

Reactivity Ratios for Acrylonitrile-Phenyl Acrylate Copolymerization Systems

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Synopsis

Reactivity ratios for various acrylonitrile-phenyl acrylate 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: $r_1 = 0.46 \pm 0.02$ and $r_2 = 0.36 \pm 0.04$ for acrylonitrile-phenyl acrylate, $r_1 = 0.73 \pm 0.02$ and $r_2 = 0.80 \pm 0.02$ for acrylonitrile-*p*-cresyl acrylate, $r_1 = 0.33 \pm 0.03$ and $r_2 = 0.9 \pm 0.02$ for acrylonitrile-*p*-chlorophenyl acrylate, $r_1 = 0.82 \pm 0.03$ and $r_2 = 1.02 \pm 0.03$ for acrylonitrile-*p*-bromophenyl acrylate, $r_1 = 1.12 \pm 0.05$ and $r_2 = 1.16 \pm 0.05$ for acrylonitrile-*o*-chlorophenyl acrylate, and $r_1 = 1.26 \pm 0.05$ and $r_2 = 0.86 \pm 0.05$ for acrylonitrile-*m*-chlorophenyl acrylate. The dependence of reactivities of the monomers upon their chemical structure was discussed.

INTRODUCTION

The classic equation for copolymer composition expresses a composition of a copolymer by a composition of monomer feed and copolymerization parameters r_1 and r_2 . To determine the r_1 and r_2 ratios, with aid of known compositions of copolymers and monomer feed, one applies various procedures, which have been discussed critically in the past by various authors.¹⁻⁵ Recently, Kelen and Tüdös⁶ have discussed the merits and drawbacks of the linear method used so far and suggested a new graphical linear method for determination of r_1 and r_2 . The distinct advantages of the Kelen-Tüdös method have encouraged us to apply it to our calculations.

EXPERIMENTAL

Acrylonitrile, azobisisobutyronitrile, and *N,N*-dimethylformamide were purified as described previously.⁷ Esters of acrylic acid were synthesized by acylation of the respective phenols with acrylyl chloride in the presence of triethylamine in benzene-pentane mixed solvent (at 0-2°C). Copolymerizations of the monomeric systems were carried out in glass tubes filled on a vacuum line and sealed at a final pressure $<10^{-4}$ mm Hg. Azobisisobutyronitrile (AIBN) (9×10^{-6} mole/cm³) was used as initiator. The temperature of the copolymer-

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izations was $60 \pm 0.1^\circ\text{C}$. Copolymers were precipitated by excess of methanol, dissolved in DMF, precipitated several times with methanol, and dried at $70^\circ\text{C}/0.1\text{ mm Hg}$.

The composition of the copolymers was determined by elemental analysis for C, H, N, Cl or Br (Mr. S. Binkowski, The Molecular and Macromolecular Research Centre, Łódź, Poland).

TABLE I
Copolymerization of Acrylonitrile (M_1) with Phenyl Acrylates (M_2)
in DMF Solution at 60°C^a

