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J. Guillot[a]; J. Vialle[a]; A. Guyot[a]
[a] Institut de Recherches sur la Catalyse C.N.R.S., Lyon, Villeurbanne, France

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Vinyl Chloride Copolymerization. Penultimate Effects with Conjugated Comonomer

J. GUILLOT, J. VIALLE, and A. GUYOT

Institut de Recherches sur la Catalyse
C.N.R.S.
Lyon-Villeurbanne, France

SUMMARY

A kinetic study of the radical copolymerization of vinyl chloride with acrylonitrile, methyl methacrylate, or styrene, using the chromatographic method, shows that penultimate effects are observed in all cases, chiefly for the acrylonitrile case ($r_{CC} = 0.03$, $r_{AC} = 3.0$). The conjugated monomer induces a stronger penultimate effect than the unconjugated vinyl chloride; this effect might be correlated with the e values of the Q-e scheme. A strong antepenultimate effect is observed on the styrene ended radicals ($r_{SSS} = 3.0$, $r_{CSS} = 20.0$, $r_{SCS} = 18.5$, $r_{CCS} = 2.7$), which might be related to a steric effect.

INTRODUCTION

In previous papers [1, 2] it has been stated that the effects of penultimate and remote units on the reactivity of the polymeric radicals are probably a general phenomenon, which may be evidenced by the study of the copolymerization kinetics chiefly in the extreme parts of the monomer feed range. The Alfrey equation, which takes into account the penultimate effects, is used:

$$n = \frac{1 + r_1' x(r_1 x + 1)/(r_1' x + 1)}{1 + (r_2'/x)(r_2 + x)/(r_2' + x)} \tag{1}$$

where n is the molar ratio of the two monomers which have been copolyerized at the time t; x is the corresponding ratio (1 upon 2) of the two monomers in the solution at the same time; and r_1, r_1', r_2, and r_2' are the reactivity ratios of the different radicals 11, 21, 22, and 12.

In the extreme part of the monomer feed range, x is large enough to make negligible the second term of the denominator, which may be reduced to unity. The simplified Eq. (1) may be used in the linear form proposed by Barb [3] from which r_1' and r_1 may be derived:

$$\frac{n-2}{x} = r_1 - \frac{1}{r_1'}\left(\frac{n-1}{x^2}\right) \tag{2}$$

The validity of this approximation obviously depends on the values of r_2 and r_2'; if they are small enough, a large range of x may be used. However, as already explained [2], when the value of the denominator is not close to unity, the Barb equation may be used by replacing n with N = kn where

$$k = 1 + \frac{r_2'}{x}\left(\frac{x + r_2}{x + r_2'}\right)$$

A number of iteration may be necessary in order to achieve the exact values of the reactivity ratios.

It is interesting to use a monomer which has low reactivity ratios in copolymerization with a number of comonomers. Vinyl chloride (C) satisfies this condition when the comonomers are conjugated monomers, such as styrene (S), methyl methacrylate (M), or acrylonitrile (A), as shown by the values published in the literature and reported in Table 1. It may be seen that the reported values of the ractivity ratios are rather dispersed although the experimental conditions are often similar, so a careful examination of the experimental results remains necessary. Further, the full range of the monomers feed has never been explored. The use of the chromatographic method, fully described elsewhere [4], allowed us to do that.

Table 1. Literature Data for the Binary Copolymerization of Vinyl Chloride (C) with Either Methyl Methacrylate (M) or Styrene (S) or Acrylonitrile (A)

