

## Reactivity Ratios for Acrylonitrile-Vinyl Chloroacetate Copolymerization Systems

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### Synopsis

Reactivity ratios for acrylonitrile-vinyl chloroacetate systems have been determined for radical copolymerization at 60°C in dimethylformamide. The values of the ratios calculated by the linear graphical method of Kelen and Tüdös were as follows:  $r_1 = 4.05 \pm 0.1$  and  $r_2 = 0.001 \pm 0.001$  for acrylonitrile (AN)-vinyl monochloroacetate (VCAC),  $r_1 = 7.0 \pm 0.25$  and  $r_2 = 0.05 \pm 0.015$  for acrylonitrile-vinyl dichloroacetate (VDAC),  $r_1 = 7.13 \pm 0.25$  and  $r_2 = 0.06 \pm 0.015$  for acrylonitrile-vinyl trichloroacetate (VTAC). The penultimate model of the copolymerization and the effect of the vinyl chloroacetate structure were discussed.

### INTRODUCTION

The theory of radical copolymerization leads to the conclusion that the composition of the copolymer is determined by the reactivity ratios,  $r_1$  and  $r_2$ , and the ratio of the concentrations of the monomers in the initial monomer feed.  $r_1$  and  $r_2$  values may be evaluated by various procedures: linear,<sup>1,2</sup> nonlinear,<sup>3-8</sup> and other copolymer composition equations.<sup>9,10</sup> Computer programming routines for calculation of  $r_1$  and  $r_2$  have been also developed.<sup>11-13</sup>

Many authors<sup>3-5,8,14</sup> have criticized the methods used for estimation of copolymerization parameters. Kelen and Tüdös<sup>15</sup> have recently discussed the linear methods, reporting a new graphical one. Its advantage is that the independent variable of the linear function varies in the range (0, 1), whereas in other linear methods it varies in the range (0,  $\infty$ ). This method has been employed in our calculations.

### EXPERIMENTAL

#### Materials and Preparation of the Comonomers

Acrylonitrile,<sup>16</sup> azobisisobutyronitrile,<sup>16</sup> and (*N,N*-dimethylformamide)<sup>16</sup> were purified as described previously. The comonomers, i.e., vinyl chloroacetate (VCAC), vinyl dichloroacetate (VDAC), and vinyl trichloroacetate (VTAC), were synthesized from acetylene and the respective chloroacetic acids in the presence of mercury salts or oxides according to the method of Wiley.<sup>17</sup> Details of the synthesis, purification, and properties of the monomers were reported previously.<sup>18</sup>

TABLE I  
Copolymerization of Acrylonitrile  $M_1$  with Vinyl Chloroacetates  $M_2$  in DMF Solution at 60°C up to Low Conversion<sup>a</sup>

Experi- ment	Comonomer	Ratio of mole fractions of monomers in mixture, $x = [M_1]/[M_2]$	Cl content of copoly- mer, wt-%	Ratio of mole fractions of monomers in copolymer, $y = d[M_1]/d[M_2]$	Conver- sion, %
1/1	VCAc	0.0000	29.50	—	4.0
2/1		0.1428	18.15	1.387	4.09
3/1		0.3333	14.14	2.455	4.50
4/1		0.6000	11.28	3.600	4.86
5/1		1.0000	9.02	5.167	4.85
6/1		1.6667	7.25	7.560	4.27
7/1		3.0000	4.43	12.916	4.66
8/1		7.0000	2.77	22.505	5.36
1/2	VDAc	0.0000	45.80	—	4.6
2/2		0.1428	29.69	1.591	2.7
3/2		0.3333	23.33	2.819	2.4
4/2		0.6000	17.67	4.657	2.3
5/2		1.0000	12.42	7.883	3.2
6/2		1.6667	8.51	12.760	4.2
7/2		3.0000	5.25	22.610	7.2
8/2		7.0000	2.56	49.384	6.7
1/3	VTAc	0.0000	56.20	—	10.1
2/3		0.1428	36.10	1.9895	3.03
3/3		0.3333	32.42	2.6298	2.38
4/3		0.6000	24.95	4.4705	3.54
5/3		1.0000	19.44	6.7399	3.42
6/3		1.6667	13.45	11.3457	4.55
7/3		3.0000	7.56	22.9234	6.68
8/3		7.0000	3.53	53.3478	8.40

<sup>a</sup> Concentration of monomer mixture = 4 mole/dm<sup>3</sup>; concentration of AIBN =  $6 \times 10^{-2}$  mole/dm<sup>3</sup>.

