

## Copolymerization Studies. III. Reactivity Ratios of Model Ethylene Copolymerizations and Their Use in $Q$ - $e$ Calculations

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### Synopsis

Monomer reactivity ratios for the copolymerization of ethylene ( $M_2$ ) with *n*-butyl acrylate, vinyl chloride, vinyl acetate, and vinyl fluoride have been measured at 1000 atm. The respective values and the experimental temperatures are  $r_1 = 11.9$ ,  $r_2 = 0.03$ , 70°C.;  $r_1 = 3.6$ ,  $r_2 = 0.24$ , 90°C.;  $r_1 = 1.08$ ,  $r_2 = 1.07$ , 90°C.;  $r_1 = 0.16$ ,  $r_2 = 4.39$ , 160°C. Price  $Q$  and  $e$  values for ethylene calculated from these reactivity ratios, uncorrected for differences in reaction pressure, are 0.03 and  $-0.43$ , respectively. New  $Q$  and  $e$  values ( $Q_0$  and  $e_0$ ) for these four comonomers were calculated on the basis of ethylene rather than styrene as the reference monomer. Assuming that the  $Q_0$  and  $e_0$  values for ethylene are 1.0 and zero, respectively, the monomer's  $Q_0$  and  $e_0$  value are as follows: *n*-butyl acrylate, 33.3,  $+1.02$ ; vinyl chloride, 4.2,  $+0.37$ ; vinyl acetate, 0.93,  $\sim 0$ ; vinyl fluoride, 0.25,  $+0.6$ . These  $Q_0$  and  $e_0$  values give calculated reactivity ratios which are in reasonable agreement with experimental ones. Good agreement is also obtained when the  $r_2$  value for the vinyl acetate/ethylene copolymerization is compared with the directly determined rate constant ratio for the addition of an ethyl radical to ethylene and to vinyl acetate, respectively, calculated from previously published data.

The free-radical polymerization of ethylene has been studied by a number of workers at autogeneous as well as high pressures.<sup>1-3</sup> Although the mechanism for the high pressure, oxygen-initiated reaction has not been precisely established,<sup>4</sup> it appears that the conventional addition polymerization mechanism is applicable to this high pressure reaction when the usual free-radical initiators are used.<sup>5</sup> In studying free-radical copolymerizations of ethylene at high pressures, therefore, one is justified in utilizing the scheme proposed by Mayo and Lewis<sup>6</sup> for relating instantaneous comonomer composition to the instantaneously formed copolymer.

A study of this sort is prompted by a number of considerations. The increasing industrial importance of ethylene copolymers, for instance, demands that accurately known monomer reactivity ratios be obtained. Also, from a theoretical point of view, such a study may be of aid in relating monomer structure to reactivity, since ethylene with its lack of substituent groups is the logical choice for the reference point of such a scheme.

With these views in mind, a study was undertaken to determine the re-

activity ratios involved when ethylene is copolymerized with *n*-butyl acrylate, vinyl acetate, vinyl chloride, and vinyl fluoride under free-radical conditions at 1000 atm. pressure.

## EXPERIMENTAL

### Monomer Purification and Polymerization Procedure

The experimental equipment and the basic experimental methods have been described previously.<sup>7</sup> Vinyl acetate and *n*-butyl acrylate (Union Carbide Chemicals Company) were purified by fractional distillation and center cuts retained for use. Vinyl fluoride (E. I. du Pont de Nemours and Company) was treated by passage through Linde #5A molecular sieves before use, and polymerization grade vinyl chloride (Union Carbide Chemicals Company) was used as obtained. Ethylene was treated for oxygen removal by passing through an activated copper column at 180°C. The oxygen level was reduced to 10 ppm by this treatment.

The liquid comonomers were weighed directly into the open autoclave. The autoclave was then sealed and thoroughly purged with high purity nitrogen (Linde Company) before the introduction of ethylene. The gaseous comonomers were admitted from small tared cylinders after the autoclave had been purged with high purity nitrogen. Pressure was maintained throughout the reaction by pumping the solvent, sulfur-free, toluene. Azobisisobutyronitrile (Westville Laboratories) was the catalyst used in the *n*-butyl acrylate, vinyl acetate, and vinyl chloride copolymerizations; the vinyl fluoride copolymerization was catalyzed by di-*tert*-butyl peroxide (Wallace and Tiernan). In all cases, the polymerizations were carried to less than 10% conversion and in most cases, less than 5%.