Comonomer 2	r_C	r_2	T (°C)	Experimental conditions	Number of experiments	Range, x = C/2	Method[b]	Ref.
S	0.02	17	60	Bulk	3	0.2-2.7	Cl	6
S	0.067	35	60	solution[a]	9	0.03-5.1	Cl	7
S	0.045	12.4	50	Emulsion	3	0.0-0.05	Cl	8
S	–	–	50	Bulk	17	0.005-0.935	Cl	9
M	0	12.5	60	–	1	–	Cl	10
M	0.1	10	68	Bulk	6	0.28-15.3	Cl	11
M	0.02	15	45	Emulsion	6	0.11-0.57	Cl	12
A	0.02	3.28	69	Bulk	3	0.43-2.35	N,Cl	13
A	–	–	40	Bulk or emulsion	24	0.008-84	–	14
A	0.074	3.7	50	Bulk	7	0.04-7.8	Cl	7
				solution[a]				
A	0.05	3.6		Bulk	23	0.01-10	N,Cl	9
A	0.04	2.7	60	Bulk	6	0.4-13	N	15

[a] Solution of monomer (50%) in acetone (50%).

[b] Chlorine or nitrogen titration.

Table 2. Charge and Results for the Vinyl Chloride (C)–Methyl Methacrylate (M) Copolymerization. Solvent: 1,2-Dichlorethane

Charge (moles)				Results				
				Kinetics, n_M	Sampling conversion (M%)	Analysis: n_M from		
M	C	Solvent	$x_M = M/C$			Cl	C	NMR
0.77	0.128	5.40	6.01	64.0				
0.78	0.208	5.55	3.75	39.0				
0.61	0.36	5.40	1.70	17.5				
0.50	0.68	5.57	0.735	9.15				
0.408	0.79	5.44	0.525	5.08	3	6.0	6.0	
0.35	1.06	5.50	0.332	3.16				
0.21	1.40	5.45	0.150	1.80	5			1.75
0.197	1.45	5.23	0.136	1.17	10	1.1	0.86	
0.107	1.10	5.40	0.11	0.71				
0.068	1.31	5.63	0.052	0.325	13	0.40	0.32	
0.0305	1.29	5.43	0.02	0.145	13	0.20	0.137	
0.0104	1.17	5.40	0.009	0.045				

II. EXPERIMENTAL RESULTS AND INTERPRETATION

Copolymerization was carried out at 60°C in rather dilute solution, under nitrogen atmosphere, using azobisisobutyronitrile as initiator with a molar concentration of about 1% of the total monomer concentration. Solvents and monomers were freshly distilled under nitrogen atmosphere before use. The kinetics of the individual monomer consumption was obtained through the chromatographic analysis of the reaction medium at various time, the solvent being used as a concentration reference. The apparatus involves a stainless steel reactor equipped with a thermostat, magnetic stirrer and taps for charge and sampling. The chromatograph is equipped with column of silicon material and filament catharometer. The areas under the chromatographic peaks were measured using an electronic integrator.

The charge of the reactors and the initial composition of the copolymers (n) are reported in Tables 2, 3, and 4 for the copolymerization of vinyl chloride (C) with M, S, and A comonomers, respectively. The kinetics results of the individual experiments are given in Figs. 1, 2, and 3 as the ratios of the initial rate of consumption of the two monomers. The values of n in Tables 2, 3, and 4 are deduced from the smoothed curves obtained.

In some cases rather large samplings were used in order to analyze the copolymers. They were precipitated with methanol, or in some cases with a mixture of water–methanol, and dried under vacuum to constant weight. The analysis includes chlorine, carbon, and nitrogen titration, or NMR spectra (60 MHz) from which other values of n, which are reported also in the tables, may be deduced.