| Expt. no. | Comonomer | Ratio of molar fractions in mono-mer feed x | Ratio of molar fractions in copoly-mer y | Conver- sion, % |
|-----------|---------------------------------|---|--|-----------------|
| 1/1 | Phenyl acrylate | 0.1428 | 0.3193 | 27.04 |
| 2/1 | | 0.3333 | 0.5489 | 14.59 |
| 3/1 | | 0.6000 | 0.7047 | 13.42 |
| 4/1 | | 1.0000 | 1.0104 | 9.39 |
| 5/1 | | 1.6667 | 1.4195 | 10.07 |
| 6/1 | | 3.0000 | 2.2123 | 8.52 |
| 7/1 | <i>p</i> -Chlorophenyl acrylate | 7.0000 | 4.3792 | 11.17 |
| 1/2 | | 0.3333 | 0.2713 | 11.66 |
| 2/2 | | 0.6000 | 0.4618 | 10.73 |
| 3/2 | | 1.0000 | 0.7271 | 14.11 |
| 4/2 | | 1.6667 | 1.0462 | 13.00 |
| 5/2 | | 3.0000 | 1.5490 | 7.79 |
| 6/2 | <i>m</i> -Chlorophenyl acrylate | 7.0000 | 2.7836 | 8.72 |
| 1/3 | | 0.3333 | 0.4101 | 17.93 |
| 2/3 | | 0.6000 | 0.7256 | 15.93 |
| 3/3 | | 1.0000 | 1.1710 | 14.95 |
| 4/3 | | 1.6667 | 2.0361 | 12.16 |
| 5/3 | | 3.0000 | 3.7427 | 10.11 |
| 6/3 | <i>o</i> -Chlorophenyl acrylate | 7.0000 | 9.1821 | 4.92 |
| 1/4 | | 0.3333 | 0.3072 | 17.85 |
| 2/4 | | 0.6000 | 0.5625 | 16.71 |
| 3/4 | | 1.0000 | 1.0040 | 15.04 |
| 4/4 | | 1.6667 | 1.6569 | 13.12 |
| 5/4 | | 3.0000 | 3.1666 | 10.04 |
| 6/4 | <i>p</i> -Bromophenyl acrylate | 7.0000 | 7.5470 | 6.02 |
| 1/5 | | 0.1428 | 0.1477 | 28.92 |
| 2/5 | | 0.3333 | 0.3172 | 19.98 |
| 3/5 | | 0.6000 | 0.4977 | 19.87 |
| 4/5 | | 1.0000 | 0.8518 | 15.29 |
| 5/5 | | 1.6667 | 1.4195 | 16.28 |
| 6/5 | Cresyl acrylate | 3.0000 | 2.6657 | 10.18 |
| 7/5 | | 7.0000 | 6.2559 | 10.10 |
| 1/6 | | 0.1428 | 0.1765 | 17.5 |
| 2/6 | | 0.3333 | 0.3562 | 14.3 |
| 3/6 | | 0.6000 | 0.6064 | 12.7 |
| 4/6 | | 1.0000 | 0.9107 | — |
| 5/6 | | 1.6667 | 1.5458 | 8.1 |
| 6/6 | | 3.0000 | 2.9714 | 7.8 |
| 7/6 | | 7.0000 | 4.8858 | 10.4 |

^a Concentration of AIBN, 9×10^{-6} mole/cm³; concentration of monomer feed, 4×10^{-3} mole/cm³.

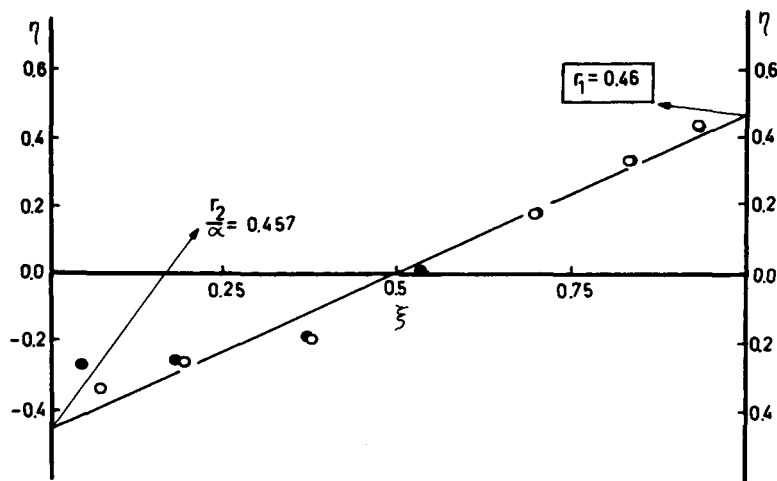


Fig. 1. Kelen-Tüdös plot for copolymerization of acrylonitrile-phenyl acrylate in DMF at 60°C: (○) eq. (1); (●) integrated eq. (1). Constant for eq. (1), $\alpha = 0.845$; correlation factor, 0.988.

