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Influence of Comonomer Functional Groups on the Reactivity Ratios of Some Phenolic Monomers

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Influence of Comonomer Functional Groups on the Reactivity Ratios of Some Phenolic Monomers

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ABSTRACT

The reactivity ratios of some halogen-substituted phenolic monomers have been determined by the linear graphical method of Kelen and Tüdős. The nature of functional groups present in the comonomer influence the order of reactivity of p-chlorophenol, p-bromophenol, and p-iodophenol. The behavior of these monomers during copolymerization reaction has been interpreted in terms of 1) different degrees of resonance stabilization of the monomers, and 2) opposite polarization caused by the substituents present in the comonomer.

INTRODUCTION

The reactivity of a monomer is greatly influenced by the nature of functional groups present in it. However, the behaviors of monomers differs in copolymerization reactions, and the classical copolymerization equation does not give an explanation of why this should be so. Keeping this fact in view, it was considered of interest to study the reactivity of some halogen-substituted phenolic monomers when they are copolymerized with aniline monomers having various types of acidic functional groups (e.g., $-SO_3H$, $-COOH$, phenolic OH). These systems

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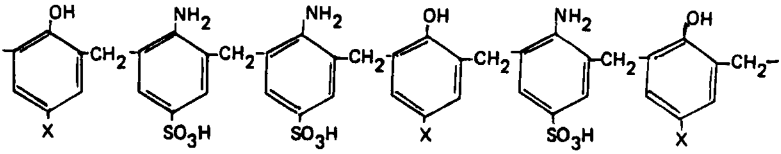
are interesting in view of the fact that such factors as 1) the electron-donating or electron-attracting nature of the substituent, 2) the resonance stabilization of the comonomers, and 3) the relative strength of acidic functional groups present in the comonomers may influence the reactivity of halogen-substituted phenolic monomers, and this is likely to be reflected in their reactivity ratios. Though reactivity ratios of various monomers have been calculated by several authors using linear [1], nonlinear [2-6], specific copolymerization equation, and computer programming routines [8], we have preferred to use the Kelen-Tüdős [9] new linear graphical method for determining these parameters because of its distinct advantages over other linear methods.

EXPERIMENTAL

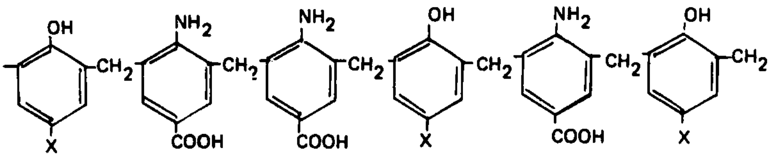
The following copolymers (1-9) have been prepared by refluxing the monomers of different feed compositions with HCHO in the presence of 2 mL of 10 N HCl for 2½ h at 130°C. The copolymer yield in most of the cases was around 70-75%.

The comonomer for Copolymers 1-3 is sulfanilic acid (SA):



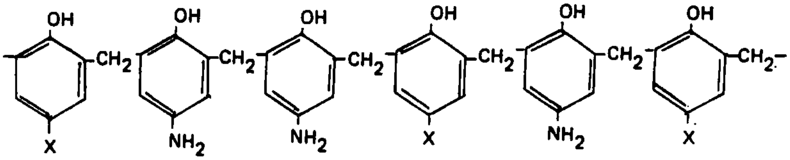
where, for Copolymer 1, X = Cl; for Copolymer 2, X = Br; and for Copolymer 3, X = I.

The comonomer for Copolymers 4-6 is p-aminobenzoic acid (PAB):



where, for Copolymer 4, X = Cl; for Copolymer 5, X = Br; and for Copolymer 6, X = I.

The comonomer for Copolymers 7-9 is p-aminophenol (PAP):



where, for Copolymer 7, X = Cl; for Copolymer 8, X = Br; and for Copolymer 9, X = I.

The compositions of the copolymers were determined by electrometric titration techniques in nonaqueous media [10]. Volhard's method has been employed to estimate the halogen content of the copolymers [11].

RESULTS AND DISCUSSION

Data concerning the composition of the copolymers and the monomer feed and the value of α for copolymerization systems 1-9 are summarized in Tables 1-3. Reactivity ratios r_1 (halogen-substituted phenols), and r_2 (sulfanilic acid (SA), or p-aminobenzoic acid (PAB), or p-aminophenol(PAP)), were calculated from the data given in the Tables 1-3, using the following equation of Kelen and Tüdős [9]:

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

where x is the ratio of mole fractions of monomer (M_1) and monomer (M_2) in the monomer feed, and y is the ratio of mole fractions M_1 and M_2 in the copolymer. Parameter α is given by

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

Equation (1) can also be expressed as a linear relationship between $[x(y-1)]/(\alpha y + x^2) = \eta$ and $x/(\alpha y + x^2) = \xi$. The variation of η with ξ is shown in Figs. 1 to 9 for copolymerization systems 1 to 9. The reactivity ratios r_1 and r_2 of the various monomers have been calculated from the linear plots and are given in Table 4.

