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Effect of Substituents on the Copolymerization Parameters of Some Phenolic Monomers

S. K. Chatterjee[a]; B. P. Singh[a]; L. S. Pachauri[a]
[a] Department of Chemistry, Delhi University, Delhi, India

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Effect of Substituents on the Copolymerization Parameters of Some Phenolic Monomers

S. K. CHATTERJEE, B. P. SINGH, and L. S. PACHAURI

Department of Chemistry
Delhi University
Delhi 110007, India

ABSTRACT

Copolymerization parameters of some halogen substituted phenolic monomers have been determined by the linear graphical method of Kelen and Tüdős. The order of reactivity of p-chlorophenol, p-bromophenol and p-iodophenol is found to be the reverse of the order of electronegativity of their halogen substituents when they are copolymerized with p-hydroxybenzoic acid. On copolymerization with p-cresol, these halogen substituted phenols have reactivity in the same order as the electronegativity of their substituents. This reversal of reactivity of phenolic monomers has been interpreted in terms of (1) opposite polarization caused by electrophilic or nucleophilic substituents present in the common monomers, and (2) the magnitude of their resonance stabilization.

The copolymerization parameters r_1 and r_2 are universally used for the characterization of monomer pairs with regard to their behavior in copolymerization. The classic copolymer equation describes the composition of the copolymer as a function of the reactivity ratios and the composition of the monomer feed. Several authors have used linear [1], nonlinear [2-6], specific copolymer composition equations [7], and computer programming routines [8] for calculating copolymerization parameters r_1 and r_2. Kelen and Tüdős [9] have recently proposed a new linear graphical method for determining these parameters. The distinct advantages of the Kelen-Tüdös [9] method over other linear methods have encouraged us to apply it to some phenolic copolymerization systems. In some preliminary investigations it was found that reactivity ratios of phenolic monomers are affected by the nature of acidic functional groups present in them, and the sequence of reactivity of comonomers were found to be of the same order as that of their acid strengths [10]. The object of the present investigation is to study the effect of various halogen substituents on the reactivity ratios of some phenolic monomers, and also to find out how the presence of electrophilic and nucleophilic substituents in the other comonomer can influence the reactivity of the halogen-substituted phenolic compounds during copolymerization. The Kelen and Tüdös [9] method has been applied to calculate the reactivity ratios. The following systems have been chosen for the present investigations: p-hydroxybenzoic acid has been condensed with formaldehyde and p-chloro-, p-bromo-, and p-iodophenols, respectively, to obtain the three different copolymers. Three other copolymers were prepared by condensing separately each of the above halogen-substituted phenolic monomers with p-cresol and formaldehyde. Several samples of each of the above six copolymers were also prepared by choosing various feed compositions.

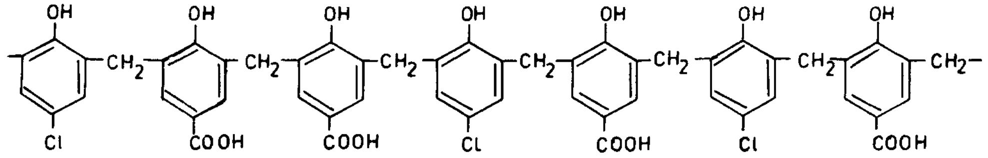
EXPERIMENTAL

Five to six samples of each of the random copolymers I-VI have been prepared by refluxing the different monomers in various molecular proportions in the presence of 2 mL of 10 N HCl as catalyst for $2\frac{1}{2}$ h at 130°C. The common monomer in Copolymers I-III is p-hydroxybenzoic acid whereas for the Copolymers IV-VI the common monomer is p-cresol. Compositions of the copolymers were determined by electrometric titration techniques [11] in nonaqueous media together with the halogen estimation of the copolymers by Volhard's method [12].