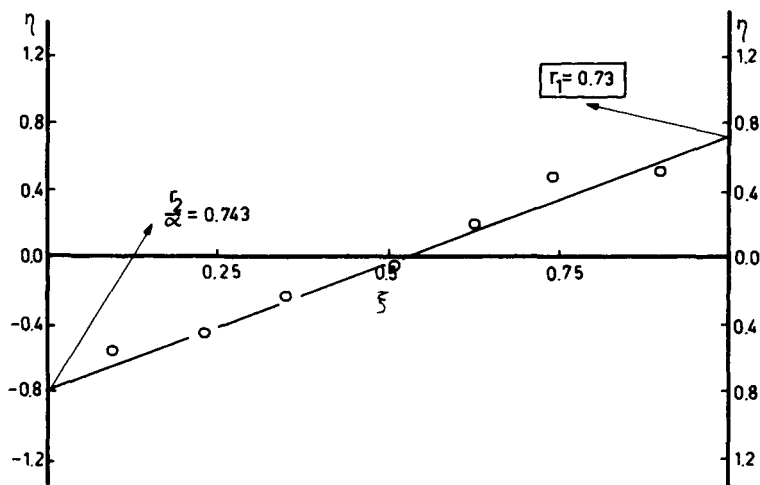


Fig. 2. Kelen-Tüdös plot for copolymerization of acrylonitrile-*p*-cresyl acrylate in DMF at 60°C. Constant for eq. (1), $\alpha = 1.076$; correlation factor, 0.984.

RESULTS AND DISCUSSION

Composition of copolymers, monomer feed, and conversions for the copolymerization systems under study are summarized in Table I. The data were used to calculate the reactivity ratios, r_1 (acrylonitrile) and r_2 (phenyl acrylates) according to eq. (1):⁶

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

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 M_1 and M_2 in the copolymer, and α is a constant. The constant α for eq. (1) can be computed from the data given in Table I from eq. (2):⁶

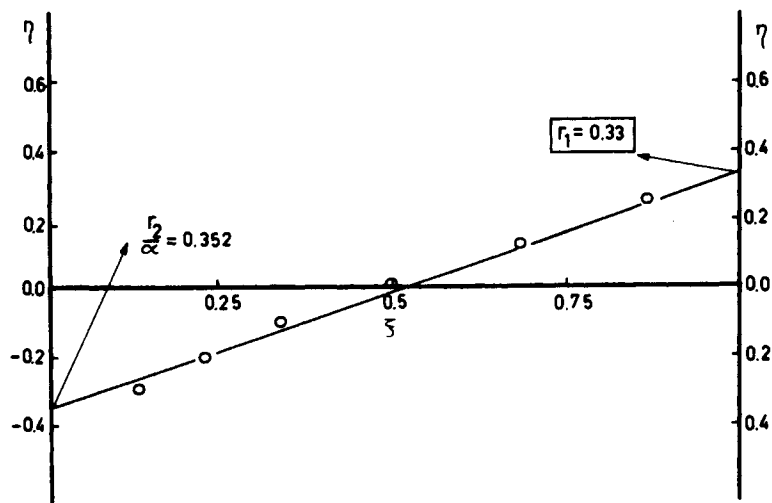


Fig. 3. Kelen-Tüdös plot for copolymerization of acrylonitrile-*p*-chlorophenyl acrylate in DMF at 60°C. Constant for eq. (1), $\alpha = 2.68$; correlation factor, 0.993.

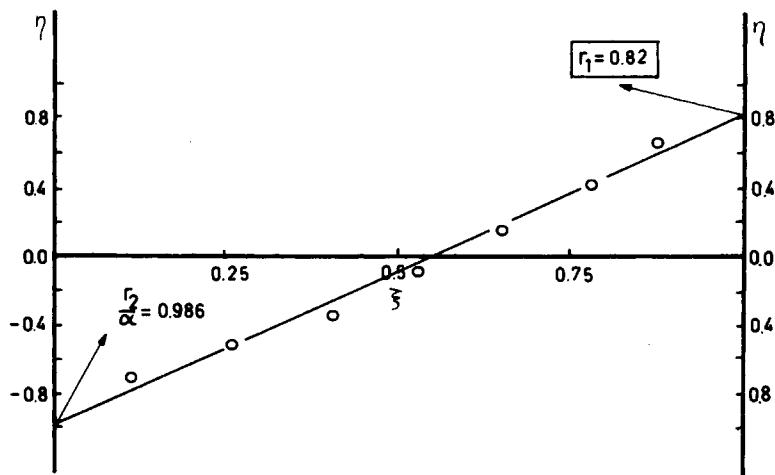


Fig. 4. Kelen-Tüdös plot for copolymerization of acrylonitrile-*p*-bromophenyl acrylate in DMF at 60°C. Constant for eq. (1), $\alpha = 1.04$; correlation factor, 0.993.

