as a Function of the Equilibrium Constants

Method	$R_1(K_1/K_2)$	$R_2(K_2/K_1)$	$R_1 \cdot R_2$
Mayo-Lewis	0.52 ± 0.14	0.50 ± 0.23	0.26
Fineman-Ross	0.45	0.35	0.16

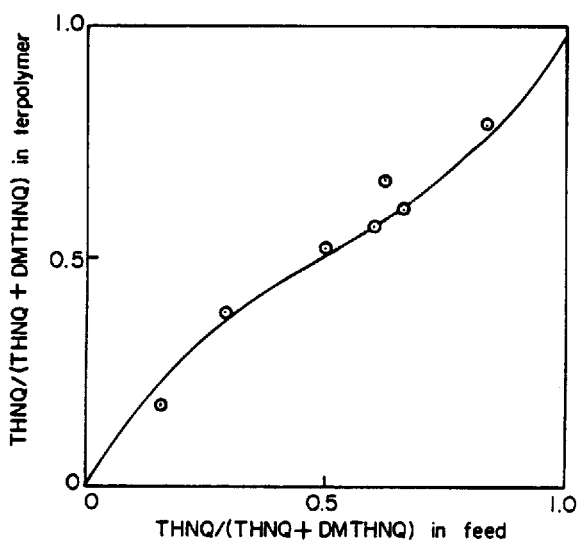


FIG. 11. Mole ratio of THNQ to [THNQ + DMTHNQ] in the terpolymerization of DVE-THNQ-DMTHNQ system in CHCl_3 at 60°C . The curve was calculated using $R_1(K_1/K_2) = 0.52$ and $R_2(K_2/K_1) = 0.50$.

EXPERIMENTAL

DVE was obtained from Merck, Sharp and Dohme and distilled before use. THNQ and DMTHNQ were prepared by the Diels-Alder reaction of benzoquinone with butadiene and 2,3-dimethylbutadiene, respectively. They were used for polymerization after three recrystallizations from benzene and petroleum ether. Reagent grade AIBN was used as the initiator after recrystallization twice from methanol. Reagent grade chloroform was used as the solvent for polymerization as received.

Polymerizations were carried out in Pyrex glass tubes which were sealed on a vacuum line under a high vacuum after repeated freeze-and-thaw cycles with liquid nitrogen. The sealed tubes were placed in an oil bath which was maintained at $60 \pm 0.05^\circ\text{C}$. The copolymers were separated and purified by precipitating into a large amount of boiling petroleum ether. The copolymers were

soluble in benzene, chloroform, acetone, THF, DMF, and DMSO.

Varian Associates analytical NMR spectrometer model A-60, Beckman DK-2A UV spectrometer and Beckman IR-10 IR Spectrometer were used for spectroscopic studies. The number-average molecular weight was measured in acetone at 37°C by Mechrolab vapor pressure osmometer Model 302.

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