A. Methyl Methacrylate Copolymers

The Fineman-Ross diagram, illustrated in Fig. 4, gives a reasonably straight line that takes into account all the experiments corresponding to values of x_M greater than 0.1, from which $r_M = 10.8$ and $r_C = 0.15$ are obtained, in good agreement with the data of Agron et al. [11] for a similar range of monomer feed, but obtained from bulk or emulsion copolymerization. The departure from the straight line for the mixtures rich in vinyl chloride suggests a penultimate effect on the C-ended radicals. Actually the use of the Barb equation gives $r_{CC} = 0.23$ and $r_{MC} = 0.09$. The same treatment applied to the mixture rich in M shows the practical absence of penultimate effect onto the M-ended radicals, with $r_{MM} = 10.5$

Table 3. Charge and Results for the Vinyl Chloride (C)–Styrene (S) Copolymerization. Solvent: 1,2-Dichlorethane

Charge (moles)				Results					
				Kinetics,	Sampling conversion		Analysis: n_S from		
S	C	Solvent	$x_S = S/C$	n_S	S%	C%	Cl	C	NMR
0.0118	1.23	4.87	0.0096	0.115	16	1.26	0.14	0.137	0.09
0.0166	1.082	4.27	0.0154	0.185	18.2	1.88	0.294	0.179	0.15
0.047	1.15	4.72	0.041	0.45	23.0	6.2	0.67	0.60	0.40
0.0284	0.95	4.45	0.030	0.345	9.5	1.7			0.25
0.113	1.37	5.3	0.0825	0.90	16.7	5.2	–	–	0.96
0.092	1.05	4.96	0.0875	0.97	11.8	3.2	2.0	1.35	0.96
0.22	0.63	4.98	0.35	2.98	18.7	3.6	6.0	4.4	3.55
0.284	0.61	4.68	0.465	3.61	19.0	4.0	19.5	6.8	3.35
0.305	0.642	4.78	0.475	3.64	11.4	1.35			3.10
0.416	0.416	5.10	1.0	5.25	11.8	4.15			4.0
0.595	0.304	4.58	1.97	6.20	10.2	3.1		46	5.0
0.593	0.065	4.49	9.13	>10	10.0	0.30		29.5	5.0
0.70	0.055	4.62	12.6	>10	–	–	59	24.3	–
0.672	0.022	4.56	30.6	>10	7.2	0.56	–	–	–

Table 4. Charge and Results for the Vinyl Chloride (C)–Acrylonitrile (A) Copolymerization. Solvent: Dimethylformamide

				Results						
Charge (moles)				Kinetics,	Sampling conversion		Analysis: n_A from			
A	C	Solvent	$x_A = A/C$	n_A	A%	C%	Cl	C	N	NMR
1.045	0.031	5.41	33.3	127.5	–	–	–	–	–	–
1.110	0.106	5.45	10.5	36.80	–	–	–	–	–	–
0.820	0.171	5.16	4.80	15.10	–	–	–	–	–	–
0.637	0.270	5.85	2.36	6.50	–	–	–	–	–	–
0.590	0.384	5.80	1.54	3.77	–	–	–	–	–	–
0.616	0.648	5.53	0.94	2.36	9.3	4.8	4.05	2.3	2.6	–
0.632	0.80	4.95[a]	0.79	1.82	–	–	–	–	–	–
0.324	0.603	5.51	0.536	1.60	16.5	5.8	2.64	1.93	2.24	2.6
0.16	0.82	5.11	0.195	0.78	–	–	–	–	–	–
0.084	1.05	4.88	0.08	0.545	19.2	3.07	0.93	0.785	0.77	0.55
0.0247	0.825	5.54	0.030	0.376	–	–	–	–	–	–
0.0191	1.00	5.30	0.019	0.316	84.0	7.25	0.314	0.25	0.256	–
0.21	0.26	No	0.81	–	–	–	5.50	5.55	5.55	–[b]
0.32	0.266	No	1.20	–	–	–	4.75	4.3	5.75	–[c]

[a] Solvent: 1,2-Dichlorethane.

[b] Corresponding literature result, n_A = 3-4 [9].

[c] Corresponding literature result, n_A = 5.2 [9].

