

# Calculation of Reactivity Ratio of Resin Copolymers Derived from Substituted Acetophenones Using Kelen–Tüdös Equation

P. L. NAYAK, S. LENKA, and P. K. NAYAK

Department of Chemistry, Ravenshaw College, Cuttack-753003, Orissa, India

## SYNOPSIS

A number of resin copolymers have been prepared by condensing some substituted acetophenones with chloro-substituted anilines, benzoic acids, and formaldehyde. The reactivity ratios of the monomers have been computed by using the Kelen–Tüdös equation. The results have been discussed taking into account the inductive, resonance, and steric effects of the substituents.

## INTRODUCTION

The development of many linear equations has greatly stimulated the study of the effects of structure in the reactivity of organic molecules. Within the past three decades, particularly, considerable progress has been made in the elucidation and disentanglement of the many interlocking factors involved in this problem. The ever increasing number of parameters, equations, factors, and interdependencies, however, present a formidable obstacle to the initiate as well as to the novice, in the application of the ideas that have been developed. Although the structure–reactivity relationship has been extensively used for the elucidation of the mechanism of many organic relations, this relationship has not been used in polymerization reactions. In the present investigation, an attempt has been made to correlate the reactivity of some phenolic monomers by calculating the reactivity ratios of copolymerization system.

There have been a number of investigations on a possible relationship between structure of the monomers and the reactivity ratios in a copolymerization system. Semiquantitative relationship between resonance stabilization of growing chain, chain ends, and electron distribution at the double bonds of unsaturated compounds and reactivity ra-

tios has been developed.<sup>1–4</sup> A reliable knowledge of copolymerization parameters is both theoretically and practically of great significance. It provides valuable information on the correlation between chemical structure and reactivity of the monomers and allows quantitative kinetic analysis of the system, the immediate practical value of which is also evident. The reactivity ratios have been determined by several methods: e.g., linear,<sup>5</sup> nonlinear,<sup>6–8</sup> computer programming routines,<sup>9</sup> etc. However, the Kelen–Tüdös linear graphical method<sup>10</sup> has been found to be one of the most suitable methods for determining copolymerization parameters for phenolic copolymerization systems.<sup>11</sup> In the present investigation, this method has been used for determining the parameters  $r_1$  and  $r_2$  for some substituted aromatic acetophenones. The linear graphical method of Fineman–Ross has also been used to compare with the results obtained by using the Kelen–Tüdös (K–T) method. The results have been discussed in the light of polarization and resonance stabilization of the monomers.

## EXPERIMENTAL

Substituted acetophenones (*o*-, *m*-, and *p*-hydroxy, *m*-, *p*-amino, and 2,4 and 2,5-dihydroxy acetophenones) have been used to copolymerize by condensing with substituted anilines, benzoic acids, and formaldehyde in the presence of 2 mL of 10(N)

HCl as catalyst for 4–8 h at 120°C. The copolymers were freed from unreacted monomers by repeated washing under inspection. The compounds were dried at vacuum.

The composition of the copolymers were determined by electrometric titration techniques in non-aqueous media,<sup>12</sup> together with halogen estimation of the copolymer by Volhard's method.<sup>13</sup>

## TREATMENT OF RESULTS

The reactivity ratios  $r_1$  (substituted aromatic acetophenones) and  $r_2$  [comonomer: *o*-, *m*-, and *p*-chloro aniline (CA), *o*-, *m*-, and *p*-chloro benzoic acids (CBA), *p*-chloro acetophenone (CAP)] have been calculated from the composition of the copolymers and their corresponding monomer feed, by using the following equations given by Kelen-Tüdös.<sup>10</sup>

$$\eta = \left( \frac{r_1 + r_2}{\alpha} \right) \epsilon - \frac{r_2}{\alpha} \quad (1)$$

where

$$\eta = X(Y - 1)(\alpha Y + X^2) \quad (2)$$

$$\epsilon = \frac{X^2}{(\alpha Y + X^2)} \quad (3)$$

$$\alpha = \frac{X_{\min} X_{\max}}{(Y_{\min} Y_{\max})^{0.5}} \quad (4)$$

where  $X$  is the ratio of mole fractions of monomers 1 ( $M_1$ ) and monomer 2 ( $M_2$ ) in the feed and  $Y$  is that of the copolymer. The value of  $r_1$  and  $r_2$  obtained are summarized in Table I.

