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## Reactivity Ratios for Some Phenolic Copolymerization Systems

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### ABSTRACT

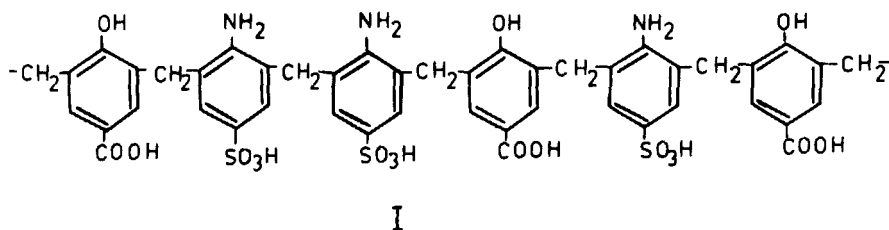
Reactivity ratios of some p-substituted aniline-p-hydroxybenzoic acid copolymerization systems have been determined by the linear graphical method of Kelen and Tüdös. It was found that the copolymerization parameters are affected by the nature of acidic functional groups present in the comonomers, and the sequence of reactivity of comonomers is found to be of the same order as that of their acid strengths.

The classical copolymer composition equation correlates copolymerization parameters  $r_1$  and  $r_2$  with the composition of a copolymer and the composition of monomer feed. Several authors [1-5] applied various procedures to evaluate the reactivity ratios  $r_1$  and  $r_2$  from the known compositions of copolymers and monomer feed. Most [1] of these procedures for the determination of reactivity ratios are not entirely satisfactory. Recently, however, Kelen and Tüdös [6] have discussed the merits and drawbacks of some of these procedures, and suggested a new graphical linear method for the determination of  $r_1$  and  $r_2$ . The distinct advantage of this method 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,  $\infty$ ). The object of the present investigation is to find out whether the Kelen-Tüdös method can be applied to determine reactivity ratios for some

simple phenolic copolymerization systems. An attempt will also be made to study how the copolymerization parameters are affected by the nature of substituents on the comonomers. The following systems have been chosen for the present investigations: p-hydroxybenzoic acid has been taken as the common monomer, and three different copolymers were prepared by condensing it with formaldehyde and one of the following monomers: sulfanilic acid, p-aminobenzoic acid, p-amino phenol. Several samples of each of these copolymers were also prepared by choosing various feed compositions.

### EXPERIMENTAL

Five samples of p-hydroxybenzoic acid (PHB)-sulfanilic acid (SA)-formaldehyde random copolymer (I) have been prepared by refluxing the components in various proportions in the presence of 2 mL of 10 N HCl as catalyst for 2½ hr at 130°C.

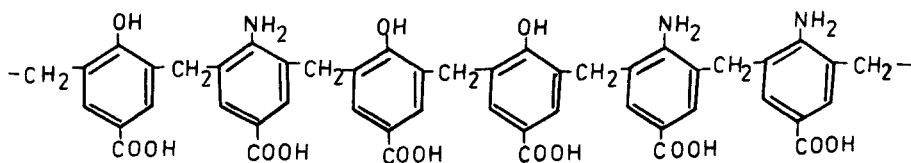


Under identical conditions, Copolymers II and III were prepared by refluxing the common monomer (PHB) with formaldehyde and one of the monomers, e.g., p-aminobenzoic acid (PAB) or p-amino phenol (PAP). Several samples of each of the above copolymers were prepared by choosing different feed compositions. Compositions of the copolymers were determined by potentiometric and conductometric titration techniques in nonaqueous media. The details of the titration procedure have been described elsewhere [7].

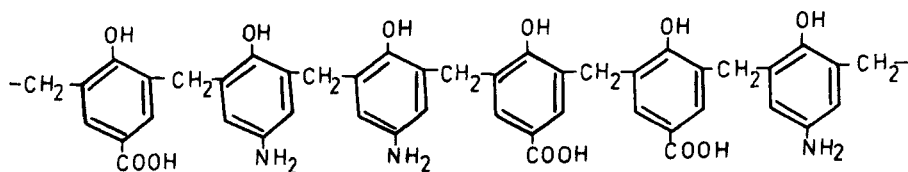
### RESULTS AND DISCUSSION

Composition of copolymers, monomer feed, and the values of  $\alpha$  for the copolymerization systems under study are summarized in Table 1. Reactivity ratios were calculated from the data given in Table 1 according to the equation of Kelen and Tüdös:

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



II



III

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  $\alpha$  is a constant. The equation parameter  $\alpha$  can be computed according to

$$\alpha = \frac{x \min^x \max}{(y \min^y \max)^{0.5}} \quad (2)$$

Equation (1) can be expressed as a linear relationship between  $x(y - 1)/(\alpha y + x^2) = \eta$  and  $x^2/(\alpha y + x^2) = \xi$ . The variations of  $\eta$  with  $\xi$  for the copolymerization systems I, II, and III are illustrated in Figs. 1, 2, and 3, respectively. In all the three figures, except at the extreme composition range, reasonably good agreement is observed between experiment and Eq. (1).

The reactivity ratios  $r_1$  and  $r_2$  have also been calculated from the Fineman-Ross equation:

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

where  $x$  and  $y$  denote the same quantities as in Eq. (1). The results are listed in Table 2. The values determined from the Kelen-Tüdös equation (Eq. 1) compares favorably with those obtained from the Fineman-Ross equation (Eq. 3) (see Table 2).

