

## Studies in Cyclocopolymerization. Relative Rates of Addition in the Free Radical-Initiated Copolymerization of 1,4-Dienes and Substituted Olefins\*

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### Synopsis

A general copolymer composition equation is developed for the cyclocopolymerization of 1,4-dienes ( $M_1$ ) and monoolefins ( $M_2$ ). The general equation relates copolymer composition to monomer feed composition in terms of five reactivity ratio parameters. When cyclization is very rapid relative to other chain propagation steps the general equation simplifies to the form:  $n = (1 + r_1x)(1 + r_cx + (r_2/x) + 2)$ , where  $n = [m_1]/[m_2]$  in the copolymer,  $x = [M_1]/[M_2]$  in the monomer feed, and  $r_1$ ,  $r_2$ , and  $r_c$  are reactivity ratios for the chain propagation steps of diene, monoolefin, and cyclized radicals, respectively. The theory is applied to the free radical initiated copolymerization of (A) divinyl ether/maleic anhydride, (B) 1,4-pentadiene/maleic anhydride, (C) divinyl ether/*N*-phenylmaleimide, (D), divinyl ether/acrylonitrile; and (E) 1,4-pentadiene/acrylonitrile. Systems A, B, and C form alternating copolymers of composition  $n = 0.5$ . For system D,  $r_1 = 0.024$ ,  $r_2 = 0.938$ ,  $r_c = 0.017$ . For system E,  $r_1 \simeq r_c \simeq 0$ ,  $r_2 = 1.13$ .

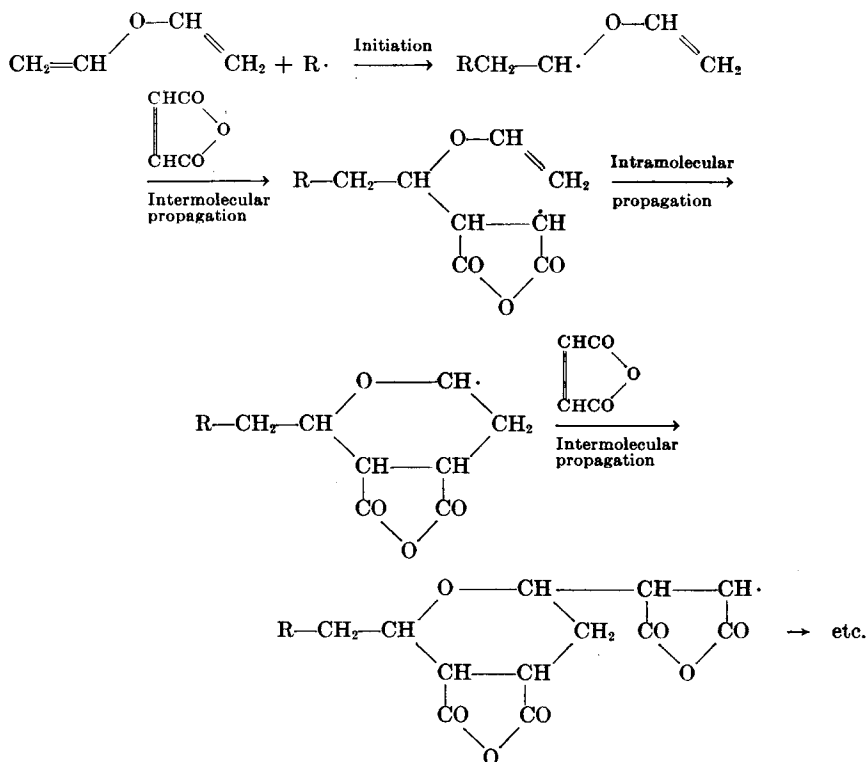
### INTRODUCTION

It has been observed that certain 1,4-dienes are capable of copolymerizing with certain monoolefins by a bimolecular alternating inter-intramolecular mechanism.<sup>1-5</sup> In these copolymers a cyclic repeating unit containing both monomers alternates with monoolefin units. The example of copolymerization of divinyl ether and maleic anhydride, shown at the top of the following page, illustrates the general course of the reaction.

