

Studies in Cyclocopolymerization. III. Copolymerization of Divinyl Ether with Certain Nitrogen-Containing Alkenes*

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Synopsis

The copolymerization of divinyl ether with fumaronitrile (A), tetracyanoethylene (B), and 4-vinylpyridine (C) has been studied, azobisisobutyronitrile being used as initiator. The compositions of the copolymers were calculated from their nitrogen and unsaturation content. Over a wide range of initial monomer composition, the mole fraction of A in the copolymers lies in the range 0.55–0.63, and the copolymers contained only 2–3% unsaturation, indicating a high degree of cyclization. The composition of the copolymers of B indicated that cyclization occurred to only a small extent, as the copolymers contained rather high unsaturation content. The values of $r_1 = 0.23$ and $r_2 = 0.12$ were obtained. The mole fraction of C in the copolymers lies between 0.85 and 0.998. If the assumption is made that $r_1 \simeq r_c \simeq 0$ and there is predominant cyclization, $r_2 = 32.0$ in this case. The difference in the composition of the copolymers is attributed to the difference between the electron density of the double bonds in A, B, and C.

INTRODUCTION

The copolymerization of 1,4-dienes with certain monoolefins has been shown to proceed by a bimolecular alternating inter-intramolecular mechanism.¹⁻⁴ In a recent paper from this laboratory,⁵ a general copolymer composition equation for this copolymerization has been presented. The derived equation which relates copolymer composition to monomer feed composition in terms of five reactivity ratio parameters is given as eq. (1):

$$n = \frac{(1 + r_1x) \left[\frac{1}{[M_2]} + \left(\frac{1}{a} \right) \left(1 + \frac{x}{r_3} \right) \right]}{\left(\frac{1}{a} \right) \left[\left(\frac{x}{r_3} \right) + \left(\frac{r_2}{x} \right) + 2 \right] + \left(\frac{1}{[M_2]} \right) \left[1 + \left(1 + \frac{r_2}{x} \right) (1 + r_cx)^{-1} \right]} \quad (1)$$

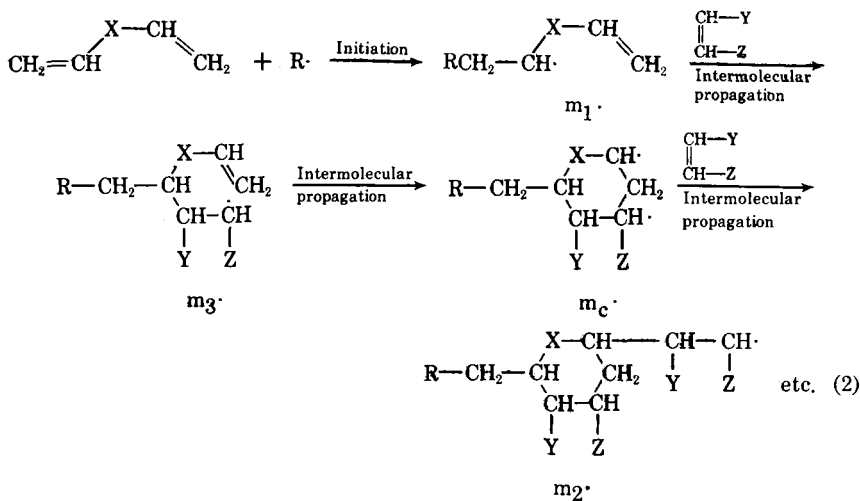
Here, $x = [M_1]/[M_2]$ is the mole fractional ratio of monomers in the feed, $n = [m_1]/[m_2]$ is the mole fractional ratio of monomers in the copolymer at

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low conversions, $r_1 = k_{11}/k_{12}$; $r_2 = k_{22}/k_{21}$; $r_3 = k_{32}/k_{31}$; $r_c = k_{c1}/k_{c2}$; and $a = k_c/k_{32}$. The reactivity ratio parameters are defined in terms of the previously proposed kinetic scheme.⁵ In certain special cases, eq. (1) can be approximated to simpler forms as previously described in detail and designated as (a), (b), and (c).

The general copolymer composition equation was further supported by the results of the most recent paper in this series,⁶ in which copolymerization of 3,3-dimethyl-1,4-pentadiene and divinyl sulfone with acrylonitrile was reported and the reactivity ratio parameters for these systems were determined.