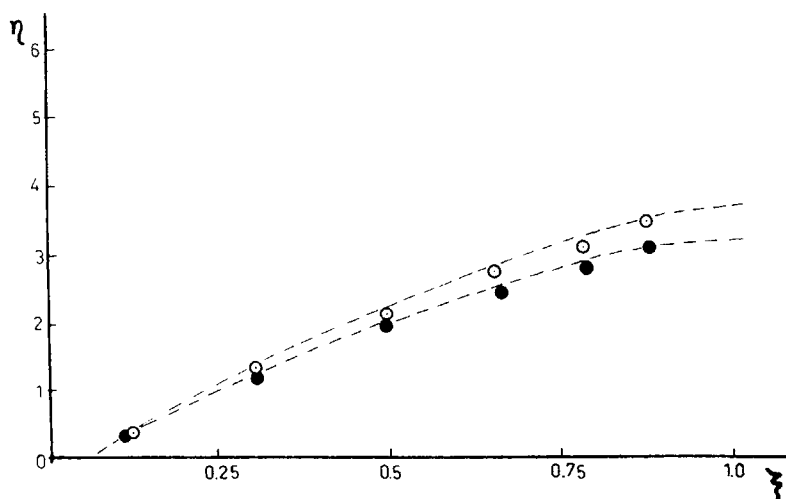


Fig. 1. Kelen-Tüdös plot for copolymerization of acrylonitrile and vinyl chloroacetate in DMF at 60°C: (O) chlorine, (●) -nitrogen.  $\alpha = 0.1012$  (Cl),  $\alpha = 0.1073$  (N).

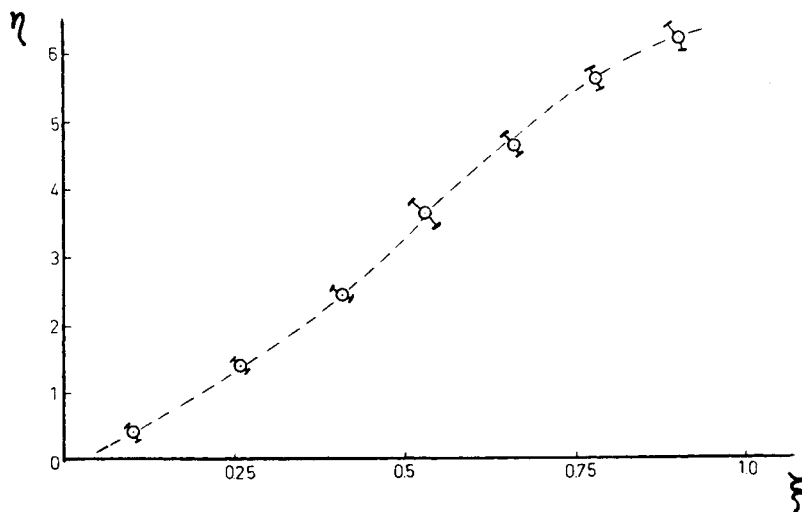


Fig. 2. Kelen-Tüdös plot for copolymerization of acrylonitrile and vinyl dichloroacetate in DMF at 60°C,  $\alpha = 0.1132$ .

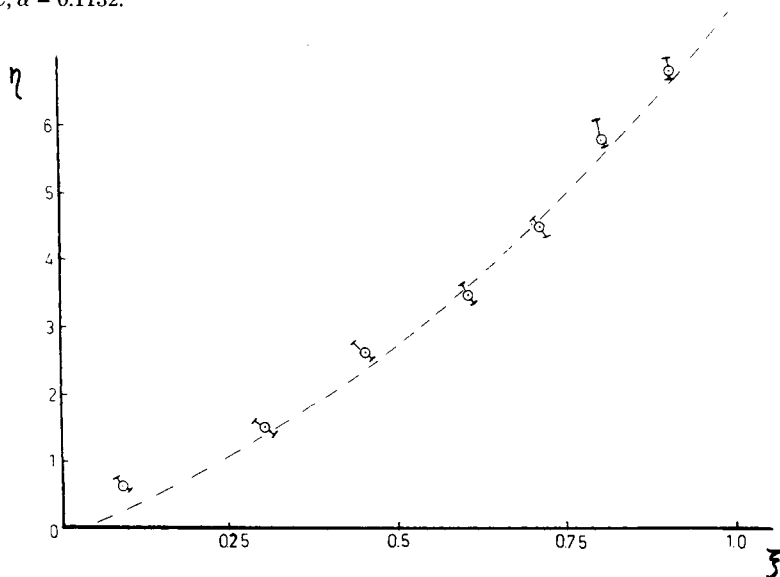


Fig. 3. Kelen-Tüdös plot for copolymerization of acrylonitrile and vinyl trichloroacetate in DMF at 60°C,  $\alpha = 0.0969$ .