TABLE 1. Composition of Halogen-Substituted Phenol (M_1) and Sulfanilic Acid (M_2) Copolymerization Systems

Feed composition in moles		Copolymer composition in moles		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	SA	PClP	SA			
0.25	0.75	0.4262	1.57	0.3333	0.2708	2.3007
0.35	0.65	0.6096	1.3904	0.5385	0.4384	
0.45	0.55	0.6795	1.3205	0.8182	0.5146	
0.55	0.45	0.6821	1.3179	1.2222	0.5176	
0.65	0.35	0.7418	1.2582	1.8571	0.5896	
0.75	0.25	0.8218	1.1782	3.0000	0.6975	

PBrP	SA	PBrP	SA			
0.2	0.8	0.3775	1.6225	0.25	0.2327	
0.3	0.7	0.3939	1.6061	0.4286	0.2453	
0.4	0.6	0.5223	1.4777	0.6667	0.3535	2.3370
0.5	0.5	0.5327	1.4673	1.0000	0.3630	
0.6	0.4	0.5553	1.4447	1.5000	0.3844	
0.7	0.3	0.7222	1.2778	2.333	0.5652	
0.8	0.2	0.8897	1.1193	4.0000	0.7869	
PIP	SA	PIP	SA			
0.2	0.8	0.1717	1.8293	0.25	0.0933	
0.3	0.7	0.1732	1.8268	0.4286	0.0948	
0.4	0.6	0.2941	1.7059	0.6667	0.1724	3.8760
0.5	0.5	0.3606	1.6394	1.000	0.2200	
0.6	0.4	0.5263	1.4737	1.5000	0.3571	
0.7	0.3	0.5842	1.4185	2.333	0.4126	
0.8	0.2	0.8329	1.1671	4.000	0.7136	

TABLE 2. Composition of Halogen-Substituted Phenol (M_1) and p-AminoBenzoic Acid (M_2) Copolymerization Systems

Feed composition in moles		Copolymer composition in moles		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	PAB	PClP	PAB			
0.2	0.8	0.2424	1.7576	0.25	0.1379	
0.3	0.7	0.2899	1.7101	0.4286	0.1695	
0.4	0.6	0.4079	1.5921	0.6667	0.2562	2.9525
0.5	0.5	0.7549	1.2451	1.0000	0.6063	
0.6	0.4	0.8641	1.1359	1.5000	0.7607	
0.7	0.3	0.8775	1.1225	2.333	0.7817	
0.8	0.2	0.9082	1.0918	4.0000	0.8318	

PBrP	PAB	PBrP	PAB			
0.2	0.8	0.3481	1.6519	0.25	0.2107	
0.3	0.7	0.4147	1.5853	0.4286	0.2616	
0.4	0.6	0.4654	1.5346	0.6667	0.3033	2.1589
0.5	0.5	0.6542	1.3458	1.0000	0.4861	
0.6	0.4	0.9030	1.0970	1.5000	0.8232	
0.7	0.3	0.9707	1.0293	2.333	0.9431	
0.8	0.2	1.0091	0.9909	4.000	1.0184	
PIP	PAB	PIP	PAB			
0.2	0.8	0.2388	1.7612	0.25	0.1356	
0.3	0.7	0.4091	1.5909	0.4286	0.2572	
0.4	0.6	0.4808	1.5192	0.6667	0.3165	3.7230
0.5	0.5	0.4850	1.5150	1.000	0.3201	
0.6	0.4	0.5542	1.4458	1.500	0.3833	
0.7	0.3	0.6033	1.3967	2.333	0.4319	
0.8	0.2	0.6944	1.3056	4.000	0.5319	

TABLE 3. Composition of Halogen-Substituted Phenol (M_1) and p-Aminophenol (M_2) Copolymerization Systems

Feed composition in moles		Copolymer composition in moles		Ratio of mole fraction of monomer in feed, $x = M_1/M_2$	Ratio of mole fraction of monomer in copolymer, $y = dM_1/M_2$	α
PClP	PAP	PClP	PAP			
0.1	0.9	0.3808	1.6192	0.1111	0.2352	
0.3	0.7	0.4358	1.5642	0.4286	0.2786	
0.5	0.5	0.4919	1.5081	1.0000	0.3262	1.2659
0.7	0.3	1.0532	0.9468	2.3333	1.1125	
0.9	0.1	1.4525	0.5475	9.0000	2.6530	