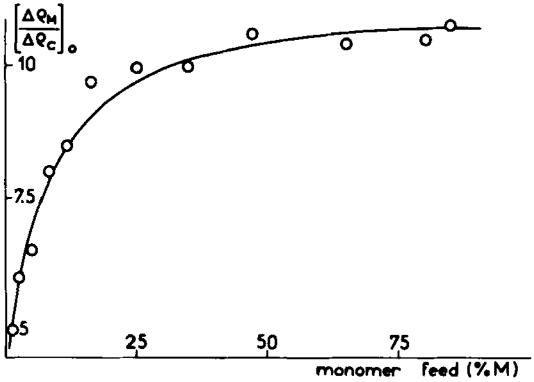

Fig. 1. Ratio of initial consumption rates vs. monomer molar feed for vinyl chloride (C)–methyl methacrylate (M) copolymerizations.

Fig. 2. Ratio of initial consumption rates vs. monomer molar feed for vinyl chloride (C)–styrene (S) copolymerizations.

and $r_{CM} = 10.0$. From these values it is possible to calculate the values of n corresponding to the experiments carried out. The calculated values are compared in Table 5 with the experimental ones. Agreement is excellent in the whole range.

Taking in account the effect of the conversion, the determination of the copolymer composition through NMR analysis or carbon and chlorine titration is in rather good agreement with the kinetic data. It may be noted, however, that chlorine titration indicates compositions slightly poorer in vinyl chloride units. This same type of discrepancy is shown in the two other systems studied, but is smaller.

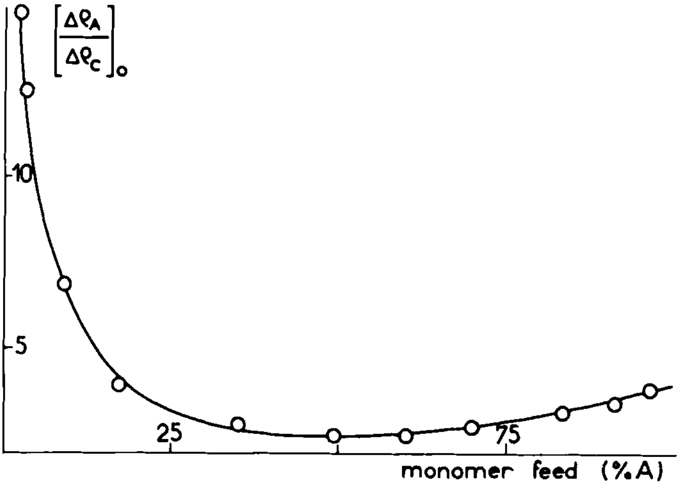

Fig. 3. Ratio of initial consumption rates vs. monomer molar feed for vinyl chloride (C)–acrylonitrile (A) copolymerizations.

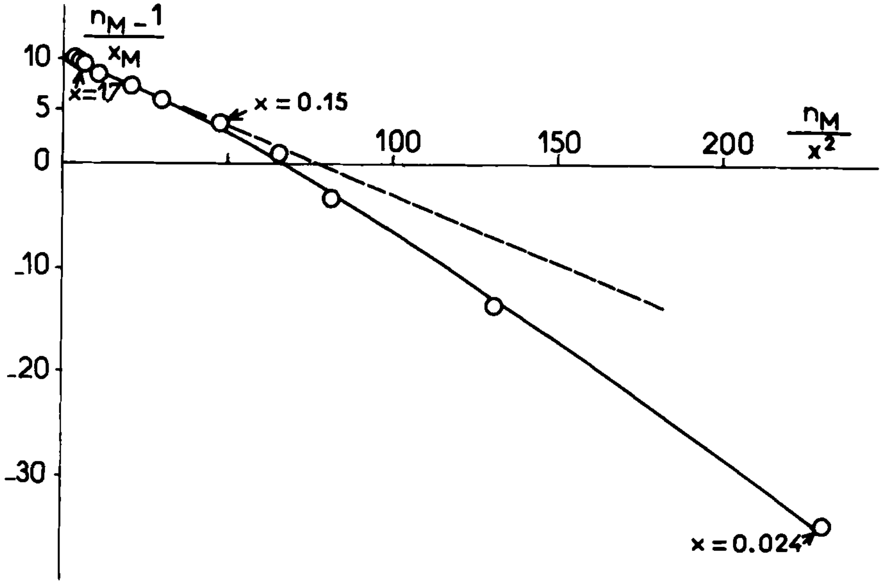

Fig. 4. Methyl methacrylate–vinyl chloride copolymerization, Fineman-Ross plot.