### Copolymerization by Radical Initiation

Copolymerization of the acrylonitrile-chloroacetate systems was initiated by AIBN ( $6 \times 10^{-5}$  mole/cm<sup>3</sup>) and carried out in sealed glass tubes in DMF solution ( $4 \times 10^{-3}$  mole/cm<sup>3</sup>) at  $60 \pm 0.1^\circ\text{C}$ . The tubes were filled by a vacuum line technique by distillation of the monomers after partial prepolymerization.

The copolymers were precipitated by an excess of methanol and purified by repeated dissolution and precipitation from solutions in DMF or DMSO. The samples were dried at  $70^\circ\text{C}/0.1$  mm Hg. The composition of the copolymers was determined by analysis for chlorine content (Mr. S. Binkowski, The Molecular and Macromolecular Research Center, Łódź, Poland).

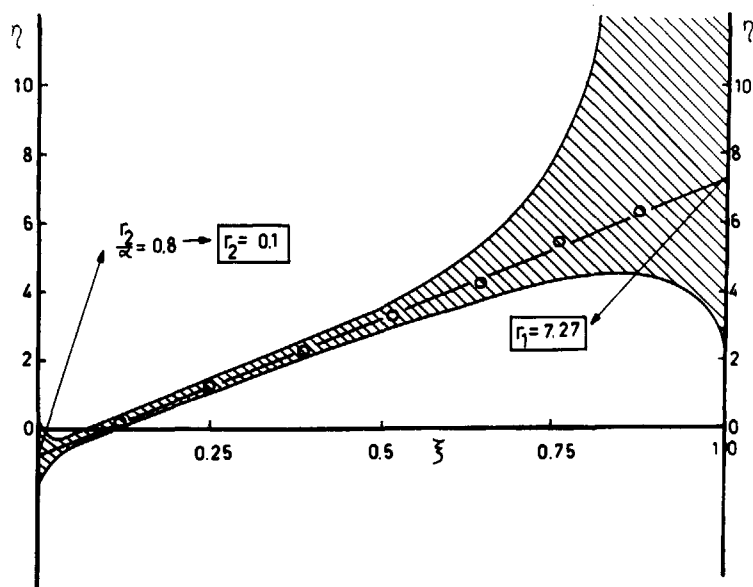


Fig. 4. Kelen-Tüdös plot for copolymerization of acrylonitrile and vinyl trichloroacetate in DMF at 60°C,  $\alpha = 0.125$  (with copolymer chlorine content).

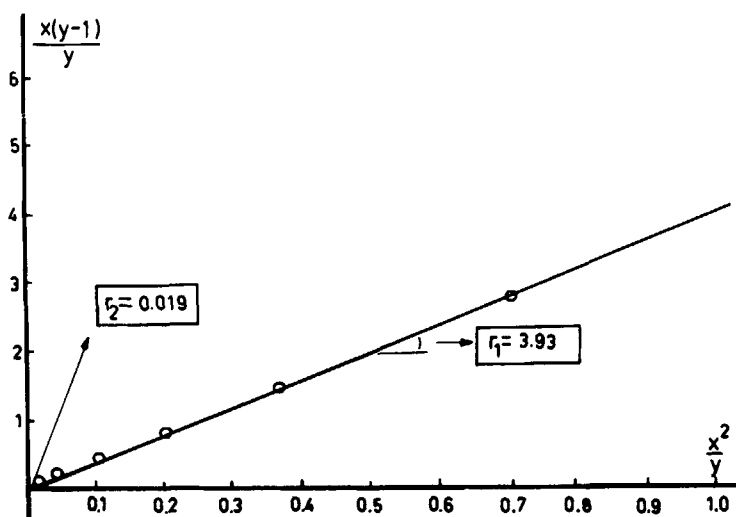


Fig. 5. Fineman-Ross plot for copolymerization of acrylonitrile and vinyl chloroacetate in DMF at 60°C.

## RESULTS AND DISCUSSION

The composition of the initial mixtures and the copolymers, the chlorine content, and conversions are summarized in Table I.

Reactivity ratios were calculated from the data given in Table I, according to Kelen and Tüdös,<sup>15</sup> by eq (1):

$$\frac{x(y-1)}{\alpha y + x^2} = \left(r_1 + \frac{r_2}{\alpha}\right) \frac{x^2}{\alpha y + x^2} - \frac{r_2}{\alpha} \quad (1)$$

TABLE II  
Copolymerization Parameters for Acrylonitrile ( $M_1$ )-Vinyl Chloroacetate ( $M_2$ ) Systems