General copolymer composition equations have been developed<sup>6,7</sup> for the cyclocopolymerization of 1,6-dienes and monoolefins, when the diene radical can cyclize directly to form a unimolecular cyclic repeating unit. It has been shown that these equations approximate to the classical binary copolymer composition equation when the cyclization of diene radicals is very rapid.

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The present work describes a general copolymer composition equation applicable to the cyclocopolymerization of 1,4-dienes and monoolefins where the cyclic repeating unit is bimolecular in construction. This equation does not approximate to the classical binary equation when cyclization is very rapid. The relevance of this theory is demonstrated experimentally for the free radical initiated copolymerization of divinyl ether/maleic anhydride, 1,4-pentadiene/maleic anhydride, divinyl ether/*N*-phenylmaleimide, divinyl ether/acrylonitrile, and 1,4-pentadiene/acrylonitrile.

Although the theory is developed for free radical... initiated copolymerization, it should also apply to appropriate ionically initiated systems and to addition copolymerizations involving nonolefinic unsaturated groups such as epoxide or carbonyl groups, if the same kinetic assumptions apply.

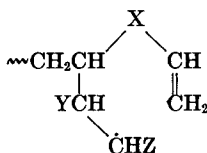
## THEORY

The kinetic scheme considered is shown in eqs. (1)–(9).

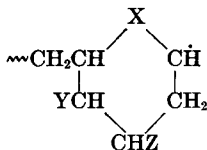




$M_1$  is the diene  $\text{CH}_2=\text{CH}-\text{X}-\text{CH}=\text{CH}_2$ , where X is  $\text{CH}_2$ , O,  $\text{SO}_2$ , etc.  $M_2$  is the monoolefin,  $\text{CHY}=\text{CHZ}$ . The  $m_1$  is the radical  $\sim\text{CH}_2\dot{\text{C}}\text{HXCH}=\text{CH}_2$ ,  $m_2$  is the radical  $\sim\text{CHY}\dot{\text{C}}\text{HZ}$ ,  $m_3$  is the radical



and  $m_c$  is the cyclized radical



The fate of the intermediate radical,  $m_3$ , is governed by the relative rate of cyclization ( $k_c$ ) and addition to monomers 1 ( $k_{31}$ ) and 2 ( $k_{32}$ ).

Although a six-membered ring is normally the most likely product of cyclization of  $m_3$ , if the terminal methylene in  $m_3$  were hindered by bulky substituents or if it were conjugated with an aromatic group, a five-membered ring might be favored. This should not, however, influence the overall kinetics.

If penultimate group effects and crosslinking reactions are neglected, the relative rate of addition of  $M_1$  and  $M_2$  is given by:

$$\begin{aligned} \frac{d[M_1]}{d[M_2]} &= \frac{d[M_1]/dt}{d[M_2]/dt} = \frac{[M_1]}{[M_2]} \\ &\times \frac{\{k_{11}[m_1] + k_{21}[m_2] + k_{31}[m_3] + k_{c1}[m_c]\}}{\{k_{12}[m_1] + k_{22}[m_2] + k_{32}[m_3] + k_{c2}[m_c]\}} \quad (10) \end{aligned}$$

or

$$n = \frac{d[M_1]}{d[M_2]} = \frac{K_{11}[m_1] + K_{21}[m_2] + K_{31}[m_3] + K_{c1}[m_c]}{K_{12}[m_1] + K_{22}[m_2] + K_{32}[m_3] + K_{c2}[m_c]} \quad (11)$$

where  $K_{ij} = k_{ij}/[M_j]$ .