Table 5. Methyl Methacrylate–Vinyl Chloride Copolymerization. Experimental and Calculated Values of n_M

x_M	0.009	0.052	0.136	0.332	0.515	0.735	1.70	3.75	6.01
n_M exp.	0.045	0.325	1.17	3.16	5.08	9.15	17.5	39.0	64.0
n_M calc.	0.047	0.332	1.16	3.32	5.25	9.4	17.7	39.4	64.0

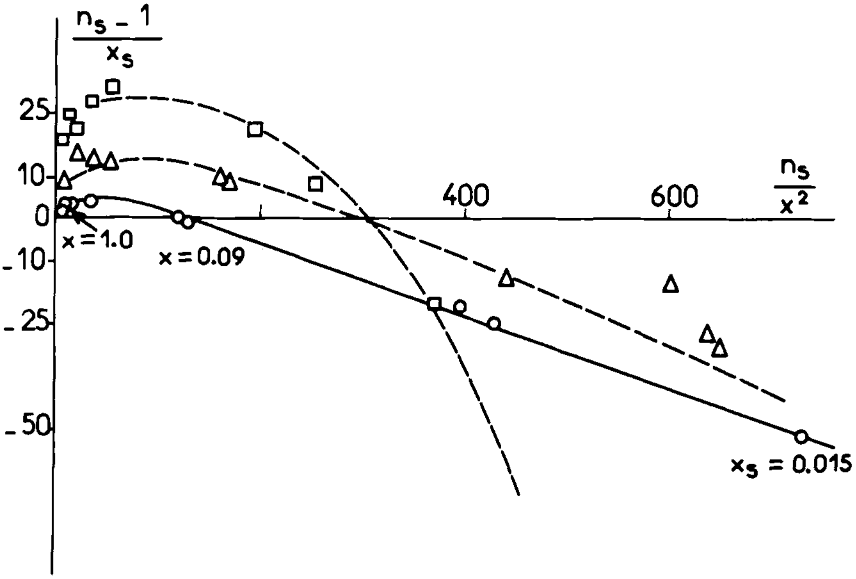

Fig. 5. Styrene–vinyl chloride copolymerization, Fineman-Ross plot. (○) This study; (△) Thomson and Raines [9]; (□) Chapin, Ham, and Fordyce [7].

B. Styrene Copolymers

The Fineman-Ross plots relative to n_S are given in Figs. 5 and 6. It may be seen that our kinetic results differ strongly from the published data. Our results from chlorine or carbon titration are closer to the literature data obtained by the same kinds of analysis. Finally, our results from NMR analysis (measurement of aromatic and others protons) are in a rather good agreement with the kinetic results. In a few cases very weak leaks have caused an enhanced consumption of vinyl chloride; the corresponding experiments, where discrepancies were noted between the final chromatographic yields and the weight of the recovered copolymer, have been eliminated. In our opinion all the data obtained from chlorine and carbon titration are questionable for these copolymers. It is known that a part of the chlorine may escape from the titration because of an unsuitable heating rate during the titration procedure. The reasonable agreement between NMR and kinetic results leads us to prefer to use these in order to deduce the reactivity ratios.