Comonomer	Simple model		Penultimate model				$E_S$	$\sigma^b$
	$r_1$	$r_2$	$r_1$	$r_1'$	$r_1'/r_1$	$Q_2^a$		
VAc	$4.05 \pm 0.1^c$	$0.001 \pm 0.001$	$3.85 \pm 0.1$	$5.55 \pm 0.5$				
	$3.93 \pm 0.2^d$	$0.019 \pm 0.01$			1.44	0.014	-0.75	-0.24
	$3.54 \pm 0.3^e$	$-0.02 \pm 0.02$						1.05
	$4.0 \pm 0.2^f$	$0.0 \pm 0.05$						
VDAc	$7.0 \pm 0.25^c$	$0.05 \pm 0.015$	$7.5 \pm 0.5$	$3.2 \pm 0.5$				
	$6.97 \pm 0.3^d$	$-0.013 \pm 0.02$			0.43	0.017	-0.15	-1.54
	$5.51 \pm 0.3^e$	$0.04 \pm 0.02$						1.94
	$7.5 \pm 0.3^f$	$0.03 \pm 0.02$						
VTAc	$7.13 \pm 0.25^c$	$0.06 \pm 0.015$	$7.5 \pm 0.5$	$2.5 \pm 0.3$				
	$6.97 \pm 0.5^d$	$-0.16 \pm 0.08$			0.33	0.027	0.27	-2.06
	$6.28 \pm 0.5^e$	$0.0023 \pm 0.08$						2.65
	$7.2 \pm 0.6^f$	$0.06 \pm 0.05$						

<sup>a</sup>  $Q_1 = 0.6$ ,  $e_1 = 1.2$ .

<sup>b</sup> Data of Hayashi and Otsu.<sup>22</sup>

<sup>c</sup> Values computed by the Kelen-Tüdös method [eq. (1)].

<sup>d</sup> Values computed by the Fineman-Ross method [eq. (3)].

<sup>e</sup> Values computed by the Fineman-Ross method [eq. (4)].

<sup>f</sup> Values computed by the Mayo-Lewis method.

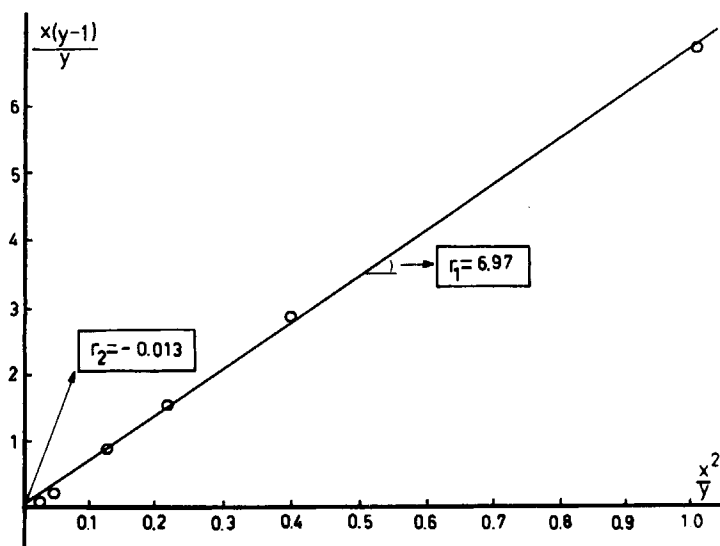


Fig. 6. Fineman-Ross plot for copolymerization of acrylonitrile and vinyl dichloroacetate in DMF at 60°C.

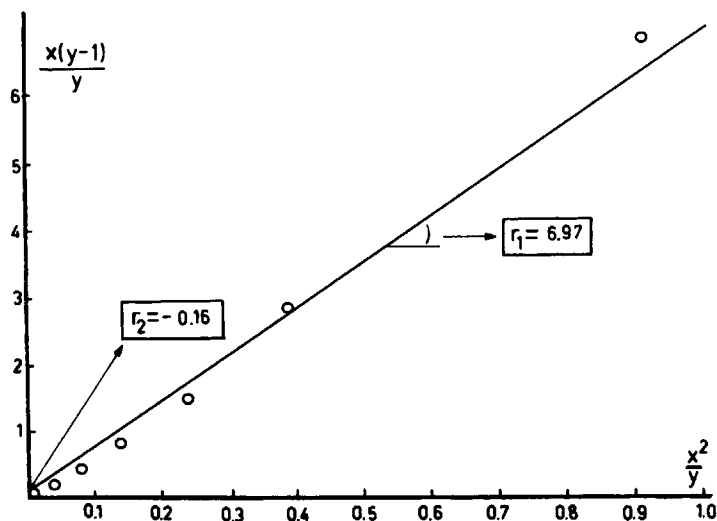


Fig. 7. Fineman-Ross plot for copolymerization of acrylonitrile and vinyl trichloroacetate in DMF at 60°C.

where  $x$  is the ratio of mole fractions of monomer 1 ( $M_1$ ) and monomer 2 ( $M_2$ ) in the monomer feed,  $y$  is the ratio of mole fractions of monomer 1 ( $d(M_1)$ ) and monomer 2 ( $d(M_2)$ ) in the copolymer, and  $\alpha$  is an equation parameter.