$$\alpha = x_{\min}x_{\max}/(y_{\min}y_{\max})^{0.5} \quad (2)$$

Equation (1) as a linear relationship between $x(y-1)/(\alpha y + x^2) = \eta$ and $x^2/(\alpha y + x^2) = \xi$ is illustrated graphically in Figures 1-6 for the acrylonitrile-phenyl acrylate copolymerization systems. The straight lines were drawn on the basis of the least-squares method. Correlation factors and constants α are given in the figure captions and in Table II. A relatively regular curvature of the experimental points with respect to the straight lines drawn is observed in Figures 1, 3, 4, and 6. In Figure 2, the deviations are occasional in nature, and in Figure 5 the best agreement between experiment and eq (1) occurs. The possibility of observing such a systematic deviation of experimental values (η, ξ) from eq. (1) for copolymer composition is one of the evident advantages of the Kelen-

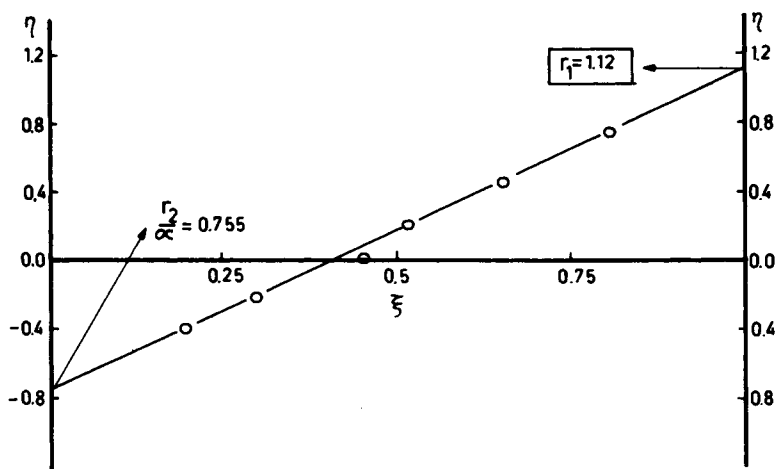


Fig. 5. Kelen-Tüdös plot for copolymerization of acrylonitrile-*o*-chlorophenyl acrylate in DMF at 60°C. Constant for eq. (1), $\alpha = 1.532$; correlation factor, 0.996.

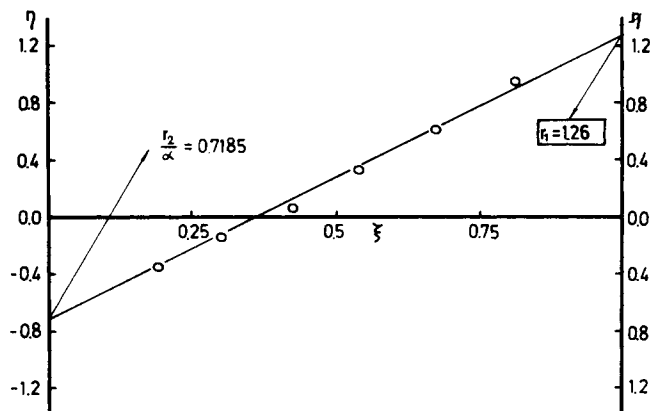


Fig. 6. Kelen-Tüdös plot for copolymerization of acrylonitrile-*m*-chlorophenyl acrylate in DMF at 60°C. Constant for eq. (1) $\alpha = 1.20$; correlation factor, 0.985.