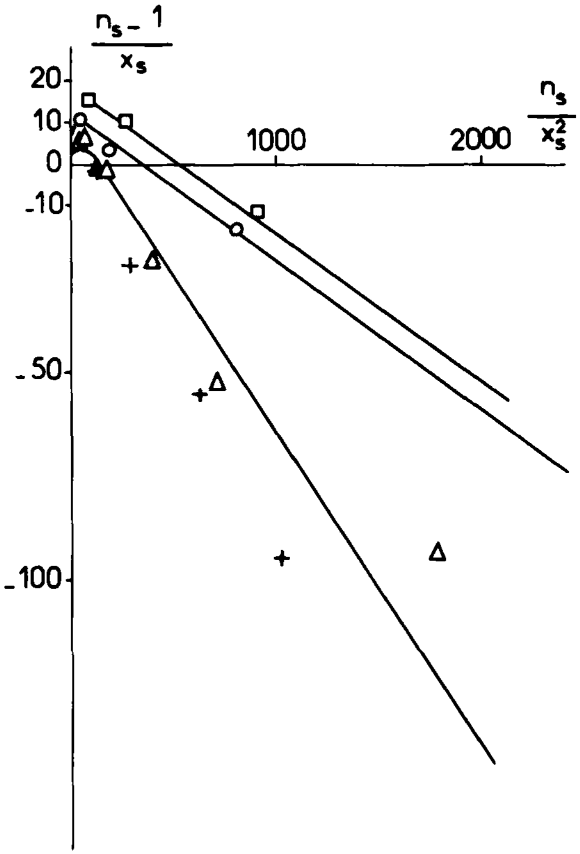

Fig. 6. Styrene–vinyl chloride copolymerization, Fineman-Ross plot. Results from kinetics (△), chlorine titration (○), carbon titration (□) and NMR (+).

The Fineman-Ross plot of Fig. 5 shows that a good straight line takes into account the experiments where $x_S < 0.1$. A corresponding plot relative to x_C shows a good straight line for $x_C > 10$. From these plots it can be deduced that there is no penultimate effect on the C-ended radicals but strong remote-unit effects on the S-ended radicals. However, the straight lines correspond only to a limited extreme part of the monomer feed range. It seems better from the kinetic point of view to use the larger intermediate range $0.08 < x_S < 2.0$. The Fineman-Ross line (Fig. 7) for this range gives $r_S = 6.5$ and $r_C = 0.06$. Penultimate effects are indicated

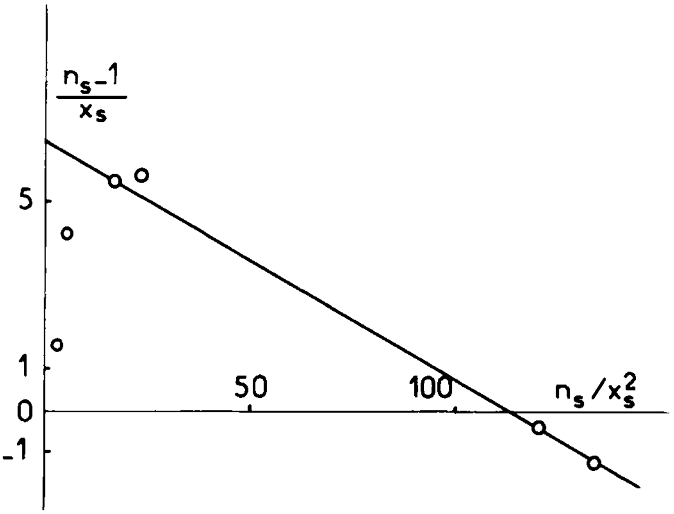

Fig. 7. Extended Fineman-Ross plot in styrene–vinyl chloride copolymerization for the intermediate range of x_S: $0.08 < x_S < 2.0$.