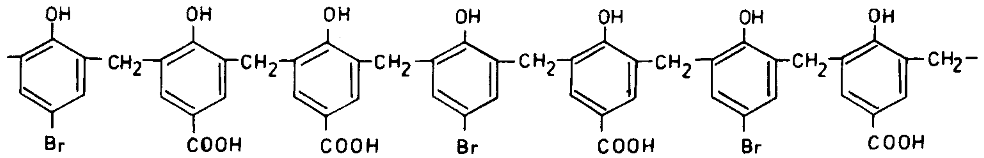
RESULTS AND DISCUSSION

The data concerning the composition of the copolymers, monomer feed, and the values of α for the Copolymerization Systems I to VI are summarized in Tables 1 and 2. These data were used in the following Kelen-Tüdös equation to calculate the reactivity ratios r_1 (halogen-substituted phenols) and r_2 (p-hydroxybenzoic acid or p-cresol):

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



(I)



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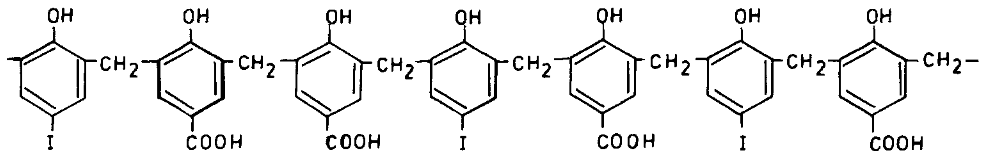

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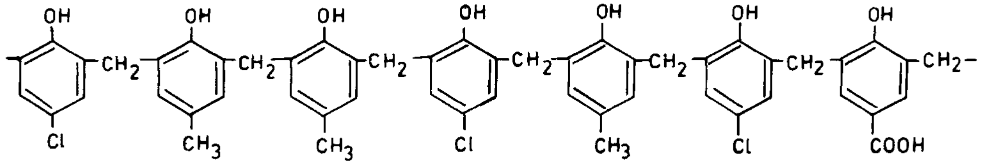

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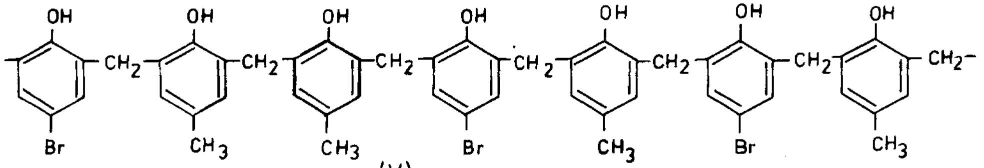

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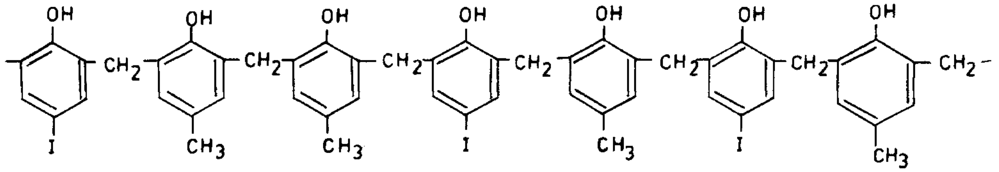

(VI)