Copolymerization of 1,6-dienes with monoolefins has been studied by many authors, and general copolymer composition equations have been developed.⁷⁻¹¹ The dienes were found to be incorporated into the copolymer chain according to the alternating intra-intermolecular propagation mechanism.¹¹ In these copolymers, the diene radical undergoes direct cyclization to form a unimolecular repeating unit. In the present system of copolymerization of 1,4-dienes with monoolefins, the monoolefin is inserted into the propagating chain before cyclization, and the propagation proceeds by a bimolecular alternating inter-intramolecular mechanism. It can be illustrated as shown in eqs. (2).



This mechanism has been widely recognized; several systems have been investigated in which the 1,4-diene was 1,4-pentadiene, divinyl sulfone, divinyl ether, divinyl dimethylsilane, or divinyl aniline and the monoolefin maleic anhydride, acrylonitrile, fumaronitrile, methyl methacrylate, *N*-phenylmaleimide, vinyl acetate, or dialkyl fumarates and maleates.

With reference to the copolymerization kinetic scheme,⁵ the fate of the intermediate radical, $\text{m}_3\cdot$, is governed by the relative rate of cyclization (k_c) and addition to the monomers 1 (k_{31}) and 2 (k_{32}). The present study was undertaken to provide further support of copolymerization by the

alternating inter-intramolecular mechanism, and to study the effect of electronic character of the monoolefin on the relative rate of cyclization. The 1,4-diene used was divinyl ether; the monoolefins used were nitrogen-containing compounds. Copolymerization of the following systems was studied: (A) divinyl ether with fumaronitrile, (B) divinyl ether with tetracyanoethylene, and (C) divinyl ether with 4-vinylpyridine.

EXPERIMENTAL

Materials

Divinyl ether was obtained from Merck, Sharp and Dohme and was freshly distilled (under nitrogen) before copolymerization (b.p. 29°C.). Fumaronitrile was obtained from Monsanto Chemical Company and was carefully recrystallized from benzene and dried under vacuum (m.p. 96°C.). Tetracyanoethylene was obtained from Aldrich Chemical Company and was recrystallized from chlorobenzene. This yielded a white-grey precipitate having m.p. 200°C. after drying overnight in a vacuum oven at 50°C. 4-Vinylpyridine was obtained from K and K Laboratories and was freshly distilled (b.p. 60°C./13 mm.) through a 12-in. Vigreux column. Dimethylformamide (Fisher reagent) was purified in the following way: 10% methanol was added and the solution was distilled under normal pressure to remove the methanol. Dimethylformamide was distilled under reduced pressure (b.p. 76°C./39 mm.). Before using 1% P_2O_5 was added, and the mixture was stirred for 0.5 hr., then distilled under reduced pressure in a nitrogen atmosphere. Benzene (Fisher reagent) was dried over sodium and distilled before using.

Polymerization

For each system, the monoolefin was weighed and the divinyl ether measured, volumetrically directly into separate 25-ml. volumetric flasks and each diluted to volume with the solvent. The total monomer concentration was 3 mole/l. The concentration of azobisisobutyronitrile (AIBN) used as initiator was 1% by weight of the total monomer concentration. The solutions of monoolefin and AIBN were transferred to 12-mm. glass tubes, and the tubes were flushed with nitrogen and cooled in a Dry Ice-acetone bath, after which the solution of divinyl ether was added. When the mixture was nearly solid, the tubes were sealed. The copolymerizations of fumaronitrile and 4-vinylpyridine with divinyl ether were carried out at $60 \pm 0.05^\circ\text{C}$. The copolymerizations of tetracyanoethylene with divinyl ether were carried out at $50 \pm 0.05^\circ\text{C}$. Reaction time was such as to allow about 10% conversion. Total volume for each polymerization was approximately 10 ml.

The polymers were precipitated in a nonsolvent, filtered through fritted glass filter funnels, and dried in a vacuum oven at 50°C. for 48 hr. prior to analysis. The fumaronitrile copolymers which were prepared in dimethylformamide were precipitated in methanol, washed with methanol and then

ethyl ether. The tetracyanoethylene copolymers, prepared in dimethylformamide, were precipitated in diethyl ether. The 4-vinylpyridine copolymers separated from solution during their polymerization in benzene and were then filtered and washed with ethyl ether. Their color varied gradually from red to yellow when the concentration of 4-vinylpyridine was decreased.

Analysis

The compositions of the copolymers were calculated from their nitrogen and unsaturation content.