### Polymer Isolation and Analysis

The pure copolymers were isolated as previously described.<sup>7</sup> Copolymer analyses were carried out by the appropriate elemental analysis. Carbon and chlorine determinations were made in these laboratories, and fluorine analyses were performed by the Clark Microanalytical Laboratories. The reduced viscosities of all copolymers were 0.2 dl./g. or greater.

## RESULTS AND DISCUSSION

Figures 1 through 4 show the resulting monomer-polymer composition curves for the four copolymerizations studied. In Table I the reactivity ratios, calculated by the method of Fineman and Ross,<sup>8</sup> are given.

From these data several interesting points are immediately apparent. The first is that even though four comonomers widely differing in reactivity were copolymerized with ethylene, three of them gave reactivity ratio products ( $r_1r_2$ ) equal to unity within experimental error and the product for the fourth, butyl acrylate, did not deviate widely from unity. This, of course,

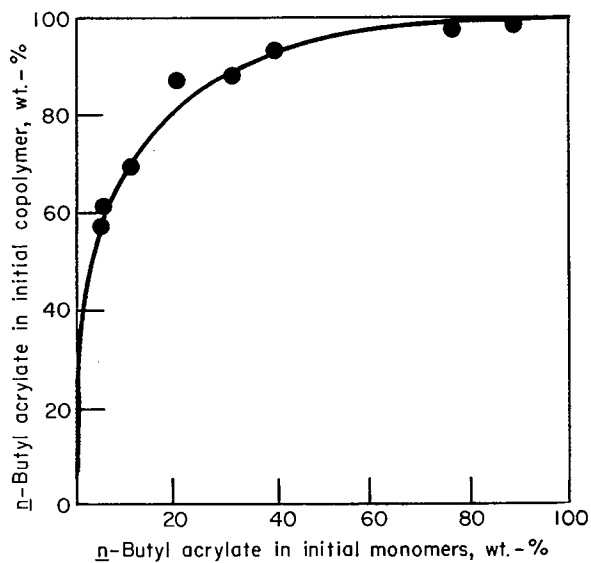
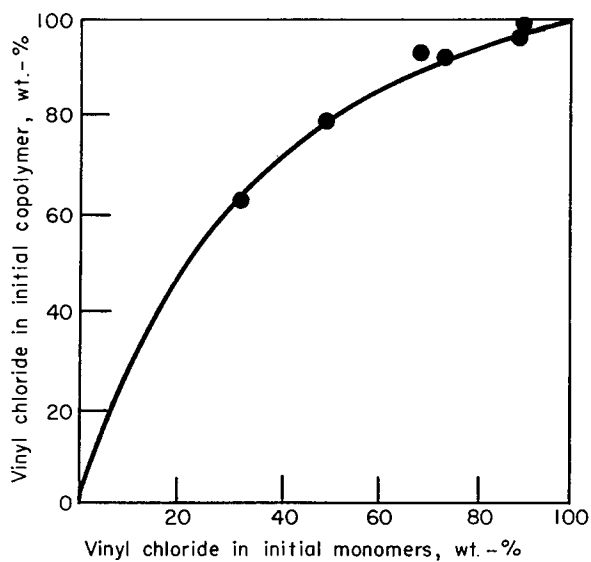
Fig. 1. *n*-Butyl acrylate-ethylene.

Fig. 2. Vinyl chloride-ethylene.

shows that these copolymerizations tend to be ideal and that truly random copolymers, with little alternating tendency, are obtained in ethylene copolymerizations. The implications arising from these phenomena are discussed below in the calculation of structure-reactivity parameters from these reactivity ratio data.