It is evident from Table 2 that the reactivity ratios vary with the substituent in the phenyl ring of comonomers having the general formula

TABLE 1. Compositions of p-Substituted Aniline ( $M_1$ ) and p-Hydroxybenzoic Acid ( $M_2$ ) Copolymerization Systems

Feed	Composition	Copolymer	Composition	Ratio of mole fraction of monomer in feed, $x = M_1/M_2$	Ratio of mole fraction of monomer in copolymer, $y = d[M_1]/d[M_2]$	$\alpha$
SA	PHB	SA	PHB			
0.9m	0.1m	1.1050	0.895	0.9000	1.2346	
0.7m	0.3m	0.9883	1.0117	2.3333	0.9769	
0.5m	0.5m	0.6533	1.3467	1.0000	0.4851	1.5196
0.3m	0.7m	0.6131	1.3869	0.4286	0.4421	
0.1m	0.9m	0.5193	1.4807	0.1111	0.3507	
PAB	PHB	PAB	PHB			
0.9m	0.1m	0.32	0.68	0.1111	0.4706	
0.2m	0.8m	0.20	0.80	0.25000	0.2500	
0.33m	0.66m	0.75	0.25	0.5000	3.0000	
0.5m	0.5m	0.57	0.43	1.0000	1.3256	0.5897
0.66m	0.33m	0.44	0.56	2.0000	0.7857	
0.8m	0.2m	0.84	0.16	4.0000	5.2500	
0.9m	0.1m	0.0948	1.9052	9.0000	11.5000	
PAP	PHB	PAP	PHB			
0.9m	0.1m	0.3794	1.6205	9.0000	0.2341	
0.7m	0.3m	0.2710	1.7290	2.3333	0.1567	
0.5m	0.5m	0.2032	1.7968	1.0000	0.1131	9.2412
0.3m	0.7m	0.1220	1.8780	0.4286	0.0650	
0.1m	0.9m	0.0948	1.9052	0.1111	0.0498	

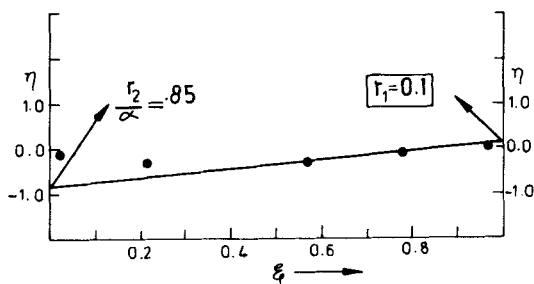


FIG. 1. Kelen-Tüdös plot of p-hydroxybenzoic acid-sulfanilic acid copolymerization system ( $\alpha = 1.5196$ ).

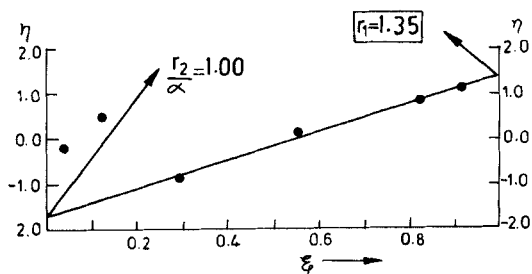


FIG. 2. Kelen-Tüdös plot for p-hydroxybenzoic acid-p-aminobenzoic acid copolymerization systems ( $\alpha = 0.5897$ ).

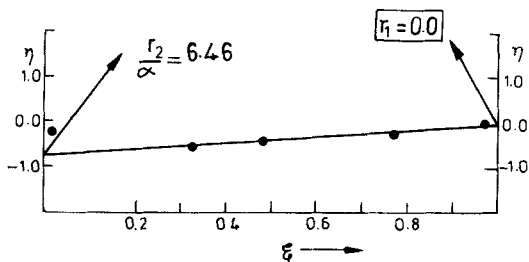
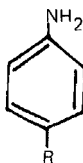


FIG. 3. Kelen-Tüdös plot for p-hydroxybenzoic acid-p-amino phenol copolymerization system ( $\alpha = 9.2412$ ).

TABLE 2. Copolymerization Parameters of p-Substituted Anilines ( $M_1$ ) with p-Hydroxybenzoic Acid ( $M_2$ )

No.	Comonomer	Equation <sup>a</sup>	$r_1$	$r_2$	$1/r_1$
1.	Sulfanilic acid (SA)	KT	0.1	1.29	10
		FR	0.1	1.30	10
2.	p-Aminobenzoic acid (PAB)	KT	1.35	1.00	0.74
		FR	1.30	1.11	0.76
3.	p-Amino phenol (PAP)	KT	0.0	6.46	-
		FR	0.0	6.11	-

<sup>a</sup>KT = Kelen-Tüdös, Eq. (1); FR = Fineman-Ross, Eq. (3).



A

where R is  $\text{SO}_3\text{H}$ ,  $\text{COOH}$ , or  $\text{OH}$ .

The relative reactivity of the "unlike and like" monomers with a given radical can be expressed in terms of the reciprocal of a reactivity ratio "r." On comparing the reciprocal of  $r_1$  for the three monomeric species, e.g., sulfanilic acid (SA), p-aminobenzoic acid (PAB), and p-amino phenol (PAP), it has been observed that the reactivity is SA ( $\text{SO}_3\text{H}$  group) > PAB (COOH group) > PAP (phenolic OH). Since the reactivity ratio  $r_1$  of p-amino phenol (PAP) has been found to be zero by both methods, not much significance can be attached to its reciprocal value.

Thus it may be concluded from this preliminary investigation that copolymerization parameters are affected by the nature of acidic functional groups present in the comonomers. The sequence of reactivity of comonomers is found to be of the same order as that of their acid strengths.

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