Making the stationary state assumption that the concentrations of radicals  $[m_1]$ ,  $[m_2]$ , and  $[m_3]$  are constant, leads to:

$$K_{12}[m_1] - K_{21}[m_2] - K_{31}[m_3] = K_{e1}[m_c] \quad (12)$$

$$K_{21}[m_2] - K_{32}[m_3] = K_{e2}[m_c] \quad (13)$$

$$k_c[m_3] = (K_{e1} + K_{e2})[m_c] \quad (14)$$

Solving for  $[m_1]$ ,  $[m_2]$ , and  $[m_3]$ , we have:

$$[m_1] = ([m_c]/K_{12}kc)(K_{e1} + K_{e2})(K_{31} + K_{32} + k_c) \quad (15)$$

$$[m_2] = ([m_c]/K_{21}k_c)\{K_{e2}kc + K_{32}(K_{e1} + K_{e2})\} \quad (16)$$

$$[m_3] = ([m_c]/kc)(K_{e1} + K_{e2}) \quad (17)$$

Substituting eqs. (15)–(17) into eq. (11) and simplifying gives:

$$n = \frac{\frac{K_{11}}{K_{12}} \left(1 + \frac{K_{31} + K_{32}}{kc}\right) + \frac{K_{31} + K_{32}}{kc} + 1}{1 + \frac{K_{31} + K_{32}}{kc} + \frac{K_{32}}{kc} \left(\frac{K_{22}}{K_{21}} + 1\right) + \left(\frac{K_{22}}{K_{21}} + 1\right) \left(\frac{K_{e1}}{K_{e2}} + 1\right)^{-1}} \quad (18)$$

This may be further simplified to give:

$$n = \frac{(1 + r_1x)\{1/[M_2] + (1/a)(1 + x/r_3)\}}{(1/a)\{(x/r_3) + (r_2/x) + 2\} + (1/[M_2])\{1 + (1 + r_2/x)(1 + r_3x)^{-1}\}} \quad (19)$$

where  $x = [M_1]/[M_2]$ ,  $r_1 = k_{11}/k_{12}$ ,  $r_2 = k_{22}/k_{21}$ ,  $r_3 = k_{32}/k_{31}$ ,  $r_c = k_{e1}/k_{e2}$ ,  $a = k_c/k_{32}$ .

Equation (19) is a differential copolymer composition equation which is applicable to the proposed scheme of cyclocopolymerization. The equation may be applied by putting  $n \simeq [m_1]/[m_2]$ , the fractional ratio of monomers combined in the copolymer at low conversions.

A similar equation can be derived relating the relative rate of addition of diene and the rate of cyclization, as follows. From eq. (10):

$$d[M_1]/dt = K_{11}[m_1] + K_{21}[m_2] + K_{31}[m_3] + K_{e1}[m_c] \quad (20)$$

Substituting eq. (12) in eq. (20) gives:

$$d[M_1]/dt = (K_{11} + K_{12})[m_1] \quad (21)$$

Then substituting eq. (15) in eq. (21) gives:

$$d[M_1]/dt = [(K_{11} + K_{12})/K_{12}kc](K_{e1} + K_{e2})(K_{31} + K_{32} + kc)[m_c] \quad (22)$$

Now the rate of cyclization is given by:

$$d[M_c]/dt = kc[m_3]$$

which may be substituted in eq. (17) to give:

$$d[M_c]/dt = (K_{e1} + K_{e2})[m_c] \quad (23)$$

From eqs. (22) and (23) we have:

$$\begin{aligned} d[M_1]/d[M_e] &= [(K_{11} + K_{12})/K_{12}k_e](K_{31} + K_{32} + k_e) \\ &= (r_1x + 1)\{([M_1]/r_3a) + ([M_2]/a) + 1\} \end{aligned} \quad (24)$$

Equation (24) applies at low conversions, where  $d[M_1]/d[m_e] \simeq [m_1]/[m_e]$ , the ratio of the total fraction of diene (unsaturated and cyclic) to the fraction of diene in cyclized units, in the copolymer.

If precise analytical methods are available for determining both the total fraction of diene in the copolymer and the fraction of either cyclic units or pendant vinyl groups, then by making a series of such measurements for different initial monomer feed compositions, values for  $r_1$ ,  $r_3$ , and  $a$  could be obtained from eq. (24). Then the remaining two parameters,  $r_2$  and  $r_e$  could be obtained from eq. (19).

In certain special cases eq. (10) may be approximated to simpler forms, as in the following examples.