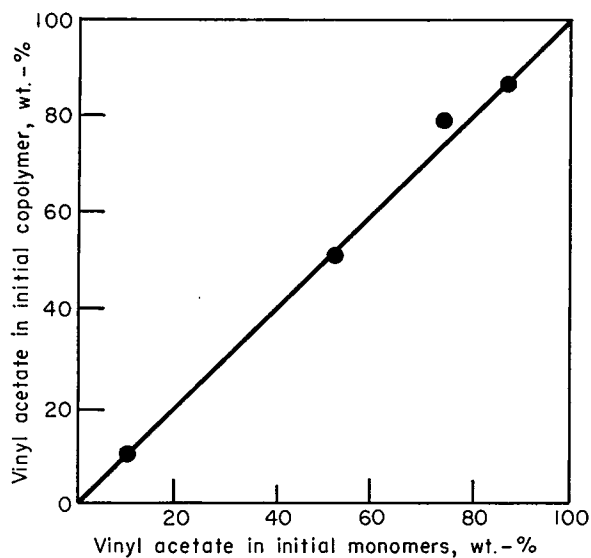


Fig. 3. Vinyl acetate-ethylene.

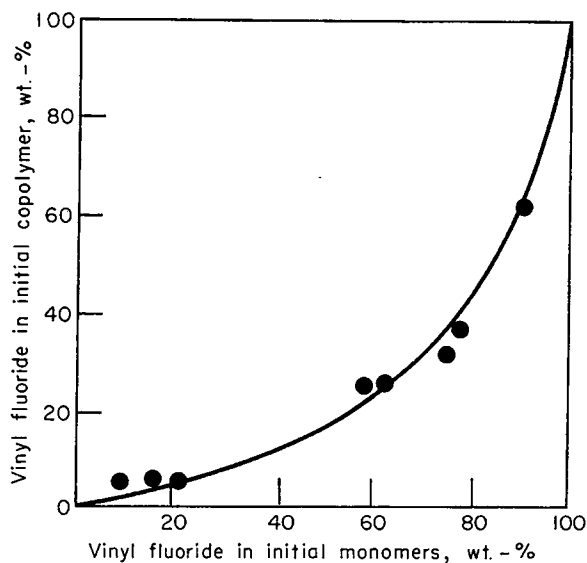


Fig. 4. Vinyl fluoride-ethylene.

Another interesting observation is the wide difference in reactivity of the two vinyl halides, ethylene lying almost midway between vinyl chloride and vinyl fluoride in double-bond reactivity. Although a difference in reactivity between vinyl chloride and vinyl fluoride is to be expected, that one is more and the other less reactive than ethylene is not easily explainable. A third point noticed from these data is that  $r_1 r_2 = 1$  for the ethyl-

TABLE I  
Reactivity Ratios for Various Monomers Copolymerizing with Ethylene ( $M_2$ )

Comonomer	Reaction temp., °C.	$r_1$	$r_2$	$r_1r_2$
<i>n</i> -Butyl acrylate	70	$11.9 \pm 2.5$	$0.03 \pm 0.01$	$0.36 \pm 0.12$
Vinyl chloride	90	$3.60 \pm 0.30$	$0.24 \pm 0.07$	$0.85 \pm 0.26$
Vinyl acetate	90	$1.08 \pm 0.19$	$1.07 \pm 0.06$	$1.16 \pm 0.21$
Vinyl fluoride*	160	$0.16 \pm 0.05$	$4.39 \pm 0.77$	$0.70 \pm 0.25$

\* Recent compositional analysis of the vinyl fluoride copolymers by NMR indicates that  $r_1$  might be as much as 15% higher and  $r_2$  15% lower than indicated in Table I.

ene-vinyl acetate copolymerization. This is rare but certainly not unique for a copolymer system.