Nitrogen. The analyses of nitrogen were done by the Kjeldahl method. The method was tested on polyacrylonitrile for the fumaronitrile and tetracyanoethylene copolymers, and on polyvinylpyridine for the copolymer of 4-vinylpyridine. A sample of each series was sent for verification to Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

Residual Unsaturation. The determination of unsaturation was carried out in the following way for the fumaronitrile/divinyl ether copolymers: About 30 mg. of polymer was dissolved in acetone and an excess of bromine solution (20%) was added. The olefin was allowed to react with Br_2 for 30 min. The polymer was then reprecipitated in methanol, filtered, and dried. On the resulting polymer, analysis for bromine was carried out by the Volhardt and Schöniger method. The percentage of unsaturation was calculated from the bromine content.

For the tetracyanoethylene-divinyl ether copolymers, determination of unsaturation was carried out by the same method and also by infrared spectroscopy with a Perkin-Elmer Model 21 spectrophotometer, vinyl ethyl ether being used as reference compound.

RESULTS AND DISCUSSION

The compositions of the copolymers have been determined over a wide range of monomer feed compositions.

Divinyl Ether-Fumaronitrile

Table I shows data for the copolymerization of divinyl ether and fumaronitrile. Over a wide range of initial monomer composition, the molar fraction of fumaronitrile in the copolymer lies in the range 0.55–0.63. These values must be compared to 0.67, which is the predicted value for 2:1 molar alternating copolymers. Table I shows also the small amount of residual unsaturation (from 2.0 to 3.5%), thus indicating the high percentage of cyclization. The results are plotted in Figure 1.

The structure of the copolymer was verified by infrared spectra which showed the following absorptions: nitrile, 2260 cm^{-1} ; unsaturated ether, 1220 cm^{-1} (small absorption);¹² and cyclic ether, 1115 cm^{-1} (very strong).¹² The structure of the copolymer is well described by a cyclic repeating unit containing both monomers, alternating with fumaronitrile units, as indicated in the theory.

TABLE I
Divinyl Ether (M_1)-Fumaronitrile (M_2) Copolymers

M_2 (monomer mole fraction)	Reaction time, hr.	Conversion, %	N in the copolymer, % ^a	Unsaturation, % by weight	m_2/m_1 ^b	m_2 (polymer mole fraction)	m_2'/m_2 ^c	η_{red} , dl./g. ^d
0.92	5	7.56	23.4	2.0	0.057	0.626	0.437	
0.8	4	11.39	22.9	2.4	0.066	0.613	0.41	0.154
0.6	2	11.69	22.9	2.45	0.068	0.613	0.41	
0.5	1.5	8.56	22.7 ^e	2.8	0.076	0.607	0.405	0.174
0.25	1.5	7.42	22.6	3.0	0.081	0.604	0.399	
0.15	2	6.71	21.8	3.1	0.08	0.59	0.332	0.138
0.05	2	3.93	20.7	3.5	0.082	0.55	0.242	0.114

^a Nitrogen percentage was corrected on the basis of 95% found for polyacrylonitrile.

^b Ratio of unsaturated ether to total ether.

^c Ratio of noncyclized fumaronitrile to total fumaronitrile in the copolymer.

^d Measured at 25°C. in dimethylformamide, $c = 0.5$ g./dl.

^e Value given by Galbraith Laboratories: 22.71%.

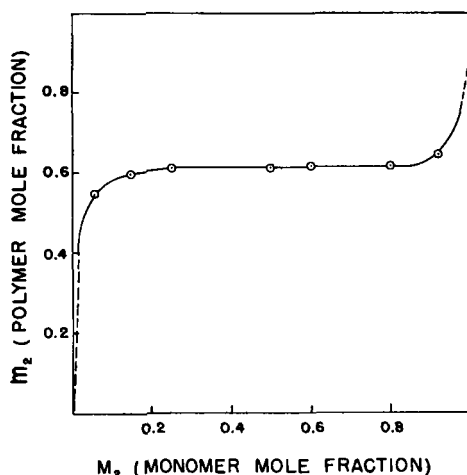


Fig. 1. Divinyl ether (M_1)-fumaronitrile (M_2) copolymers.

The composition of the copolymer was studied as a function of the total monomer feed concentration. The relative composition in monomers was kept constant: $[M_1] = [M_2] = 0.5$. These results are shown in Table II.