The Fineman-Ross method permits two linear graphical equations for the evaluation of the parameters as represented below:

$$\frac{X(Y - 1)}{Y} = r_1 \left( \frac{X^2}{Y} \right) - r_2 \quad (5)$$

$$\frac{Y - 1}{X} = r_1 - r_2 \left( \frac{Y}{X^2} \right) \quad (6)$$

where  $X$  and  $Y$  have the same meaning. The values are tabulated in Table I.

However, in applying the approximation  $Y - dm_1/dm_2$ , a systematic error is committed, which can be lowered by keeping conversion as low as possible. Since in the present investigation, the degree

of conversion is much higher it is important to deduce the degree of error.

The relative error of approximation in percent may be defined as

$$\delta = \frac{|\eta - \eta(\epsilon)|}{(r_1 + r_2/\alpha) \times 100} \quad (7)$$

where  $\eta(\epsilon)$  is the value of  $\eta$  obtained from Eq. (1) on substitution of Eq. (3) and  $n$  is the value obtained from Eq. (2).

## RESULTS AND DISCUSSION

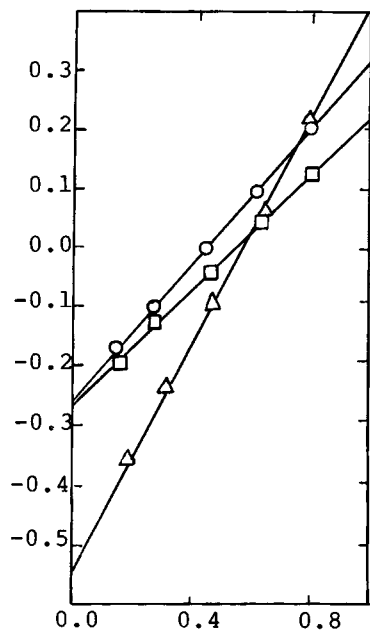
The reactivity ratios  $r_1$  (hydroxy and amino-substituted acetophenones) and  $r_2$  (different aromatic substrates) have been calculated by using the Fineman-Ross and Kelen-Tüdös equations. The data is presented in Table I for comparison. The Kelen-Tüdös plot for the copolymerization systems are shown in Figures 1–7. Figures 1 and 2 show the K-T plot for copolymerization of *p*-hydroxy and *p*-amino acetophenone (PHAP, PAAP), respectively, with *o*-, *m*-, and *p*-substituted chlorobenzoic acids (OCBA, MCBA, PCBA) in the presence of formaldehyde as condensing agent. Figure 3 shows the plot for copolymerization of 2,4- and 2,5-hydroxy acetophenones (RAP, QAP) with *o*- and *p*-chlorobenzoic acids. Figure 4 shows the copolymerization of *o*-, *m*-, and *p*-hydroxy acetophenones with *p*-chloro acetophenone. Figures 5–7 represent the copolymerization of *o*-hydroxy, *m*-hydroxy, and *m*-amino acetophenone (OHAP, MHAP, MAAP), respectively, with *o*-, *m*-, and *p*-chloro anilines (OCA, MCA, PCA).

The errors involved in the calculation of reactivity ratios are shown in Table II for the copolymerization systems: RAP-OCBA-F, RAP-PCBA-F, QAP-OCBA-F, and QAP-PCBA-F. This has also been furnished graphically in Figure 8 as a plot of error (in percentage) against molar ratio of monomer feed composition.