### **$Q$ and $e$ Values for Ethylene Based on Styrene ( $Q = 1.0$ , $e = -0.8$ )**

The calculation of Alfrey and Price<sup>9</sup>  $Q$  and  $e$  values for ethylene from these data presents a problem, since it is known that reactivity ratios are affected by the application of high pressures.<sup>7</sup> It has been shown, however, that the methyl methacrylate/acrylonitrile and styrene/acrylonitrile copolymerizations tend simply to become more ideal ( $r_1r_2$  tends toward unity) as pressure is increased to 1000 atm., with the result that the  $e$  values of a comonomer pair tend toward each other with increasing pressure while the  $Q$  values are relatively unaffected.<sup>7</sup> The generality of this phenomenon has not been firmly established, but the possible utility of having even approximate  $Q$  and  $e$  values for ethylene would seem to justify the inclusion of these calculated values at this point. These are presented in Table II.

TABLE II  
 $Q$  and  $e$  Values for Ethylene

Comonomer	$Q$	$e$	Reference
<i>n</i> -Butyl acrylate <sup>a</sup>	0.04	-0.41	Alfrey et al. <sup>10</sup>
Vinyl chloride	0.01	-0.57	Thompson and Raines <sup>11</sup>
Vinyl acetate	0.03	-0.30	Alfrey et al. <sup>10</sup>
Average	0.03	-0.43	

<sup>a</sup> The comparison monomer was actually methyl acrylate.<sup>10</sup>

The very low  $Q$  value for ethylene is certainly to be expected. This finding corresponds with the fact that the activation energy for the addition of an ethyl radical to ethylene is 8.6 kcal./mole,<sup>12</sup> while the addition of an ethyl radical to styrene requires only 4.0 kcal./mole activation energy.<sup>13</sup>

### **$Q$ and $e$ Values Based on Ethylene as the Reference Monomer**

It has been suggested that the double bond of ethylene would provide the most reasonable reference point for the  $Q$ - $e$  scheme;<sup>10</sup> however, no quan-

titative data on ethylene copolymerizations have been available heretofore. Indeed, it would seem that ethylene copolymerizations at high pressure might provide a most useful method for the determination of relative monomer reactivities, since the perturbing effects of alternation due to double-bond polarity differences in the comonomers are at a minimum here. It is of interest, therefore, to determine  $Q$  and  $e$  values for these comonomers using ethylene as the reference monomer.

Since the  $e$  value of a vinyl monomer is related to the electron-donating or electron-withdrawing characteristics of the pendant group on the double bond, one may assume that the  $e$  value for ethylene is zero. Even though subsequent work may indicate that a slight shift in this  $e$  value is desired solely to augment the self-consistency of the scheme, the choice  $e = 0$  for ethylene is advantageous and provides a reasonable starting value from which to work. When the  $Q$  value for ethylene is chosen to be equal to unity, then the equations relating reactivity ratios to  $Q$  and  $e$  values become

$$r_1 = (Q_0)_1 \exp \{ -(e_0)_1^2 \} \quad (1)$$

$$r_2 = 1/(Q_0)_1 \quad (2)$$

for ethylene as monomer 2, where the subscript zero denotes the ethylene-based  $Q$ - $e$  values.

One important advantage which is obtained with the use of this system instead of the styrene-based system is illustrated in eq. (2). Here it is seen that the  $Q_0$  value for a monomer is a rate constant ratio requiring no adjustment due to differences in double-bond polarity as is required when styrene is used as the reference monomer. A comparison of  $Q_0$  values is therefore a more straightforward measure of monomer reactivity than a comparison of  $Q$  values.

It will also be noted that here the copolymerization ideality (the proximity of  $r_1 r_2$  to unity) depends only on the  $e_0$  value of the comonomer, and, since ethylene resides at the zero point of the  $e$  scale, a relatively large (positive or negative)  $e_0$  value is required to remove  $r_1 r_2$  very far from unity. The experimental  $r_1 r_2$  values given in Table I bear this out,  $r_1 r_2$  being close to unity for ethylene copolymerizations with vinyl acetate, vinyl chloride, and vinyl fluoride; only with *n*-butyl acrylate, whose  $e$  value is highly

TABLE III  
Comparison of Calculated  $Q$  and  $e$  Values with Ethylene as the Reference Monomer ( $Q_0$  and  $e_0$ ) with  $Q$  and  $e$  Values with Styrene as the Reference