In the range $[M_1] + [M_2] = 1.1\text{--}4.5$ mole/l., the composition of the copolymer remains constant. The reactivity ratios r_1 , r_2 , and r_c could be obtained from eq. (3)⁵

$$m_1/m_2 = (1 + M_1r_1/M_2) \times (1 + M_1r_c/M_2) / [r_cM_1/M_2 + r_2M_2/M_1 + 2] \quad (3)$$

by using a digital computer method similar to that applied by Tidwell and Mortimer.¹³ However, since this system approximates an alternating system, in which the molar ratio of olefin to diene approximates 2:0, the results most nearly fit special case (b)⁵ in which both eqs. (1) and (3) reduce to eq. (4).

$$n = 1/2 \quad (4)$$

Also, in this case, it seems that one must assume a kinetic effect of the penultimate unit. Such effects have been investigated for a few sys-

TABLE II
Variation of Total Monomer Concentration for
Divinyl Ether-Fumaronitrile Copolymerization

$[M_1] + [M_2]$, mole/l.	N, % by weight	m_2 (molar fraction in polymer)
1.106	22.8	0.61
3.0	22.7	0.607
4.5	22.47	0.604

tems^{14,15} and in particular for the copolymerization of fumaronitrile with styrene. The authors established that the rates of the copropagation steps are influenced by electrostatic repulsion between the nitrile groups in the monomer and the nonterminal nitrile groups in the attacking polymer radical. They developed a new composition equation, reduced to eq. (5) in the particular case of the fumaronitrile ($r_2 = 0$):¹⁶

$$r_1 = [(n - 1)/x^2 r_1'] + [(n - 2)/x] \quad (5)$$

where $r_1 = k_{111}/k_{112}$ and $r_1' = k_{211}/k_{212}$.

Application of eq. (5) to the fumaronitrile-divinyl ether copolymerization led to negative values of r_1 and r_1' , showing the inadequacy of this kinetic model. The systems to which eq. (5) was applied did not show any cyclization, which is not the case for the fumaronitrile-divinyl ether system. More exact values would be obtained if a new kinetic equation were derived for the divinyl ether-fumaronitrile copolymerization. Such an equation should take into account both cyclization and influence of the penultimate unit in order to give a complete description of the copolymerization.

TABLE III
Divinyl Ether (M_1)-Tetracyanoethylene (M_2) Copolymers

M_2 (monomer mole fraction)	Reaction time, min.	Conversion, %	N, % by weight	m_2 (polymer mole fraction)	η_{red} , dl./g. ^a
0.25	50	5.71	23.69	0.392	0.0514
0.40	60	9.30	25.91	0.442	—
0.50	60	11.51	27.32 ^b	0.477	0.067
0.60	25	6.37	28.51	0.506	—
0.80	30	4.45	31.11	0.574	—
0.90	30	5.75	33.16	0.64	0.0553

^a Solvent: DMF; 25°C.; $c = 0.5$ g./dl.

^b Value given by Galbraith Laboratories: 27.34%.

Divinyl Ether-Tetracyanoethylene

Table III shows data for the copolymerization of divinyl ether and tetracyanoethylene. The copolymer composition was quite different from that expected on the basis of an alternating bimolecular mechanism ($m_2 = 0.67$). Furthermore, the infrared spectrum showed a strong absorption in the 1630 cm^{-1} unsaturation region, suggesting that a cyclization occurred to only a small extent. These results are plotted in Figure 2.

The reactivity ratios r_1 and r_2 were determined by the Alfrey-Price equation, eq. (6).

$$r_2 = \frac{M_1}{M_2} \left[\frac{m_2}{m_1} \left(1 + \frac{M_1}{M_2} r_1 \right) - 1 \right] \quad (6)$$

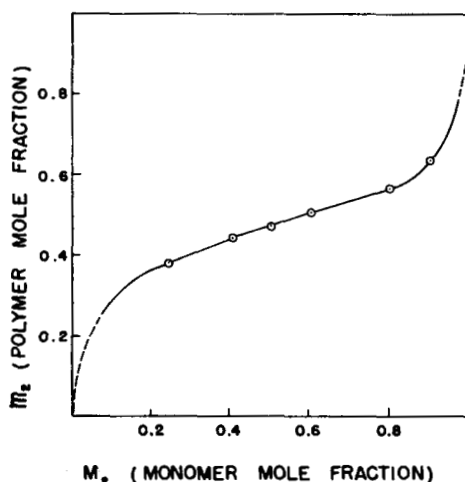


Fig. 2. Divinyl ether (M_1)-tetracyanoethylene (M_2) copolymers.