The equation parameter can be computed according to eq. (2):<sup>15</sup>

$$\alpha = \frac{x_{\min} x_{\max}}{y_{\min} y_{\max}} \quad (2)$$

where  $x_{\min}$ ,  $x_{\max}$  are minimal and maximal mole fractions, respectively, of mo-

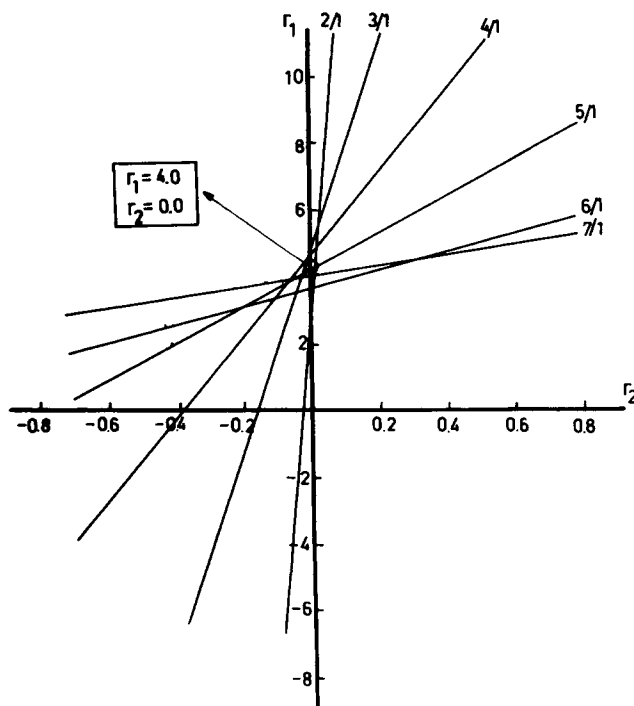


Fig. 8. Mayo-Lewis plot for copolymerization of acrylonitrile and vinyl chloroacetate in DMF at 60°C. The numbers of individual straight lines correspond to the numbers of experiments given in Table I.

nomers 1 and 2 in the monomer feed;  $y_{\min}$ ,  $y_{\max}$  are minimal and maximal mole fractions, respectively, of monomers 1 and 2 in the copolymer.

The relation  $x(y - 1)/\alpha y + x^2 = \eta$  for the system AN-VCAc is shown in Figure 1 as a function of  $x^2/\alpha y + x^2 = \xi$  for the data listed in Table II and also for the experimental values of the copolymer nitrogen content. Points corresponding to the chlorine content of the copolymer are given with the assumed experimental error of  $\pm 3\%$ . A linear least-squares fit for these points is given in Figure 1 (correlation factor = 0.9944), the intercept on the ordinate determining the corresponding values of  $r_1$  and  $r_2/\alpha$ . Experimental points obtained from the nitrogen content of the copolymer can also be fitted to a straight line with a correlation factor of 0.9949. The points based on chlorine and nitrogen contents of the copolymer both exhibit a curved deviation from the straight-line plots.

The relations  $\eta = f(\xi)$  for the systems AN-VDAc and AN-VTAc are presented in Figures 2 and 3, respectively, with the assumed chlorine content determination error of  $\pm 3\%$ . Within the limits of the assumed error, characteristic deviations from the calculated straight lines (CF = 0.9975 and CF = 0.9798) are observed in Figure 2 and convex deviations can be observed on Figure 3.

The experimental error of the chlorine content determination is  $\pm 1\%$  and this error was then taken into account when computing the reactivity coefficients listed in Table II. It can be seen from Figure 1 that the relation  $\eta = f(\xi)$  for the same copolymer sample is different depending upon whether the data are based on chlorine and nitrogen contents; these differences increase with the increasing VCAc content in the copolymer. Those differences can be ascribed to the dif-