On comparing  $r_1$  and  $r_2$  values obtained from the Kelen-Tüdös equation [Eq. (1)] and the Fineman-Ross method [Eqs. (5) and (6)], a great deal of discrepancy can be observed. However, taking the mean value of the results obtained from both equations, i.e., by eliminating the uncertainties in slope measurement, it coincides well with the K-T values. The reciprocal of reactivity ratio, expressing the relative strength of different monomers when they are copolymerized with a given monomer, are presented in Table I.

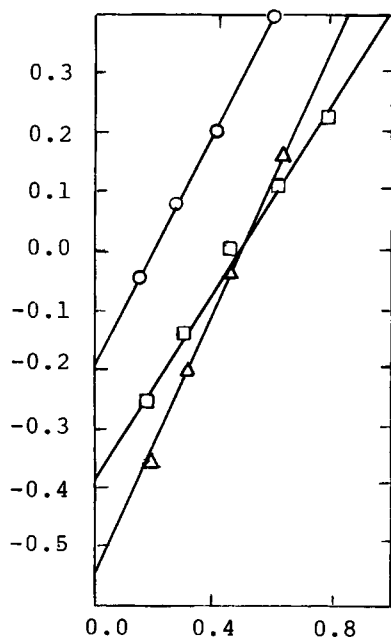
**Table I Monomer Reactivity Ratio Values of Reactants: Compared**

Copoly- merization System	Fineman-Ross Method						Kelen-Tüdös Equation			
	Method A		Method B		Mean Value		$r_1$	$r_2$	$1/r_1$	$1/r_2$
	$r_1$	$r_2$	$r_1$	$r_2$	$r_1$	$r_2$				
PHAP-OCBA-F	0.42	0.41	0.42	0.405	0.41	0.405	0.4013	2.469	2.4919	
PHAP-MCBA-F	0.21	1.4	0.215	1.2	0.2125	1.3	1.368	4.5455	0.731	
PHAP-PCBA-F	0.31	0.22	0.315	0.2057	0.3125	0.2129	0.2142	3.1746	4.6655	
PAAP-OCBA-F	0.52	0.47	0.55	0.46	0.535	0.465	0.4613	1.8519	2.1678	
PAAP-MCBA-F	0.4	0.81	0.39	0.805	0.395	0.8075	0.815	2.5641	1.227	
PAAP-PCBA-F	0.7	0.15	0.7	0.147	0.7	0.1485	0.1443	1.3333	6.93	
RAP-OCBA-F	0.5	0.7	0.5	0.722	0.5	0.711	0.5351	2.0	1.8688	
RAP-PCBA-F	0.4	0.775	0.375	0.778	0.388	0.776	0.4568	2.381	2.1891	
QAP-OCBA-F	0.22	0.47	0.25	0.5	0.235	0.485	0.3367	3.3614	2.97	
QAP-PCBA-F	0.38	0.3	0.4	0.375	0.39	0.338	0.281	2.5641	3.5587	
PCAP-OHAP-F	0.6	0.5	0.526	0.55	0.563	0.525	0.5574	2.1505	0.794	
PCAP-MHAP-F	0.5	0.8	0.905	0.463	0.952	0.631	0.4905	2.1739	2.0887	
PCAP-PHAP-F	1.0	0.45	0.6	0.81	0.8	0.613	0.8451	0.9615	1.1833	
OHAP-OCA-F	0.105	0.28	0.117	0.27	0.111	0.275	0.2801	9.0909	3.5702	
OHAP-MCA-F	0.157	0.59	0.1492	0.713	0.1531	0.6515	0.6945	6.4516	1.4399	
OHAP-PCA-F	0.12	0.32	0.143	0.333	0.1315	0.3265	0.3279	7.4074	3.0497	
MHAP-OCA-F	0.095	2.2	0.097	2.1	0.096	2.15	2.2053	10.0	0.4535	
MHAP-MCA-F	0.08	0.653	0.101	0.678	0.0905	0.6655	0.6454	11.4286	1.5494	
MHAP-PCA-F	0.07	0.97	0.12	1.52	0.095	1.245	1.3457	10.5263	0.7431	
MAAP-OCA-F	0.44	0.32	0.44	0.317	0.44	0.3185	0.3182	2.2599	3.1427	
MAAP-MCA-F	0.03	0.672	0.07	0.673	0.05	0.6725	0.6315	80.0	1.5835	
MAAP-PCA-F	0.02	0.8	0.01	0.93	0.015	0.865	0.8337	66.6667	1.1995	