TABLE 1. Composition of p-Substituted Phenol (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, $y = dM_1/dM_2$	α
PClP	PHB	PClP	PHB			
0.75m	0.25m	0.9936	1.0064	3.0000	0.9873	3.8937
0.55m	0.45m	0.4565	1.5435	1.2222	0.2958	
0.45m	0.55m	0.4199	0.5801	0.8182	0.2657	
0.35m	0.65m	0.3333	1.6667	0.5385	0.2000	
0.25m	0.75m	0.1252	1.8748	0.3333	0.0668	
PBrP	PHB	PBrP	PHB			
0.80m	0.20m	1.0336	0.9664	4.0000	1.0695	2.3507
0.70m	0.30m	0.9894	1.0106	2.3333	0.9790	
0.60m	0.40m	0.7445	1.2555	1.5000	1.2555	
0.50m	0.50m	0.6394	1.3606	1.0000	0.4699	
0.40m	0.60m	0.5093	1.4907	0.6667	0.3417	
0.30m	0.70m	0.4896	1.5104	0.4286	0.3242	
0.20m	0.80m	0.2894	1.7106	0.2500	0.1692	
PIP	PHB	PIP	PHB			
0.75m	0.25m	0.5748	1.4252	3.0000	0.4033	6.0162
0.65m	0.35m	0.5524	1.4476	1.8571	0.3816	
0.55m	0.45m	0.5136	1.4864	1.2222	0.3455	
0.45m	0.55m	0.3462	1.6538	0.8182	0.2093	
0.35m	0.65m	0.2029	1.7971	0.5385	0.1129	
0.25m	0.75m	0.1282	1.8718	0.3333	0.0685	

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 the parameter α is given by

$$\alpha = \frac{x_{min} x_{max}}{(y_{min} y_{max})^{0.5}}$$

Equation (1) can be expressed in the form of a linear relationship between η and ξ where

TABLE 2. Compositions of p-Substituted Phenol (M_1) and p-Cresol (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, $d = dM_1/dM_2$	α
PClP	PC	PClP	PC			
0.9m	0.1m	1.0886	0.9114	9.0000	1.1944	1.8912
0.7m	0.3m	0.7056	1.2944	2.3333	0.5451	
0.5m	0.5m	0.6735	1.3265	1.0000	0.5077	
0.3m	0.7m	0.5601	1.4399	0.4286	0.3890	
0.1m	0.9m	0.3793	1.6207	0.1111	0.2340	
PBrP	PC	PBrP	PC			
0.9m	0.1m	1.5810	0.4190	9.0000	3.7733	1.1442
0.7m	0.3m	0.9884	1.0116	2.3333	0.9771	
0.5m	0.5m	0.8191	1.1809	1.000	0.6936	
0.3m	0.7m	0.6996	1.3004	0.4286	0.5380	
0.1m	0.9m	0.3366	1.6634	0.1111	0.2024	
PIP	PC	PIP	PC			
0.75m	0.25m	0.8648	1.1352	3.0000	0.7618	2.7156
0.65m	0.35m	0.7086	1.2914	1.8571	0.5487	
0.55m	0.45m	0.6430	1.3570	1.2222	0.4738	
0.45m	0.55m	0.5555	1.4445	0.8182	0.3846	
0.35m	0.65m	0.4705	1.5295	0.5385	0.3076	
0.25m	0.75m	0.3022	1.6978	0.3333	0.1780	

$$\eta = x(y - 1)/(\alpha y + x^2)$$

$$\xi = x^2/(\alpha y + x^2)$$

For the Copolymerization Systems I to VI the variation of η with ξ have been shown in Figs. 1 to 6, respectively. A reasonably good agreement could be seen between the experimental points and Eq. (1) for most of the copolymerization systems.

The reactivity ratio (r_1) obtained for the various halogen-substituted phenolic monomers during their copolymerization with the common monomer p-hydroxybenzoic acid and p-cresol, respectively, are given in Table 3. It is possible to arrange the order of reactivity of a series of monomers with a given radical by comparing the reciprocal of

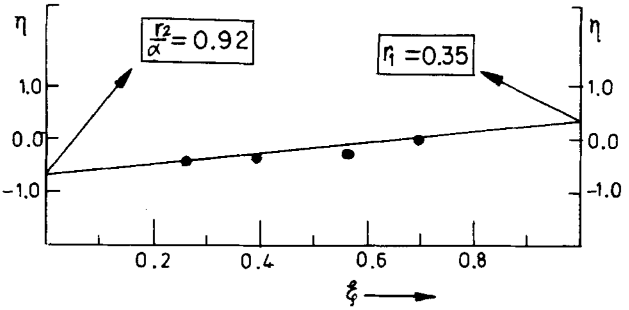

FIG. 1. Kelen-Tüdös plot for copolymerization of p-hydroxybenzoic acid and p-chlorophenol.