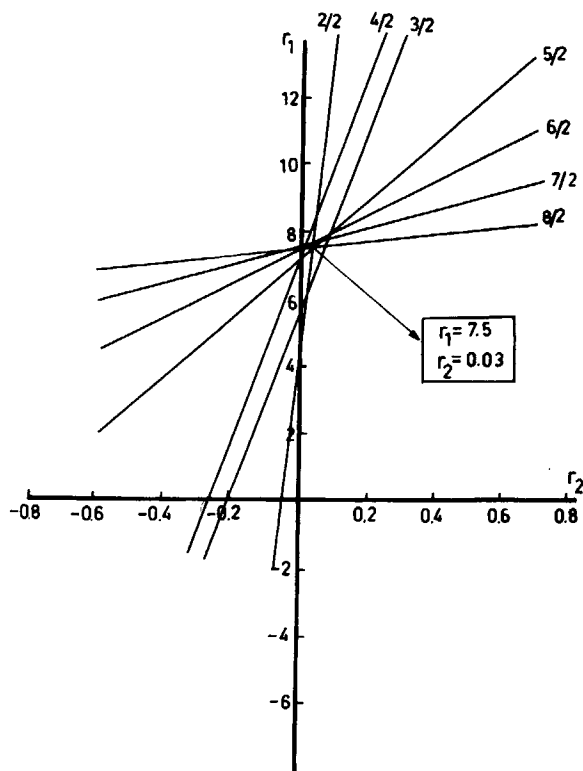


Fig. 9. Mayo-Lewis plot for copolymerization of acrylonitrile and vinyl dichloroacetate in DMF at 60°C. The numbers of individual straight lines correspond to the numbers of experiments given in Table I.

ferences in the molecular weight of the two comonomers. Therefore, it is not advisable to take the nitrogen content as a basis for determining the composition of the copolymer, and especially for such systems as AN-VDAc and AN-VTAc. Figure 4 depicts the function  $\eta = f(\xi)$  for the system AN-VTAc, using the nitrogen content error of  $\pm 3$  percent. The error of the determination of the values of  $r_1$  and  $r_2$  at the comonomer molecular weight ratio  $M_{\text{VTAc}}/M_{\text{AN}} = 3.573$  and with increasing VTAc content of the copolymer can be seen to increase considerably. The nitrogen-based experimental points all lie on a straight line cutting off a value of  $r_1 = 7.27$ , which is in good agreement with the value of  $r_1 = 7.13$  obtained from the data based on the chlorine content, although the characteristic curvature of the graph seen in Figure 3 is not observed in this case.

The Kelen-Tüdös method gives a graphic dependence  $\eta = f(\xi)$  between the composition of the starting monomer feed and the copolymer composition, where  $\xi$  is in the range (0–1); thus the distribution of experimental points is uniform (Figs. 1–4) and hence estimation of their deviation from the straight line is possible. This method therefore gives information as to whether the experimental results are in agreement with the simple copolymer composition equation. To evaluate the results obtained by the Kelen-Tüdös method in comparison with other generally used methods of determining the  $r_1$  and  $r_2$  values, the data from Table I was used to draw Fineman-Ross<sup>1</sup> plots and Mayo-Lewis<sup>9</sup> plots.



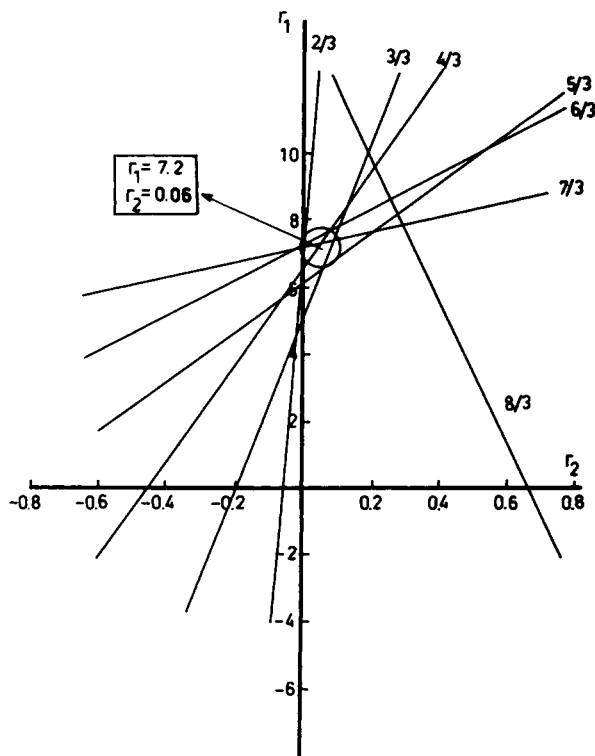


Fig. 10. Mayo-Lewis plot for copolymerization of acrylonitrile and vinyl trichloroacetate in DMF at 60°C. The numbers of individual straight lines correspond to the numbers of experiments given in Table I.

Figures 5–7 show Fineman-Ross plots for the systems AN-VCAc, AN-VDAc, and VTAc based on eq. (3):<sup>1</sup>

$$x(y-1)/y = r_1(x^2/y) - r_2 \quad (3)$$

where  $x$  and  $y$  have the same meaning as in eq. (1).

The  $r_1$  and  $r_2$  values calculated from eq. (3) are listed in Table II. The values of  $r_1$  obtained by this method are in good agreement with the  $r_1$  values obtained by the Kelen-Tüdös method. However, the  $r_2$  values differ considerably (Figs. 5–7) from the corresponding  $r_2$  values obtained from Figures 1–3, and for the systems AN-VDAc and AN-VTAc even negative  $r_2$  values have been obtained. The negative values of reactivity coefficients determined by the Fineman-Ross method have been explained in the literature<sup>19</sup> as being due to certain errors in elementary analysis determinations.