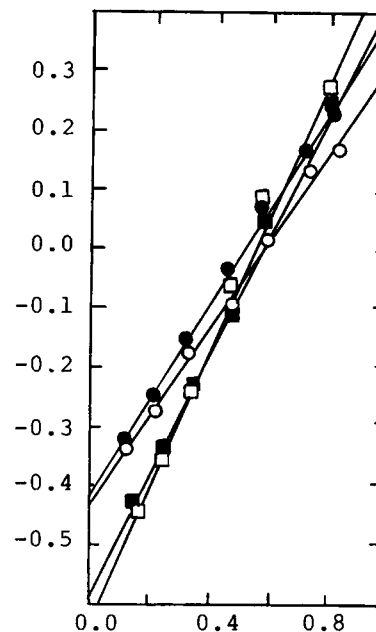


**Figure 1** Kelen-Tüdös plot for the copolymerization systems. ○, PHAP-PCBA-F; □, PHAP-MCBA-F; △, PHAP-OCBA-F.

In the copolymerization of PHAP and PAAP with chlorobenzoic acids, the reactivity ( $1/r_1$ ) has the following order: PCBA > OCBA > MCBA. This is in agreement with their relative degrees of resonance

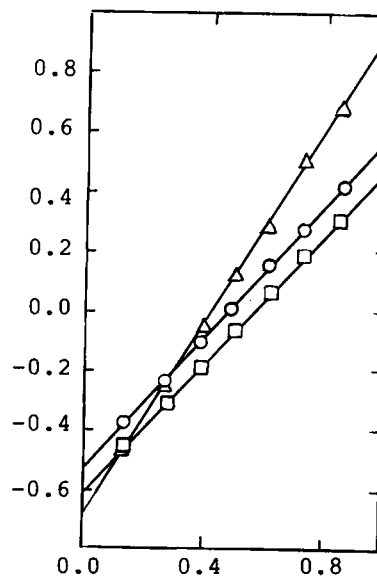


**Figure 2** Kelen-Tüdös plot for the copolymerization systems. □, PAAP-PCBA-F; ○, PAAP-MCBA-F; △, PAAP-OCBA-F.

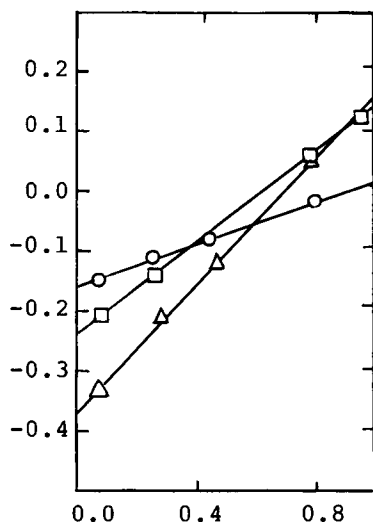


**Figure 3** Kelen-Tüdös plot for the copolymerization systems. ○, QAP-OCBA-F; ●, QAP-PCBA-F; □, RAP-OCBA-F; ■, RAP-PCBA-F.

stabilization. The trend in  $1/r_1$  and PAAP follows the reverse order, which can be attributed to the presence of electron withdrawing  $-\text{COCH}_3$  groups. However, for PAAP it follows the order  $m$ - >  $o$ -