(a) If  $k_e \gg k_{32}$  so that  $a$  is very large and cyclization is the predominant reaction of the radicals  $m_3$ , then eq. (19) gives:

$$n = (1 + r_1x)(1 + r_ex)/[r_ex + (r_2/x) + 2] \quad (25)$$

This is equivalent to considering the addition of monoolefin to diene radicals to be a concerted bimolecular step proceeding through a cyclic transition state and producing the cyclic repeating unit.

(b) If in addition there is a strong alternating tendency so that  $(r_1, r_2, r_e) \rightarrow 0$  then eq. (25) reduces in the limit to  $n = 1/2$ . This predicts an alternating copolymer composition of 2:1 molar in contrast to 1:1 for the similar limiting case of the classical binary copolymer composition equation.

(c) If the diene has a negligible tendency to add to its own radicals and  $r_1 \simeq r_e \simeq 0$ , and there is also predominant cyclization, then eq. (25) gives:

$$n = 1/[(r_2/x) + 2] \quad (26)$$

A plot of  $1/n$  against  $1/x$  should be linear with a slope  $r_2$  and an intercept 2.0.

The application of each of these special cases of the theory is shown for experimental systems in the section on results.

It has been suggested<sup>8</sup> that in reactivity ratio calculations involving nonconjugated dienes the diene concentration should be expressed in equivalents of double bond per liter and not moles per liter. This is so only if the double bonds of the diene act as independent units, and then, to be rigorous, the diene concentration should still be expressed in moles/liter but there should be statistical factors of 2 associated with each of the rate expressions involving diene. This factor does affect the magnitude of the reactivity ratios but not the analytical form of the copolymer composition equation. For example, in eq. (25),  $r_1 = 2r_1^*$ ,  $r_e = 2r_e^*$ ,  $r_2 = r_2^*/2$ , where  $r_n$  is derived for  $[M_1]$  in moles/liter, and  $r_n^*$  is derived with  $[M_1]$  in equivalents double bond/liter.

## EXPERIMENTAL

### Materials

Monomers and solvents were all readily obtainable in high purity directly or after applying conventional purification techniques.

### Polymerization

The monomers and azobisisobutyronitrile initiator were weighed directly into 25 ml. volumetric flasks and diluted to volume with the solvent. Total monomer concentrations were in the range 2–6 moles/l. The solution was transferred by hypodermic syringe to 9 mm. glass tubes, and the tubes were flushed with nitrogen and sealed. The tubes were heated in a water bath at  $50 \pm 0.05^\circ\text{C}$ ., for the appropriate time. The polymer was precipitated in a nonsolvent and dried in a vacuum oven at  $50^\circ\text{C}$ . for at least 24 hr. prior to analysis.

The acrylonitrile copolymers which were prepared in dimethylformamide solution, were precipitated in water or methanol. The maleic anhydride and *N*-phenylmaleimide copolymers were precipitated in dry heptane or ether. In all cases care was taken to ensure that the isolated polymer was free of solvents and monomers.

In all copolymerization systems except those in DMF solution the copolymer partially precipitated from solution during polymerization, but the copolymer after isolation was soluble in dimethyl formamide.

### Analysis

Elemental analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tennessee. The compositions of the acrylonitrile and *N*-phenylmaleimide copolymers were calculated from their nitrogen content. The compositions of the other copolymers were calculated from their carbon and hydrogen contents.

The copolymers containing maleic anhydride were found almost invariably to be associated with water. This water content was up to 5% w/w and was probably present combined in maleic acid units. From C and H contents, the fractions of combined water and hence the true copolymer compositions were calculated.

Some of the maleic anhydride copolymers were completely hydrolyzed by heating in water. The clear solutions were evaporated to dryness and dried to constant weight *in vacuo* at  $60^\circ\text{C}$ . These hydrolyzed samples were then analyzed for C and H and the calculated compositions in terms of maleic acid units were in good agreement with those calculated for the anhydride copolymers after correction for water content.

## RESULTS AND DISCUSSION

The relative compositions of the copolymers from various systems have been determined at low conversions and over a wide range of initial mon-

omer feed compositions. The initiator used throughout was azobisisobutyronitrile (AIBN) and the polymerizations were run at 50°C.