The differences in the  $r_1$  and  $r_2$  values obtained by the two quoted linear methods by use of the same experimental data can be the results of different statistical weights of the experimental points considered in the Kelen-Tüdös and Finemann-Ross methods. This is also supported by the change of the  $r_1$  and  $r_2$  values computed by the Fineman-Ross method after interchanging the comonomer indices and/or after transforming eq. (3) into the form:

$$(y-1)/x = r_1 - r_2(y/x^2) \quad (4)$$

The values of  $r_1$  and  $r_2$  calculated from eq. (4) are also listed in Table II.

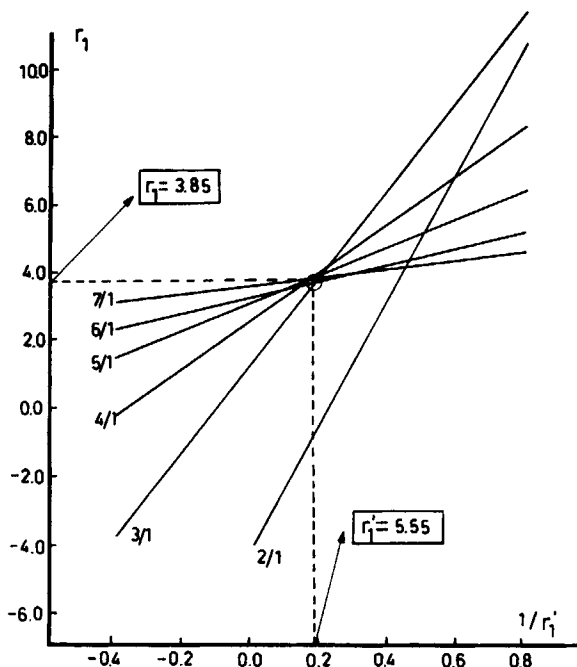


Fig. 11. Merz-Barb plot for copolymerization of acrylonitrile and vinyl chloroacetate in DMF at 60°C. The numbers of individual straight lines correspond to the numbers of experiments given in Table I.

The Fineman-Ross plots (Figs. 5–7) indicate that the characteristic deviations of the experimental points from linearity are much less pronounced than those observed on the Kelen-Tüdös plots (Figs. 1–3).

Figures 8–10 show the graphical method of determining the  $r_1$  and  $r_2$  values by using the Mayo-Lewis<sup>9</sup> copolymer composition integral equation for the data listed in Table I (low percentage conversion). The  $r_1$  and  $r_2$  values obtained by the above method are listed in Table II and are in very good agreement with the corresponding values obtained by the Kelen-Tüdös method. Considerable scatter of the intersection points of the different experimentally derived straight lines is to be observed. The greatest scatter is for the AN-VTAc system for which (Fig. 3) the largest deviation of the points from the straight line were found earlier. Such deviations as those to be seen in Figures 1–3 are present in Figures 8–10 in the form of the above mentioned scatter of intersection points.

These deviations are not accidental but can be due to the penultimate effect present in the copolymerization of acrylonitrile and vinyl chloroacetates. The presence of such an effect was checked by using the Merz<sup>20</sup> and Barb<sup>21</sup> scheme which, in our case, where it is assumed that  $r_2 = r_2' = 0$ , can be put simply as:

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

The values of the  $r_1'$  coefficients accounting for the penultimate effect can be determined from Figures 11–13. It is evident from Table II that ratio  $r_1'/r_1$  decreases with increasing number of chlorine atoms in the ester group substituents of the vinyl chloroacetates used.

The average values of the Alfrey-Price<sup>23</sup> parameters  $Q_2$  and  $e_2$  (Table II) were

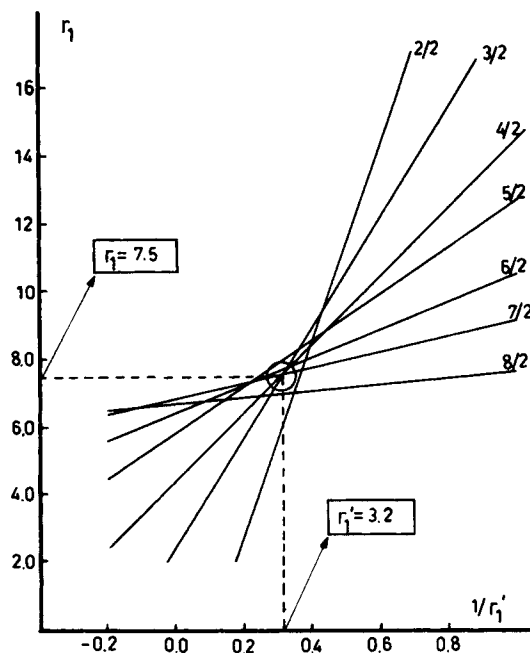


Fig. 12. Merz-Barb plot for copolymerization of acrylonitrile and vinyl dichloroacetate in DMF at 60°C. The numbers of individual straight lines correspond to the numbers of experiments given in Table I.