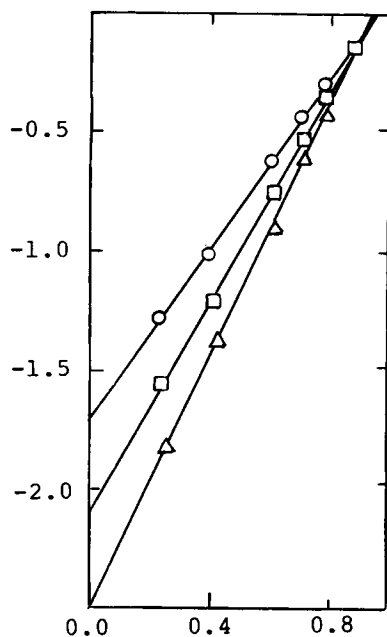
**Figure 4** Kelen-Tüdös plot for the copolymerization systems. ○, PCAP-OHAP-F; □, PCAP-MHAP-F; △, PCAP-PHAP-F.



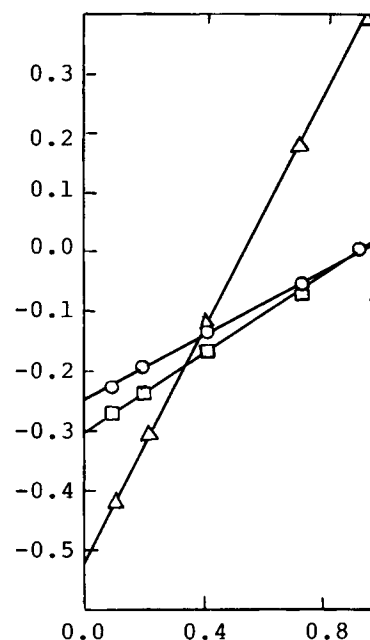
**Figure 5** Kelen-Tüdös plot for the copolymerization systems. ○, OHAP-OCA-F; □, OHAP-PCA-F; △, OHAP-MCA-F.

> *p*-, the change of which can only be attributed to a steric factor.

The reciprocal of reactivity ( $1/r_1$ ) for the copolymerization of 2,4-dihydroxy acetophenone, follows the order PCBA > OCBA. But when 2,5-dihydroxy acetophenone is copolymerized, the trend is OCBA



**Figure 6** Kelen-Tüdös plot for the copolymerization systems. ○, MHAP-OCA-F; □, MHAP-MCA-F; △, MHAP-PCA-F.



**Figure 7** Kelen-Tüdös plot for the copolymerization systems. ○, MHAP-OCA-F; □, MHAP-MCA-F; △, MHAP-PCA-F.

> PCBA, i.e., the reverse order of their base strength. This trend can be well explained taking into account phenomena like resonance stabilization of monomeric units, influence of electron attracting or donating groups present, directive influence of substituents on polarization, as well as the steric factors.<sup>14,15</sup> In case of 2,4-dihydroxy acetophenone, the  $-\text{COCH}_3$  group interacts with hydroxyl groups causing the system to be highly polarized, however, with 2,5-dihydroxy acetophenone the  $-\text{OH}$  groups being para to each other, thereby rendering the molecule weakly polarized, which directs the substituted benzoic acids to follow reverse order as their basic strengths.