Table I shows data for the copolymerization of 1,4-pentadiene and maleic anhydride in tetrahydrofuran.

TABLE I  
1,4-Pentadiene ( $M_1$ )-Maleic Anhydride ( $M_2$ ) Copolymers<sup>a</sup>

$M_2$ (monomer) mole frac.	$m_2$ (polymer) mole frac.	Reaction time, hr.	Conversion, %
0.249	0.67	17.5	11.1
0.335	0.70	17.5	14.4
0.500	0.655	17.5	20.5
0.667	0.67	17.5	23.7
0.833	0.64	23.0	22.0

<sup>a</sup> [AIBN] =  $7.3 \times 10^{-3}$  mole/l.; total initial monomer concentration: 1.6–3.1 mole/l.

Over a wide range of initial monomer feed composition,  $[m_2]$  in the copolymer lies in the range 0.64–0.70 with a mean value of 0.67 which is the predicted value for 2:1 molar alternating copolymers, the special case (b) of the theory section.

Data for the copolymerization of divinyl ether and maleic anhydride are given in Table II.

TABLE II  
Divinyl Ether ( $M_1$ )-Maleic Anhydride ( $M_2$ ) Copolymers<sup>a</sup>

$M_2$ (monomer) mole frac.	$m_2$ (polymer) mole frac.	[AIBN] $\times$ $10^3$ , mole/l.	Reaction time, hr.	Conversion, %
0.175	0.70	6.0	3.5	4.5 <sup>b</sup>
0.484	0.70	5.4	3.5	5.7
0.504	0.69 <sup>c</sup>	5.9	5.5	4.0
0.683	0.70	9.8	3.5	3.3
0.904	0.65	6.6	52.5	4.2
0.976	0.65	8.7	52.5	4.1

<sup>a</sup> Total initial monomer concentration: 2.0–2.8 mole/l.

<sup>b</sup>  $[\eta]_{inh} = 0.505$ .

<sup>c</sup> Calc. from standard base titration.

Again over a wide variation in initial monomer feed composition, the copolymer composition is approximately constant at 2:1 molar. The mean value for  $[m_2]$  (mole frac.) in the copolymer is 0.68.

Table III shows results from the copolymerization of divinyl ether and *N*-phenylmaleimide.

For the three experiments the mean value of  $[m_2]$  is 0.70 mole fraction, which is within 5% of the predicted value of 0.67 for alternating copolymers.

TABLE III  
 Divinyl Ether ( $M_1$ )-*N*-Phenylmaleimide ( $M_2$ ) Copolymers<sup>a</sup>

$M_2$ (monomer) mole frac.	$m_2$ (polymer) mole frac.	(AIBN) $\times$ $10^3$ , mole/l.	Reaction time, hr.	Yield, %	$[\eta]_{inh}$
0.166	0.720	2.9	$\sim 30$	34.3	—
0.500	0.674	3.2	$\sim 30$	14.2	0.23
0.665	0.717	2.4	$\sim 30$	10.8	0.27

<sup>a</sup> Total initial monomer concentration 1.6–2.4 mole/l.

The overall range in values of  $[m_2]$  for all of the three copolymerization systems considered above is 0.64–0.72 which is  $\pm 4.5\%$  of the theoretical value of 0.67, demonstrating the strong tendency in these copolymerizations to form alternating 2:1 copolymers.

Systems of the type under consideration which do not form constant composition copolymers but where cyclization predominates over side reactions (branching or crosslinking) should be described by eq. (25) at low conversions. The copolymerization of divinyl ether and acrylonitrile appears to be an example of this sort of behavior. Figure 1 illustrates the best fit of the data for this system to eq. (25), obtained by using a digital computer method similar to that applied by Tidwell and Mortimer<sup>9</sup> for the classical binary copolymer composition equation.

The method is essentially a least-squares fit of the data to eq. (25) by a nonlinear (Gauss-Newton) procedure, starting from initial estimates of the values of  $r_1$ ,  $r_2$ , and  $r_c$  obtained manually by curve fitting.