calculated from eqs. (6) and (7) by using the  $r_1$  and  $r_2$  values obtained by the Kelen-Tüdös method and also by use of the data quoted in the literature.<sup>22,24,25</sup>

$$r_1 r_2 = \exp \{-(e_1 - e_2)^2\} \quad (6)$$

$$r_1 = Q_1/Q_2 \exp \{-e_1(e_1 - e_2)\} \quad (7)$$

The unpublished data cited by Young<sup>26</sup> obtained for the system AN-VCAc ( $r_1 = 0.34$ ,  $r_2 = 0.09$ ) and for the system AN-VDAc ( $r_1 = 0.25$ ,  $r_2 = 0.18$ ) have not been used in the above calculations.

The values of  $Q_2$  and  $e_2$  (Table II) agree well with the ideal  $Q$ - $e$  scheme, i.e., the values of  $Q_2$  increase with increasing number of chlorine atoms ( $Q_2$  for VAc = 0.22<sup>22</sup>), while the overall monomer reactivity increases slightly.

The decrease of the negative values of  $e_2$  with increasing number of chlorine atoms ( $e_2$  for VAc = 0.59<sup>22</sup>) indicates the growth of the electron-acceptor effect of the ester group.

The obtained results make it possible to draw the following conclusions as to the relationship between the chemical structure of the monomers and their reactivity. For a simple copolymerization scheme, the relative reactivity of the vinyl chloroacetates ( $\log 1/r_1$ ) as determined in relation to the polyacrylonitrile radical, can be described by the linear (CF = 0.983) Taft equation:<sup>27</sup>

$$\log (1/r_1) - \log (1/r_1)_{\text{VAc}} = (0.139 \pm 0.006)E_S \quad (8)$$

where  $E_S$  is a measure of the steric hindrance effect of the substituent and  $\log (1/r_1)_{\text{VAc}} = -0.594$ . The  $\log (1/r_1)_{\text{VAc}}$  values were originally taken from the paper

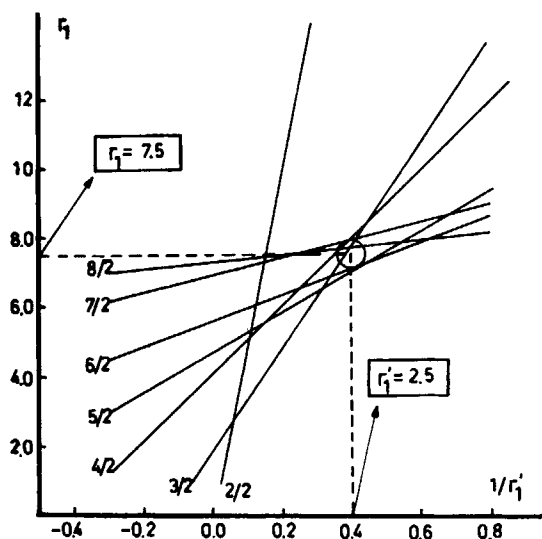


Fig. 13. Merz-Barb plot for copolymerization of acrylonitrile and vinyl trichloroacetate in DMF at 60°C. The numbers of individual straight lines correspond to the numbers of experiments given in Table I.

of Mayo and co-workers<sup>28</sup> ( $r_1 = 4.05 \pm 0.3$ ,  $r_2 = 0.061 \pm 0.013$ ) and then computed by using the Kelen-Tüdös relation to give  $r_1 = 4.05 \pm 0.2$  and  $r_2 = 0.16 \pm 0.03$ . Equation (8) indicates that in the simple copolymerization scheme the change of the vinyl chloroacetate substituent does not change the inductive effect of the reaction with the polyacrylonitrile radical, the reactivity changes being due to steric effects.

If we take the penultimate effect into consideration, the relative reactivity of vinyl chloroacetates ( $\log 1/r_1$ ) as determined in relation to the polyacrylonitrile radical, can be described by the linear ( $CF = 0.983$ ) Taft equation:<sup>27</sup>

$$\log (1/r_1') = (0.22 \pm 0.01)\sigma^* - 0.96 \quad (9)$$

where  $\sigma^*$  is a measure of the inductive effect of the substituent. The values  $\rho^* = 0.22$  and  $\delta = 0.139$  would seem to suggest that the rate of the reaction of vinyl chloroacetates with polyacrylonitrile radical is only very slightly influenced by changes in the substituents in their ester groups.

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