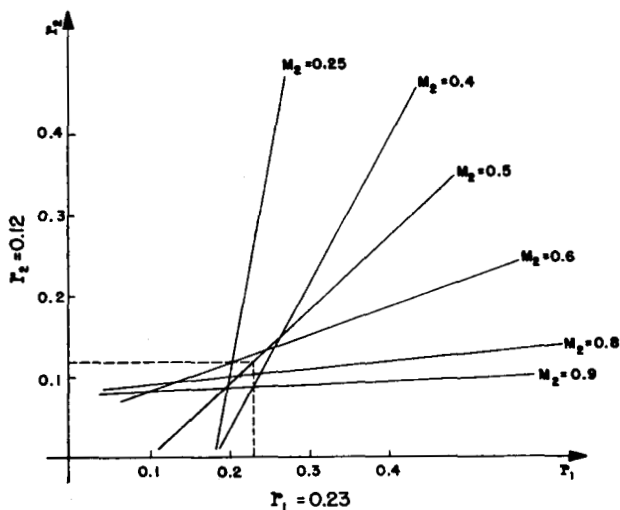


Fig. 3. Evaluation of r_1 and r_2 for divinyl ether-tetracyanoethylene copolymerization

The plot of r_2 against r_1 is shown in Figure 3. The values obtained were $r_1 = 0.23$, $r_2 = 0.12$. The linear method of Fineman and Ross¹⁷ gave the values $r_1 = 0.2$; $r_2 = 0.11$ (Fig. 4).

Divinyl Ether-Vinylpyridine

Table IV shows data for the copolymerization of divinylether and 4-vinylpyridine. The mole fraction of 4-vinylpyridine in the copolymer lies between 0.85 and 0.998 indicating a high value of r_2 . These results are plotted in Figure 5.

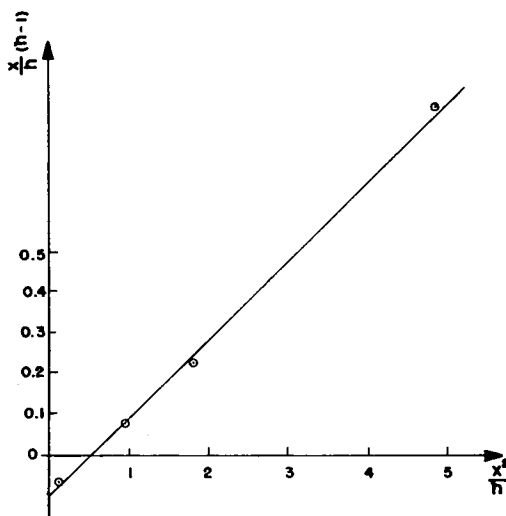


Fig. 4. Evaluation of r_1 and r_2 by Fineman and Ross method for divinyl ether-tetracyanoethylene copolymerization. $(x/n)(n-1) = (x^2/n)(r_1 - r_2)$; $r_1 = 0.2$; $r_2 = 0.1$.

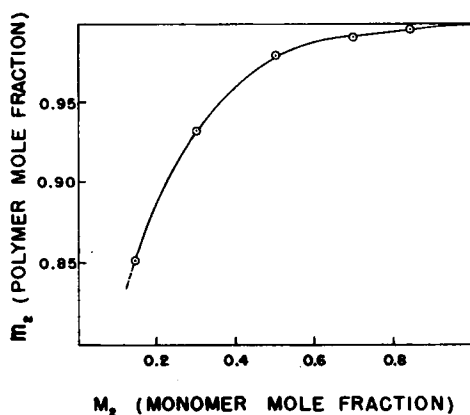


Fig. 5. Divinyl ether (M_1)-4-vinylpyridine (M_2) copolymers.