The solid line in Figure 1 is drawn for  $r_1 = 0.024$ ,  $r_2 = 0.938$ , and  $r_c = 0.017$ . These are the values for which  $\sum \Delta^2$ , the sum of the squares of the

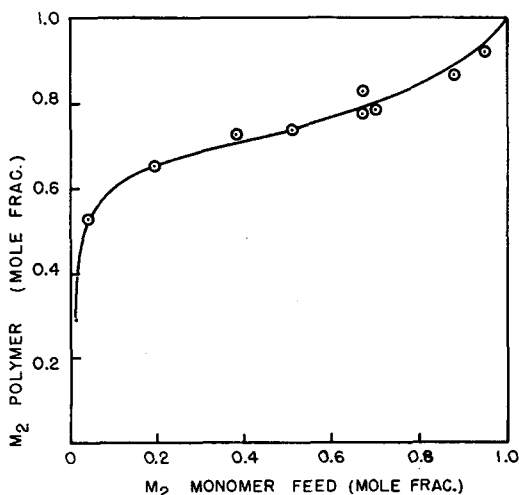


Fig. 1. Divinyl ether ( $M_1$ )-acrylonitrile ( $M_2$ ) copolymers. Points are experimental. Line calculated for:  $r_1 = 0.024$ ;  $r_2 = 0.938$ ;  $r_c = 0.017$ .



differences between observed and computed values of  $n$  was a minimum. For the initial estimates  $r_1 = 0.04$ ,  $r_2 = 0.90$ , and  $r_c = 0.01$ ,  $\sum \Delta^2$  was reduced from 0.246462 to 0.0851882 in three iterations of the computing cycle.

Attempts to fit data for the copolymerization of 1,4-pentadiene and acrylonitrile in dimethylformamide solution to eq. (25) by the method described above led to extremely low or negative values for  $r_1$ , depending on the initial estimates. Since 1,4-pentadiene does not homopolymerize under these conditions it was thought that this may be a case where cyclization is predominant but  $r_1 \approx 0$ , so that eq. (26) should fit the data.

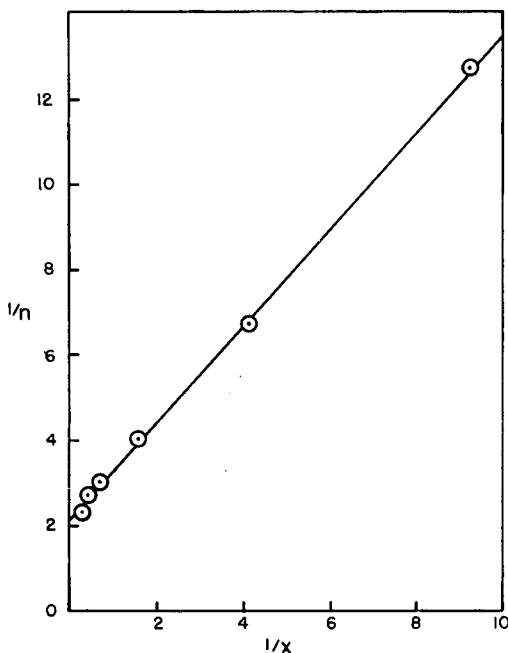


Fig. 2. 1,4-Pentadiene ( $M_1$ )-acrylonitrile ( $M_2$ ) copolymers.  $r_2 = 1.129$ .

In Figure 2 a plot is shown of  $1/n (= [m_2]/[m_1])$  against  $1/x (= [M_2]/[M_1])$  for these results. The plot is linear as predicted. The line in Figure 2 is the best fit for the experimental points from a linear regression computation and has a slope  $r_2 = 1.13$ . The intercept at  $1/n = 2.15$  is close to the theoretical 2.00. It is interesting to note that the equivalent limiting case ( $r_1 = 0$ ) of the classical binary equation predicts that  $1/n$  should vary linearly with  $1/x$  but that the intercept should be 1.00, and it is clear that this case does not fit the present results.