Tüdös method. This is due to the variability of the independent variable in the range (0,1). However, it is not possible to define the reasons for the deviations observed (Figs. 1, 3, 4, and 6) on the basis of the series of experiments carried out for one concentration of monomer feed yet. In Figure 1 η, ξ values derived from the integral form⁸ of eq. (1) with regard to the conversion factors are given. The error made by neglecting the conversion (Table I) is not significant, and exists within the region of errors shown for the ratios, r_1 and r_2 , computed through eq. (1) and summarized in Table II.

The complete agreement of the r_1 and r_2 values calculated from eq. (1) and those obtained from the Mayo-Lewis⁹ integral copolymer composition equation indicates that the application of the Kelen-Tüdös differential copolymer composition equation to experimental results obtained for higher degrees of conversion (Table I) is justified.⁸

Results given in Table I have been also used to calculate the values of r_1 and

r_2 by using the Fineman-Ross¹⁰ linear methods based on eqs. (3) and (4):

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

and

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

where x and y denote the same quantities as in eq. (1). Results obtained are listed in Table II. The corresponding values obtained from eqs. (3) and (4) in general differ from one another, but their average values agree well with those determined by the Kelen-Tüdös method.

Correlation coefficients of the linear relationships (3) and (4) are higher than those obtained for the linear relationship (1), which implies that the some experimental data are better described by the Fineman-Ross straight-line relationship. This fact points to a higher sensitivity of the Kelen-Tüdös method for the determination of the deviation of the experimentally obtained copolymer composition from those derived from the classical copolymer composition equation.

It follows from Table II that the reactivity ratios vary with the substituent in the phenyl ring of comonomers having the general structure I

TABLE II
Copolymerization Parameters of Acrylonitrile (M_1) with Phenyl Acrylates
(M_2) in DMF at 60° C

| Comonomer | Equation ^a | r_1 | r_2 | Correlation factor | Q_2^b | e_2 | $\Delta\sigma_R^+{}^c$ |
|---------------------------------|-----------------------|-------------|-------------|--------------------|---------|-------|------------------------|
| <i>p</i> -Chlorophenyl acrylate | KT | 0.33 ± 0.03 | 0.94 ± 0.02 | 0.9930 | 0.50 | 0.12 | } |
| | FR3 | 0.39 | 1.03 | 0.9982 | | | |
| | FR4 | 0.31 | 0.85 | 0.9982 | | | |
| | ML | 0.35 ± 0.10 | 0.90 ± 0.10 | — | | | |
| Phenyl acrylate | KT | 0.46 ± 0.02 | 0.36 ± 0.04 | 0.9880 | 0.26 | -0.15 | } |
| | FR3 | 0.38 | 0.33 | 0.9980 | | | |
| | FR4 | 0.52 | 0.45 | 0.9995 | | | |
| | ML | 0.40 ± 0.05 | 0.35 ± 0.05 | — | | | |
| <i>p</i> -Cresyl acrylate | KT | 0.73 ± 0.02 | 0.80 ± 0.02 | 0.9851 | 0.33 | 0.45 | } |
| | FR3 | 0.68 | 0.75 | 0.9982 | | | |
| | FR4 | 0.63 | 0.63 | 0.9897 | | | |
| | ML | 0.78 ± 0.15 | 0.80 ± 0.15 | — | | | |
| <i>p</i> -Bromophenyl acrylate | KT | 0.82 ± 0.03 | 1.02 ± 0.03 | 0.993 | 0.44 | 0.78 | } |
| | FR3 | 0.70 | 0.93 | 0.998 | | | |
| | FR4 | 0.89 | 1.13 | 0.999 | | | |
| | ML | 0.80 ± 0.15 | 1.0 ± 0.15 | — | | | |
| <i>o</i> -Chlorophenyl acrylate | KT | 1.12 ± 0.05 | 1.16 ± 0.05 | 0.9960 | — | — | } |
| | FR3 | 1.11 | 1.16 | 0.9990 | | | |
| | FR4 | 1.12 | 1.16 | 0.9999 | | | |
| | ML | 1.12 ± 0.10 | 1.16 ± 0.10 | — | | | |
| <i>m</i> -Chlorophenyl acrylate | KT | 1.26 ± 0.05 | 0.86 ± 0.05 | 0.9850 | — | — | } |
| | FR3 | 1.34 | 0.93 | 0.9997 | | | |
| | FR4 | 0.95 | 0.62 | 0.9479 | | | |
| | ML | 1.25 ± 0.10 | 0.85 ± 0.10 | — | | | |

^a KT = Kelen-Tüdös, eq. (1); FR3 = Fineman-Ross, eq. (3); FR4 = Fineman-Ross, eq. (4); ML = Mayo-Lewis method.