on each side of the range. Using the Barb equation, one obtains $r_{CC} = 0.10$, $r_{SC} = 0.03$ and $r_{SS} = 6.8$, $r_{CS} = 6.0$. However, these values do correctly represent the part of the range rich in styrene if $x_S < 0.5$. Thus, an antepenultimate effect is indicated. From a procedure [1] based on the Ham equation [16] for antepenultimate effect and fully described in the following paper [17], one obtains $r_{SSS} = 3.0$, $r_{CSS} = 20.00$ and $r_{SCS} = 18.5$, $r_{CCS} = 2.7$. These values are not very precise, because in the corresponding range the rate of vinyl chloride consumption is very low and badly measured. However, by taking in account these penultimate and antepenultimate effects, one may calculate again the copolymer compositions and compare them with the experimental ones (Table 6). It may be seen that the agreement is rather good up to $x_S = 2$. The same procedure might be extended in order to search for an anteantepenultimate effect; however, after $x_S > 5$ the experimental results of the kinetics are not precise enough to test the procedure. Thus, the possibility of such an effect remains, or there may be another kind of effect that accounts for the observed discrepancies.

Table 6. Styrene–Vinyl Chloride Copolymerization. Experimental and Calculated Values of n_S

x_S	0.0096	0.0154	0.03	0.0875	0.35	0.465	1.0	1.97	9.13	12.6	30.6
n_S exp.	0.115	0.185	0.345	0.97	2.98	3.61	5.25	6.20	>10 (29[a])	>10 (25[a])	>10
n_S calc.	0.107	0.178	0.36	0.99	2.90	3.42	5.32	8.4	30	40	94

[a] From carbon titration.

C. Acrylonitrile Copolymers

In this case the Fineman-Ross diagram (Fig. 8) does not show any linear part. Again, our kinetic results are quite different from those of the literature and also from our results from element titration, and again these last results are closer to those of the literature; the agreement is rather good for bulk experiments (Table 4, two last lines). The NMR results are less reliable in this case because of the poor resolution of the spectra. However, for the reasons quoted above, we think that the kinetic results are the most reliable. From the more linear fit of the results relative to the intermediate range, the successive application of the Barb equation to the results of both the two extreme ranges and a few iterations lead to the values $r_{AA} = 4.0$, $r_{CA} = 2.5$ and $r_{CC} = 0.03$, $r_{AC} = 3.0$. Thus, penultimate effects are observed for both the A- and C-ended radicals and no antepenultimate effect is necessary to account for all the experimental results. The n values calculated from these values are in good agreement with the experimental ones

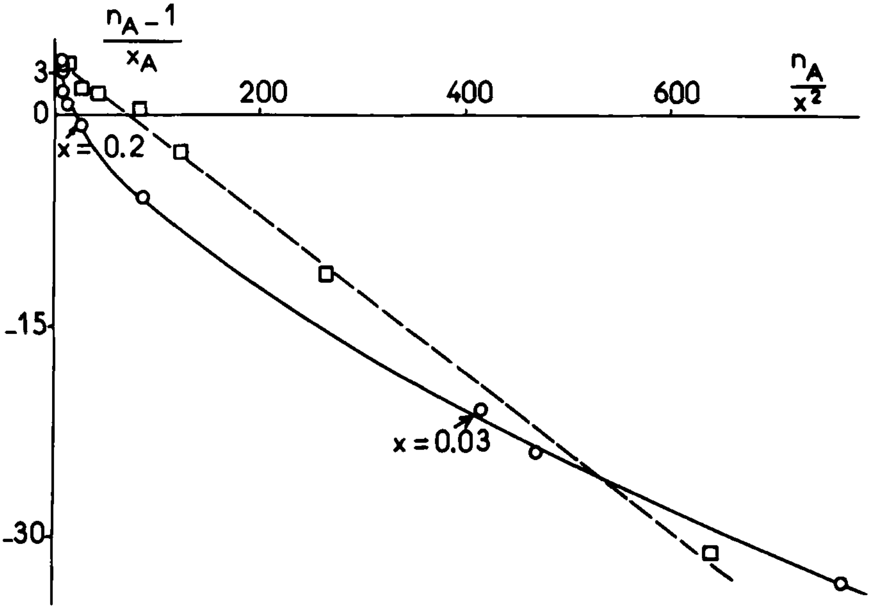

Fig. 8. Acrylonitrile–vinyl chloride copolymerization, Fineman-Ross plot. (□) Thomson and Raines [9]; (○) this study.