In all of the copolymerization systems considered above the proposed cyclic structure of the copolymers is supported by their solubility in dimethylformamide, the absence of gelation even at high conversion under the conditions of these experiments, and the presence of little or no ab-

sorption in the infrared at  $6.1\mu$  for C = C. Further confirmation of the cyclic structure of the copolymers has been obtained by Butler.<sup>5</sup>

The fact that our theoretical expressions in their respective limiting cases, when cyclization is predominant over linear propagation of the radicals  $m_3$ , adequately describe the experimental data provides strong support for believing that the postulated mechanism of cyclocopolymerization is essentially correct.

When further values of reactivity ratios for similar systems become available, a comparison of their magnitudes should give valuable information on the influence of the structure of the monomers on the structure of the copolymers. It would be particularly interesting if some data could be fitted to the general equations, eqs. (19) and (24), giving the relative rates of cyclization and linear propagation.

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The digital computer program was written and run by Mrs. Eleanore Todarro at the University of Florida Computing Center.

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### Résumé

On a développé une équation générale pour la composition des copolymères obtenus dans la cyclocopolymérisation des 1,4-diènes ( $M_1$ ) et des monooléfines ( $M_2$ ). L'équation générale relie la composition du copolymère à la composition du mélange réactionnel en employant cinq paramètres du rapport de réactivité. Quand la cyclisation est très rapide par rapport aux autres étapes de propagation de chaîne, l'équation générale devient plus simple:  $n = (1 + r_1x)(1 + r_2x)/((r_2x + (r_2/x) + 2)$  où  $n = (m_1)/(m_2)$  dans le copolymère,  $x = (M_1)/(M_2)$  dans le mélange réactionnel et  $r_1$ ,  $r_2$ , et  $r_c$  sont les rapports de réactivité pour les étapes de propagation de la chaîne du diène, de la monooléfine et des radicaux cyclisés respectivement. On a appliqué la théorie à la copolymérisation, initiée par des radicaux libres, des systèmes (A) éther divinylque/anhydride maléique (B), 1,4-pentadiène/anhydride maléique (C) éther divinylque/*N*-phenylmalimide (D) éther divinylque/acrylonitrile et (E) 1,4-pentadiène/acrylonitrile. Les systèmes A, B et C donnent des copolymères alternés de composition  $n = 0.5$ . Pour le système D,  $r_1 = 0.024$ ,  $r_2 = 0.938$ ,  $r_c = 0.017$ . Pour le système E,  $r_1 \simeq r_c \simeq 0$ ,  $r_2 = 1.13$ .

### Zusammenfassung

Eine allgemeine Copolymerzusammensetzungsgleichung wird für die Cyclocopolymerisation von 1,4-Dienen ( $M_1$ ) und Monoolefinen ( $M_2$ ) entwickelt. Die allgemeine Gleichung bildet eine Beziehung zwischen der Copolymerzusammensetzung und der Zusammensetzung des Monomeransatzes mit 5 Reaktivitätsverhältnisparametern. Bei im Verhältnis zu den anderen Kettenwachstumsschritten sehr rascher Cyclisierung nimmt die allgemeine Gleichung folgende einfache Form an:  $n = (1 + r_1x)(1 + r_2x)/[r_2x + (r_2/x) + 2]$ , wo  $n = m_1/m_2$  im Copolymeren,  $x = [M_1]/[M_2]$  im Monomeransatz und  $r_1$ ,  $r_2$ , und  $r_c$  die Reaktivitätsverhältnisse für den Kettenwachstumsschritt des Diens, des Monoolefins bzw. der cyclisierten Radikale sind. Die Theorie wird auf die radikalisch gestartete Copolymerisation von Divinyläther/Maleinsäureanhydrid (A), 1,4-Pentadien/Maleinsäureanhydrid (B), Divinyläther/*N*-Phenylmaleinimid (C), Divinyläther/Acrylnitril (D) und 1,4-Pentadien/Acrylnitril (E) angewendet. Die Systeme A, B, und C bilden alternierende Copolymere mit der Zusammensetzung  $n = 0,5$ . Für das System D ist  $r_1 = 0,024$ ,  $r_2 = 0,938$ ,  $r_c = 0,017$ . Für das System E ist  $r_1 \cong r_c \cong 0$  und  $r_2 = 1,13$ .

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