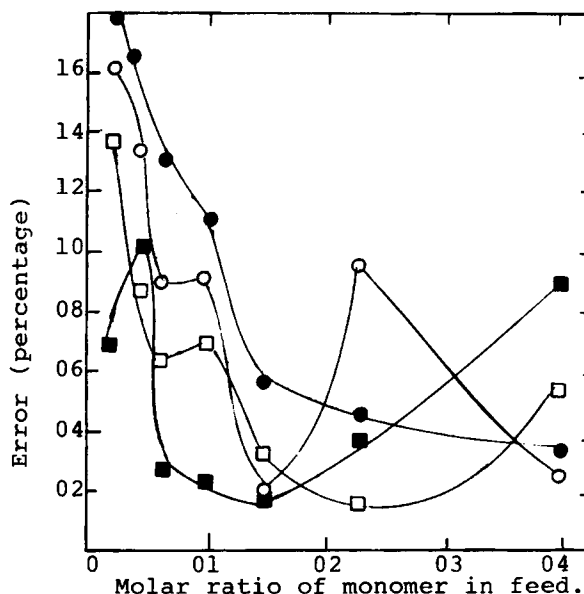
When MHAP and MAAP are copolymerized with chloro anilines, the reactivity ( $1/r_1$ ) follows the order MCA > PCA > OCA. Both the  $-\text{OH}$  and  $-\text{NH}_2$  groups being present meta to an electron-withdrawing  $-\text{COCH}_3$  group causes the system to be very weakly polarized, making a reversal in the order of base strength. Again from the data available, it is observed that  $1/r_1$  values are much higher with MHAP than with MAAP. This can be related to greater resonance stabilization of MHAP than MAAP along with the presence of a phenolic-OH group that renders it more susceptible to attack by a strong base; the relative order being their basic

strength, as evidence from the  $1/r_2$  values shows in Table I.

However, with OHAP the order follows as OCA > PCA > MCA, which can be easily explained. Further, it is well known that the chain growth in phenolic polymerization proceeds in a electrophilic attack of benzylic cations on phenolic molecules.<sup>16</sup> One can expect two types of end groups, e.g., the benzylic cations and the activation of the end ring for further cationic attack due to intramolecular hydrogen bonding, the second factor being predominant with OHAP. Furthermore, one would expect the order of reactivity PCA > OCA > MCA toward electrophilic attack by  $-\text{CH}_2\text{OH}$  group. Clearly the degree of resonance stabilization of monomers and polariza-

**Table II Degree of Error (Percentage) in Using Kelen-Tüdös Equation for Copolymerization of Dihydroxy Acetophenones**

Copolymerization System	Molar Ratio of Monomer Composition in		Error Percentage
	Feed	Copolymer	
RAP-OCBA-F	0.25	0.2891	13.04
	0.4286	0.456	13.40
	0.6666	0.6471	8.88
	1.0	0.854	9.06
	1.5	1.184	5.68
	2.3333	1.51	9.58
RAP-PCBA-F	4.0	2.54	2.44
	0.25	0.27	16.07
	0.4286	0.4014	16.57
	0.6666	0.5811	12.98
	1.0	0.78	10.93
	1.5	1.2	1.97
QAP-OCBA-F	2.3333	1.496	4.68
	4.0	2.22	3.38
	0.25	0.3513	6.79
	0.4286	0.4711	8.69
	0.6666	0.6523	6.3
	1.0	0.7858	6.87
QAP-PCBA-F	1.5	1.0281	5.72
	2.3333	1.4198	1.25
	4.0	1.7218	5.31
	0.25	0.2572	17.81
	0.4286	0.4711	10.8
	0.6666	0.8318	3.69
	1.0	1.01	2.22
	1.5	1.2734	1.64
	2.3333	1.7174	3.67
	4.0	1.72	8.955



**Figure 8** Kelen-Tüdös plot for the copolymerization systems. Plot of percentage of error vs. molar ratio of monomer feed composition for the copolymerization systems. ○, RAP-OCBA-F; ●, RAP-PCBA-F; □, QAP-OCBA-F; ■, QAP-PCBA-F.

tion are more dominant factors, and the overlapping effect of both plays the most crucial role.

Further a look at Table II shows the errors in the range of 1–16%, which can be attributed to the mode of calculation itself. Thus it can be well concluded that Kelen-Tüdös linear graphical methods (as seen from coincidence with Fineman-Ross and theoretical explanations) is well suited for the calculation of reactivity ratios of phenolic and other monomers in case of condensation polymerization process.

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