Table 7. Acrylonitrile–Vinyl Chloride Copolymerization. Experimental and Calculated Values of n_A

x_A	0.019	0.08	0.195	0.536	0.94	2.36	4.8	10.5	33.3
n_A exp.	0.316	0.545	0.78	1.60	2.36	6.5	15.1	36.8	127
n_A calc.	0.300	0.525	0.765	1.45	2.50	6.3	14.3	36.2	125

(Table 7). It is to be noted that in this case the penultimate effect on the C-ended radicals is very strong; obviously it is responsible for the failure of a Fineman-Ross straight line to fit even a limited range of experimental results.

III. DISCUSSION

The above results show that of the three cases studied only the C-M case is reasonably accounted for by the usual copolymerization theory. In the other cases the Fineman-Ross plot shows a definite curvature in the medium range of the monomer feed composition. A straight line may be observed only in one of the extreme ranges in the C-S case; however, the choice of this region for the determination of the reactivity ratios would mask the penultimate effect operative on the C-ended radical. On the other hand, the initial choice of the straight line to determine the more reasonable values of the reactivity ratio is rather arbitrary (for instance in Fig. 7) and would be expected to lead to rather arbitrary values for the penultimate or antepenultimate effect, but iteration procedures actually correct the consequences of a bad initial choice, and lead to unequivocally defined values.

In some cases the kinetic data are not very accurate because of the very low consumption of the vinyl chloride monomer, for instance. An accurate determination of the copolymer composition that takes into account the monomer consumption would be useful. As pointed out by Johnston [18], the reactivity ratios may be obtained from such different functions as W(1) and W(2), the weight fractions of units 1 and 2 in the copolymer, and $\bar{L}_n$, the number-average sequence length. NMR studies are in progress in our laboratory [19]. Preliminary results show that for the styrene rich copolymer $\bar{L}_{nS}$ values are rather low and correspond to r_S values of less than 10, in agreement with the present results.

The present results confirm the generality of the penultimate effects which are observed in all cases. It may be noted that a conjugated unit always induces a rather important effect on the unconjugated vinyl chloride-ended radical, but the reverse is not true except in the case of the S-C copolymers. There is no penultimate effect on the M-ended radicals and the effect is limited for the A-ended radicals. On the other hand, the penultimate effect of an A unit on the C-ended radical is dramatic and is the reverse of that of the M or S unit; it induces a preferential addition of a C unit, while the two other units induce the addition of the conjugated monomer. Further, the effect of an S penultimate unit is larger than that of an M unit. These observations suggest that a correlation might be possible between these penultimate effects and the e values of the Q-e scheme. It may be observed that in the case of the M-C, the e values are not very different ($e_C = 0.20$ and $e_M = 0.40$); the corresponding penultimate effect is also very limited. The e value of acrylonitrile is positive and high ($e_A = 1.20$) and that of styrene is negative ($e_S = -0.80$). On the basis of the Q-e scheme, a larger penultimate effect would be expected for the styrene. However, the case of the S-C copolymer is a special one because it shows a large antepenultimate effect onto the styrene radical. Careful examination of the four reactivity ratios points out that the probability of S-S diad is very low and that the probability of the S-S-S triads is much greater. At the present time it is not possible to give a satisfactory explanation, but tentatively it might be suggested that a steric effect is involved. It has been shown by Riess and Benoit [20] that polystyrene possesses a helical 3_1 conformation in solution, stable up to about 70°C; the third S unit of a triad might induce the helical conformation to be formed, thus decreasing the steric hindrance for the addition of a vinyl chloride unit. Such an explantation would also account for the more remote units effects suggested by the very strong curvature of the Fineman-Ross plot.

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