An attempt to use the digital computer method⁵ for obtaining values for the reactivity ratios, r_1 , r_2 , and r_c , from eq. (3) gave negative values for r_1 or r_2 , depending upon the initial estimates. However, when $1/n$ ($= [m_2]/[m_1]$) was plotted against $1/x$ ($= [M_2]/[M_1]$), using the results from Table IV (the last point was neglected since a very small error in determining $[m_2]$ results in an enormous difference in $1/n$) a straight line was obtained with an intercept of 2.0 as predicted from eq. (7).

$$n = 1/[(r_2/x) + 2] \quad (7)$$

Equation (7) is the form to which eq. (1) reduces in the special case when the diene has a negligible tendency to add to its own radical, that is,

TABLE IV
 Divinyl Ether (M₁)-4-Vinylpyridine (M₂) Copolymers

M ₂ (monomer molar fraction)	Reaction time, hr.	Conversion, %	N, % by weight ^a	m ₂ (polymer molar fraction)
0.15	5	6.1	11.9	0.848
0.30	4	5.6	12.45	0.931
0.50	1.3	3.68	13.1 ^b	0.975 ^c
0.70	2	9.65	13.2	0.987
0.85	1	7.53	13.3	0.998

^a Percentage of nitrogen was corrected on the basis of the calculated nitrogen percentage in 4-vinylpyridine homopolymer, and of the nitrogen percentage found: 12.65%.

^b Value given by Galbraith Laboratories: 12.40%.

^c $\eta_{\text{red}} = 0.30$ dl./g. at 25°C. in DMF for the concentration $c = 0.5$ g./dl.

$r_1 \simeq r_c \simeq 0$, and there is also predominant cyclization. The slope of the line gave a value of 32.0 for r_2 . It is reasonable to assume that under these conditions, divinyl ether has little tendency to add to its own radical, and since crosslinking was not observed, that there was also predominant cyclization.

The monomer reactivity ratios, r_1 and r_2 were also estimated by assuming $r_c \simeq r_1$, and substituting r_1 for r_c in eq. (3). Plots of r_1 versus r_2 were then made. Each experiment with a given feed ratio gives a curved line; the intersection of several of these lines allows an approximate evaluation of r_1 and r_2 . By use of this method, r_1 was found to be 0.032 and r_2 was found to be 32.1.

From the results obtained it is interesting to compare the behavior of *p*-chlorostyrene,¹⁸ 4-vinylpyridine, acrylonitrile,⁵ fumaronitrile, and tetracyanoethylene in their copolymerization with divinyl ether, as shown in Table V.

The ease with which divinyl ether adds to the monoolefins increases from 4-vinylpyridine to tetracyanoethylene. *p*-Chlorostyrene leads only to the homopolymer.¹⁹

The same order of reactivity is obtained when comparing the copolymerization rates as shown in Table VI. Tetracyanoethylene reacts most

 TABLE V
 Relative Composition of the Copolymers ([M] = [M₂] = 0.5)

Monoolefin	m ₁ ^a	e ^b
<i>p</i> -Chlorostyrene ^c	0.0000	-0.3
4-Vinylpyridine	0.025	-0.19
Acrylonitrile	0.251	+1.11
Fumaronitrile	0.393	>1.2
Tetracyanoethylene	0.523	>1.2

^a m₁ is the molar fraction of divinyl ether in the copolymer.

^b Value of e with respect to styrene.²⁰

^c Data of Allen and Butler.¹⁹

TABLE VI
 Relative Copolymerization Rates

Monoolefin ^a	Temp., °C.	Reaction time, min.	Conversion, %
4-Vinylpyridine	60	80	3.68
Fumaronitrile	60	90	8.56
Tetracyanoethylene	50	60	11.56

^a Initial feed monomer molar fraction: $[M_1] = [M_2] = 0.5$.

rapidly with divinyl ether and is incorporated into the copolymer to a greater extent than any other monoolefin studied, and also produces the most nearly alternating copolymer. The electron acceptor effect of the four $\text{—C}\equiv\text{N}$ groups of the tetracyanoethylene decreases the electronic density of the double bond and thus increases the affinity of the divinyl ether for the tetracyanoethylene.

It is interesting to compare these conclusions with the values of e , a measure of polarity. The effect of the cyanide groups becomes obvious when the copolymerization rates are compared with the copolymer compositions. This effect is strengthened when the number of cyanide substituents increases, thus decreasing the electronic density of the double bond to which they are attached and making it more active in its reaction with the diene.

The steric effect does not seem to be very important. Otherwise, the order in the copolymerization rates would be the reverse of that observed. Therefore, the electronic effect is predominant in these systems. The relative rate and composition of the copolymers may be explained on the basis of polarity: the greater the difference in polarity between the two comonomers, the greater the copolymerization rate and the greater the degree of incorporation of monoolefin in the copolymer.