Monomer	$Q_0$	$e_0$	$Q$	$e$	Reference
<i>n</i> -Butyl acrylate <sup>a</sup>	33.3	+1.02	0.42	+0.6	Alfrey et al. <sup>10</sup>
Vinyl chloride	4.2	+0.37	0.04	-0.17	Thompson and Raines <sup>11</sup>
Vinyl acetate	0.93	~0	0.03	-0.3	Alfrey et al. <sup>10</sup>
Vinyl fluoride	0.25	+0.6	—	—	

<sup>a</sup> Compared with methyl acrylate.

positive, does the reactivity ratio product vary much from ideality. The  $Q_0$  and  $e_0$  values are given in Table III and compared with  $Q$  and  $e$  values calculated on the styrene basis ( $Q = 1.0$ ,  $e = -0.8$ ) where possible.

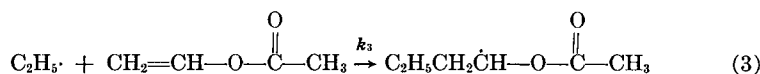
In order to determine if these values are reasonable, reactivity ratios have been calculated for the various copolymerizations possible with the chosen comonomers and compared with experimental values. This comparison is given in Table IV. It will be noted that, although the calculated values refer to high pressure reactions, the degree of agreement is at least sufficient to show that  $Q_0$  and  $e_0$  values are reasonable.

TABLE IV  
Reactivity Ratios Calculated from  $Q_0$  and  $e_0$  Values

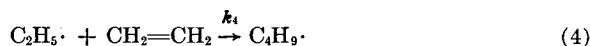
Monomer 1	Monomer 2	$r_1$		$r_2$	
		Expt.	Calc.	Expt.	Calc.
<i>n</i> -Butyl acrylate <sup>a</sup>	Vinyl chloride	5.0	4.0	—	0.16
<i>n</i> -Butyl acrylate <sup>a</sup>	Vinyl acetate	$9.0 \pm 2.5$	12.6	$0.1 \pm 0.1$	0.03
Vinyl chloride	Vinyl acetate	2.1	3.7	0.3	0.22

<sup>a</sup> Compared with methyl acrylate.

It is of further interest to compare the results obtained here with those recently published by James and MacCallum<sup>13</sup> on the rates of addition of ethyl radicals to various monomers. When a value of  $10^{14}$  cm.<sup>3</sup>/mole-sec. is taken as the bimolecular rate constant for the recombination of ethyl radicals,<sup>12</sup> one obtains a value of  $k_3 = 1.0 \times 10^7$  cm.<sup>3</sup>/mole-sec. for the reaction



at 90°C. From the activation energies and frequency factors tabulated by Metcalfe and Trotman-Dickenson,<sup>12</sup> the rate constant for the reaction



is calculated to be  $5.0 \times 10^6$  cm.<sup>3</sup>/mole-sec., also at 90°C. The ratio  $k_4/k_3 = 0.5$ . The directly comparable value ( $r_2$ ) for the analogous homo- and cross-propagation reactions in the copolymerization of ethylene with vinyl acetate is 1.07. This is quite reasonable agreement, considering the experimental pressure difference which would, if anything, make agreement even closer.

## CONCLUSIONS

The high pressure copolymerization of ethylene with *n*-butyl acrylate, vinyl chloride, vinyl acetate, and vinyl fluoride give monomer reactivity ratios from which  $Q$  and  $e$  values may be calculated on the basis of ethylene as the reference monomer ( $Q = 1.0$ ,  $e = 0$ ). These new  $Q$ - $e$  values form

an internally consistent scheme judging from calculated reactivity ratios. Although high reaction pressures have to be used in order to obtain a wide range of copolymer compositions, this practical disadvantage may be offset by the fact that a better reference standard becomes available. The close agreement of the  $r_2$  value for the vinyl acetate/ethylene copolymerization with the directly determined rate constant ratio ( $k_4/k_3$ ) indicates that data obtained by either method may be useful in attempts to relate monomer structure with reactivity.