^b $Q_1 = 0.6$, $e_1 = 1.2$.

^c Data of Brown and Okamoto.¹⁸

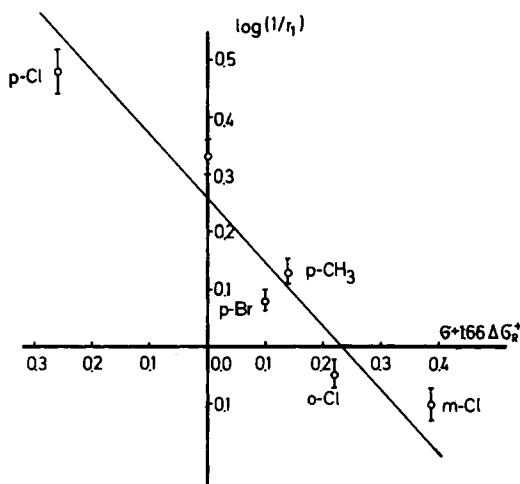
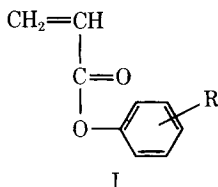


Fig. 7. Yukawa-Tsuno relationship for phenyl acrylates for copolymerization with acrylonitrile.



where R is H, *p*-CH₃, *p*-Cl, *p*-Br, *o*-Cl, or *m*-Cl.

For reactive series with vinyl monomers the rule of variation of activation energy has been stated,^{11,12} most frequently either in form of Hammett's equation¹³ [eq. (5)]

$$\log(1/r_1) = \rho\sigma + \gamma E_R \quad (5)$$

or Taft's equation¹⁴ [eq. (6)],

$$\log(1/r_1) = \rho^*\sigma^* + \delta E_s \quad (6)$$

where σ and E_R are Hammett's polar and Yamamoto-Otsu's resonance constants for a substituent,¹² respectively; σ^* and E_s are Taft's polar and steric constants for a substituent,^{14,15} respectively; and ρ , γ , ρ^* , and δ are reaction constants.

In the series of copolymerizations of acrylonitrile with phenyl acrylates examined by us, the dependence of reactivities of the comonomers M₂ with respect to the polyacrylonitrile radical on the parameters of their structure cannot be described by eq. (5). It is believed that the reactivities of this monomers in relation to polyacrylonitrile radical are defined both by polar and steric effects of the substituents in a phenyl ring. In this case, one would rather expect to observe polar and resonance effects like for the series of phenyl methacrylates.¹⁶ However, such correlation in the series of phenyl acrylates does not occur. A group of phenyl substituents, particularly those of different mesomeric character, exhibit rather stronger or weaker action than it could be suspected from a common value σ . Hence, in our opinion, for substituents in a phenyl ring it is necessary to apply Hammett's equation modified by Yukawa and Tsuno:¹⁷

$$\log(1/r_1) = \rho(\sigma + \gamma\Delta\sigma_R^+) \quad (7)$$

where ρ , σ , and γ are as defined previously and $\Delta\sigma_R^+$ is the difference between Brown's constant σ^+ for a substituent¹⁸ and Hammett's constant σ for a substituent.

The result of using eq. (7) for the series of phenyl acrylates is presented in Figure 7. By Jaffe's criterion¹⁹ (correlation factor = 0.956) the relationship given may be recorded as a linear function with good correlation:

$$\log(1/r_1) = -0.98(\sigma + 1.66\Delta\sigma_R^+) \quad (8)$$

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