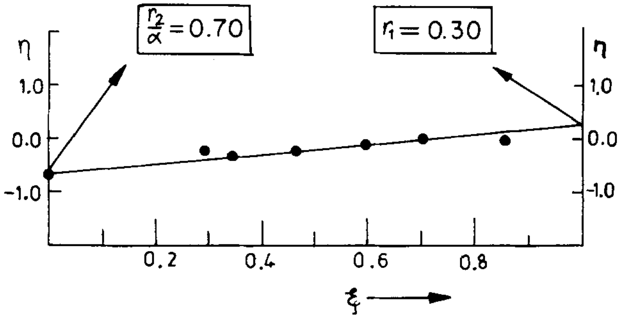

FIG. 2. Kelen-Tüdös plot for copolymerization of p-hydroxybenzoic acid and p-bromophenol.

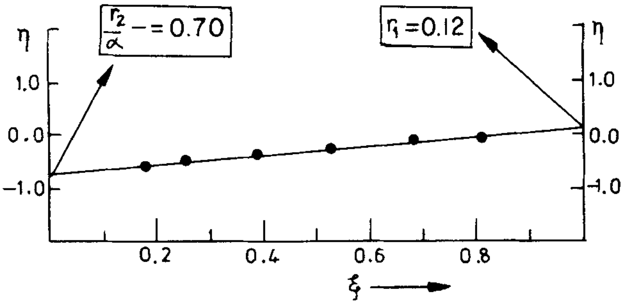

FIG. 3. Kelen-Tüdös plot for copolymerization of p-hydroxybenzoic acid and p-iodophenol.

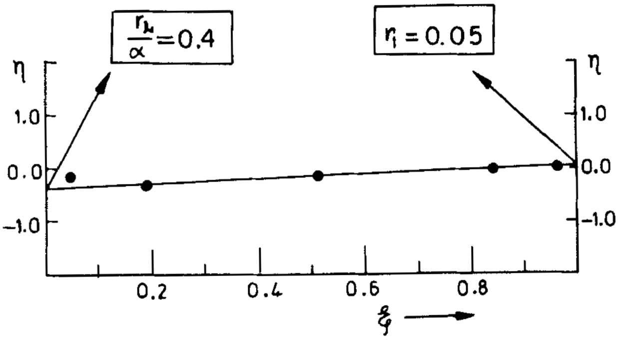

FIG. 4. Kelen-Tüdös plot for copolymerization of p-cresol and p-chlorophenol.

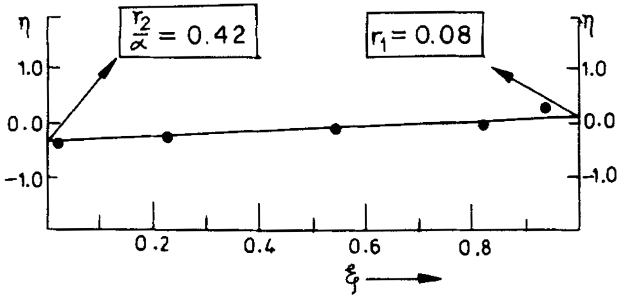

FIG. 5. Kelen-Tüdös plot for copolymerization of p-cresol and p-bromophenol.

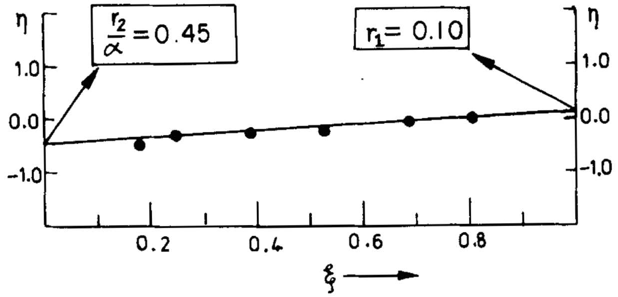

FIG. 6. Kelen-Tüdös plot for copolymerization of p-cresol and p-iodophenol.