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### Résumé

Les rapports des réactivités monomériques pour la copolymérisation d'éthylène ( $M_2$ ) avec l'acrylate de *n*-butyle, chlorure de vinyle, acétate de vinyle et fluorure de vinyle ont été mesurés à 1000 atm. Les valeurs respectives et les températures expérimentales sont  $r_1 = 11.9$ ,  $r_2 = 0.03$ , 70°C.;  $r_1 = 3.6$ ,  $r_2 = 0.24$ , 90°C.;  $r_1 = 1.08$ ,  $r_2 = 1.07$ , 90°C.;  $r_1 = 0.16$ ,  $r_2 = 4.39$ , 160°C. Les valeurs  $Q$  et  $e$  de Price pour l'éthylène calculées aux dépens de ces rapports de réactivités, non-corrigés pour les différences dans la pression de réaction sont 0.03 et  $-0.43$  respectivement. De nouvelles valeurs de  $Q$  et  $e$  ( $Q_0$  et  $e_0$ ) pour ces quatre comonomères ont été calculées en utilisant l'éthylène au lieu du styrène comme monomère de référence. Supposant que les valeurs  $Q_0$  et  $e_0$  pour l'éthylène soient 1.0 et zéro respectivement, les valeurs  $Q_0$  et  $e_0$  des monomères sont les suivants: acrylate de *n*-butyle, 33.3, + 1.02; chlorure de vinyle, 4.2, + 0.37; acétate de vinyle, 0.93,  $\sim 0$ ; fluorure de vinyle, 0.25, + 0.6. Ces valeurs de  $Q_0$  et  $e_0$  donnent des rapports de réactivités calculés qui concordent de façon raisonnable avec les valeurs expérimentales. Un bon accord est également obtenu lorsque la valeur  $r_2$  pour la copolymérisation acétate de vinyle/éthylène est comparée avec le rapport des constantes de vitesse directement déterminé dans le cas de l'addition d'un radical éthyle à l'éthylène et à l'acétate de vinyle, respectivement, calculé des données publiées précédemment.



### Zusammenfassung

Monomerreaktivitätsverhältnisse wurden für die Copolymerisation von Äthylen ( $M_2$ ) mit *n*-Butylacrylat, Vinylchlorid, Vinylacetat und Vinylfluorid bei 1000 Atm bestimmt. Die betreffenden Werte sowie die Versuchstemperaturen sind  $r_1 = 11,9$ ,  $r_2 = 0,03$ ,  $70^\circ\text{C}$ ;  $r_1 = 3,6$ ,  $r_2 = 0,24$ ,  $90^\circ\text{C}$ ;  $r_1 = 1,08$ ,  $r_2 = 1,07$ ,  $90^\circ\text{C}$ ;  $r_1 = 0,16$ ,  $r_2 = 4,39$ ,  $160^\circ\text{C}$ . Nach Price daraus berechnete  $Q$ - und  $e$ -Werte betragen ohne Korrektur für Druckunterschiede 0,03 bzw.  $-0,43$ . Neue  $Q$ - und  $e$ -Werte ( $Q_0$  und  $e_0$ ) wurden für die vier Comonomeren mit Äthylen als Bezugsmonomerem an Stelle von Styrol berechnet. Unter der Annahme dass die  $Q_0$ - und  $e_0$ -Werte für Äthylen 1,0 bzw. Null sind, ergeben sich für die  $Q_0$ - und  $e_0$ -Werte der Monomeren folgende Zahlen: *n*-Butylacrylat, 33,3, + 1,02; Vinylchlorid 4,2, + 0,37; Vinylacetat 0,93,  $\sim 0$ ; Vinylfluorid 0,25, + 0,6. Diese  $Q_0$ - und  $e_0$ -Werte liefern berechnete Reaktivitätsverhältnisse, die eine brauchbare Übereinstimmung mit den experimentellen Werten zeigen. Gute Übereinstimmung wird auch beim Vergleich des  $r_2$ -Wertes für die Vinylacetat-Äthylencopolymerisation mit dem direkt bestimmten, aus früher veröffentlichten Daten berechneten, Verhältnis der Geschwindigkeitskonstanten der Addition eines Äthylradikals an Äthylen und Vinylacetat erhalten.

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