The same explanation may serve to describe the relative importance of the cyclization. It has been observed that the comonomer plays a role in the yield of cyclization of the nonconjugated 1,6-dienes. The larger the

 TABLE VII
 Effect of Polarity Difference of Comonomers on Cyclization of 1,6-Diene

Comonomer	e	Δe	k_c/k_{12}^a
Acrylic anhydride ^b	1.2	0.2	7.1
Methyl methacrylate	1.0		
Styrene	-0.8		
Acrylic anhydride	1.2	2.0	0.25

^a Ratio of the cyclization rate constant of the 1,6-diene to the rate constant of the addition of the 1,6-diene (2) to the monoolefin (1).

^b Data of Smets et al.¹⁰

TABLE VIII
Effect of Polarity Difference of Comonomers on Cyclization in 1,4-Diene

Monoolefin ^a	Cyclization, %
Acrylonitrile ^b	100
Fumaronitrile	96.3
Tetracyanoethylene	18.4

^a Initial monomer concentration: $[M_1] = [M_2] = 0.5$.

^b Data of Barton et al.⁵

difference in polarity between the diene and the monoolefin, the lower the cyclization yield, as shown in Table VII.

In the same way, the percentage of cyclization in the copolymerization of a 1,4-diene with a monoolefin may be related to the polarity difference of the two monomers. It is observed that the percentage of cyclization decreases when the polarity difference between the two monomers increases, as shown in Table VIII.

However, it should be pointed out that for the 1,6-diene, k_c is compared with k_{12} ; and for the 1,4-diene, k_c is compared with k_{31} .⁵ It can be considered that the addition reaction of the radical $m_3\cdot$ and a diene molecule is more favored as the difference in their polarity is increased. This is what is observed upon going from acrylonitrile to tetracyanoethylene. However the steric effect cannot be neglected and probably has an important role in the intermediary step of cyclization. Both factors must be taken into account. Their relative importance is difficult to determine.

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Résumé

La copolymérisation de l'éther divinylque avec le fumaronitrile (A), le tétracyanoéthylène (B) et la 4-vinylpyridine (C) a été étudiée utilisant l'asobisisobutyronitrile comme initiateur. La composition des copolymères a été calculée au départ de leur teneur en azote et en insaturation. Sur une grande gamme de compositions en monomères initiaux la fraction molaire de A dans les copolymères se situe entre 0.55 et 0.63, les copolymères contenaient uniquement 2-3% d'insaturation, ce qui indique un degré élevé de cyclisation. La composition des copolymères de (B) indiquaient une cyclisation peu prononcée ainsi que le montrait la teneur élevée en insaturation des copolymères obtenus. Les valeurs de $r_1 = 0.23$ et $r_2 = 0.12$ ont été obtenues. La fraction molaire de (C) dans les copolymères se situe entre 0.85 et 0.998. En admettant que r_1 est environ égal à r_c est environ égal à 0, et en admettant également qu'il y a essentiellement cyclisation, $r_2 = 32.0$ dans ce cas ci. La différence de composition des copolymères est attribuée à la différence entre les densités électroniques des doubles soudures dans (A), (B) et (C).

Zusammenfassung

Die Copolymerisation von Divinyläther mit Fumaronitril (A), Tetracyanäthylen (B) und 4-Vinylpyridin wurde mit Azobisisobutyronitril als Initiator untersucht. Die Zusammensetzung der Copolymeren wurde aus ihrem Stickstoff- und Doppelbindungsgehalt berechnet. Über einen weiten Bereich der Ausgangszusammensetzung der Monomerenmischung liegt der Molenbruch von (A) in den Copolymeren im Bereich von 0,55 – 0,63 und die Copolymeren enthalten nur 2-3% Doppelbindungen, was für einen hohen Cyclisierungsgrad spricht. Die Zusammensetzung der Copolymeren von (B) zeigte, dass Cyclisierung nur in geringem Ausmass auftritt, da die Copolymeren ziemlich stark ungesättigt waren. Es wurden die Werte $r_1 = 0,23$ und $r_2 = 0,12$ erhalten. Der Molenbruch an (C) in den Copolymeren liegt zwischen 0,85 und 0,998. Für den Fall, dass $r_1 \simeq r_c \simeq 0$ und dass vorwiegend Cyclisierung eintritt beträgt $r_2 = 32,0$. Die Zusammensetzungsunterschiede der Copolymeren werden auf Unterschiede in der Elektronendichte der Doppelbindungen in (A), (B) und (C) zurückgeführt.

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