TABLE 3. Reactivity Ratios for Copolymerization Systems I to VI[a]

S. No.	Comonomer	r_1	r_2	$1/r_1$
	Common Monomer: p-Hydroxybenzoic acid (M_2)			
I	p-Chlorophenol (M_1)	0.35	2.8035	2.85
II	p-Bromophenol (M_1)	0.30	1.6454	3.33
III	p-iodophenol (M_1)	0.12	4.2113	8.33
	Common Monomer: p-Cresol (M_2)			
IV	p-Chlorophenol (M_1)	0.05	0.7565	20.0
V	p-Bromophenol (M_1)	0.08	0.4806	12.5
VI	p-Iodophenol (M_1)	0.10	1.2220	10.0

[a] Calculations are based on the Kelen-Tüdös equation.

their reactivity ratios. The reciprocal of r_1 values for the three halogen-substituted phenolic monomers when they are copolymerized with the common monomer p-hydroxybenzoic acid followed the order (see Table 3) p-iodophenol ($1/r_1$) > p-bromophenol ($1/r_1$) > p-chlorophenol ($1/r_1$). Evidently the order of reactivities of the phenolic monomers is the reverse of the order of electronegativity of their halogen substituents. However, when these halogen-substituted phenolic monomers are copolymerized with p-cresol, the reciprocal of r_1 values are found to be in the order (see Table 3) p-chlorophenol ($1/r_1$) > p-bromophenol ($1/r_1$) > p-iodophenol ($1/r_1$).

As expected, the reactivity of the halogen-substituted phenols is in the same order as the electronegativity of their substituents. Therefore, it is obvious that the nature of substituent in the common monomer can bring about a reversal of the order of reactivity of halogen-substituted phenolic monomers.

These interesting observations can be interpreted in terms of two factors, e.g., (1) degree of resonance stabilization of the common monomers, and (2) influence of the electron-attracting and electron-donating groups present in them. Because of the presence of the COOH group p-hydroxy benzoic acid is expected to have a higher degree of resonance stabilization compared to p-cresol. Whether on the addition of a monomer to a growing chain a positive or negative chain-end occurs depends on the substituent of the monomers. As a result of resonance stabilization and the electron-attracting nature of the COOH group, electrons of the phenyl radical in p-hydroxybenzoic acid probably take part in the electronic system of the substituents. This leads to a certain negative overcharge which is missing from the double bond, and therefore causes the double bond to have a positive overcharge of the same magnitude. If one assumes that such a polarization is possible, then a chain end at which there happens to be a structural unit with an electron-attracting substituent should prefer a monomer with an electron-donating substituent. Since iodine is less electronegative than bromine and chlorine, therefore p-iodophenol should react more readily with p-hydroxybenzoic acid than p-bromophenol and p-chlorophenol. This was the actual trend of reactivity observed when these phenolic monomers were copolymerized with p-hydroxybenzoic acid.

However, the presence of an electron-donating group such as CH_3 should polarize the molecule in the opposite sense. Thus a growing chain end with a structural unit containing an electron-donating substituent (e.g., CH_3) prefers to add a monomer with an electron-attracting substituent. Since chlorine is more electronegative than bromine or iodine, therefore p-chlorophenol should react more readily with p-cresol than p-bromophenol and p-iodophenol. This was the order of reactivity actually observed in the Copolymerization Systems IV to VI.

Thus it may be concluded that the rate of addition of the monomers in a copolymerization reaction depends on the combination of both the effects, e.g., (1) opposite polarization caused by the electron-donating or electron-withdrawing substituents present in the common monomer, and (2) the magnitude of their resonance stabilization.

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