PBrP	PAP	PbrP	PAP			
0.1	0.9	0.2987	1.7013	0.1111	0.1756	
0.3	0.7	0.4753	1.5247	0.4286	0.3117	1.7779
0.5	0.5	0.8472	1.1528	1.0000	0.7349	
0.7	0.3	1.1818	0.8182	2.3333	1.4444	
0.9	0.1	1.2860	0.7140	9.0000	1.8011	
PIP	PAP	PIP	PAP			
0.25	0.75	0.2224	1.7776	0.3333	0.1251	
0.35	0.65	0.5863	1.4433	0.5385	0.3853	
0.45	0.55	0.7856	1.2144	0.8182	0.6469	1.7792
0.55	0.45	1.1775	0.8225	1.2222	1.4316	
0.65	0.35	1.2589	0.7411	1.8571	1.6987	
0.75	0.25	1.4326	0.5674	3.0000	2.5249	

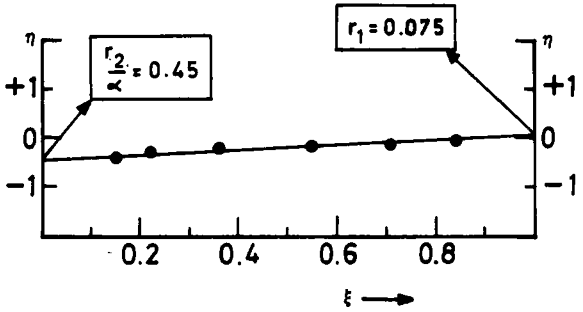


FIG. 1. Kelen-Tüdős plot for copolymerization of sulfanilic acid and p-chlorophenol.

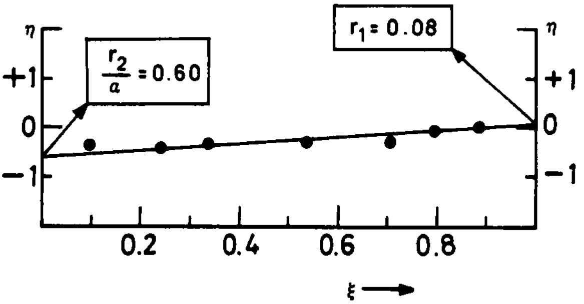


FIG. 2. Kelen-Tüdős plot for copolymerization of sulfanilic acid and p-bromophenol.

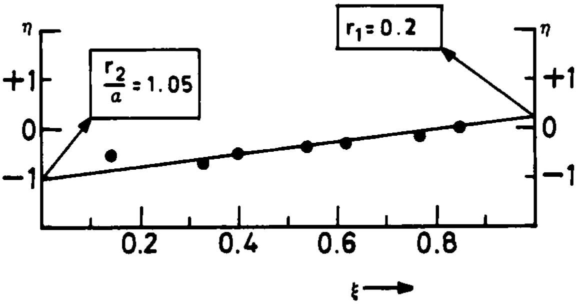


FIG. 3. Kelen-Tüdős plot for copolymerization of sulfanilic acid and p-iodophenol.

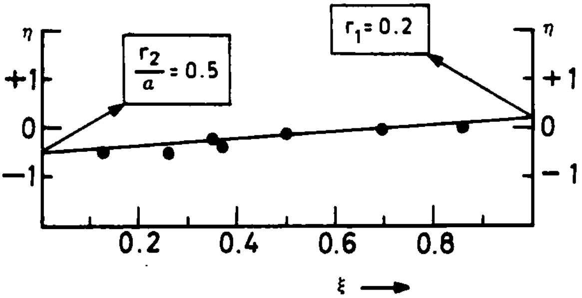


FIG. 4. Kelen-Tüdös plot for copolymerization of p-aminobenzoic acid and p-chlorophenol.

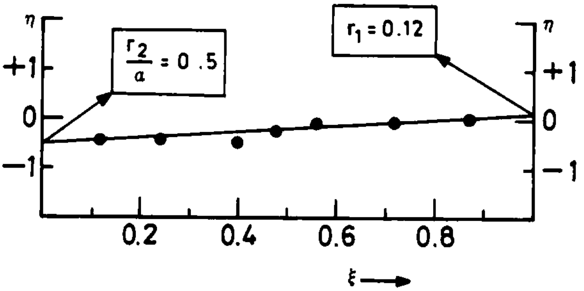


FIG. 5. Kelen-Tüdös plot for copolymerization of p-aminobenzoic acid and p-bromophenol.

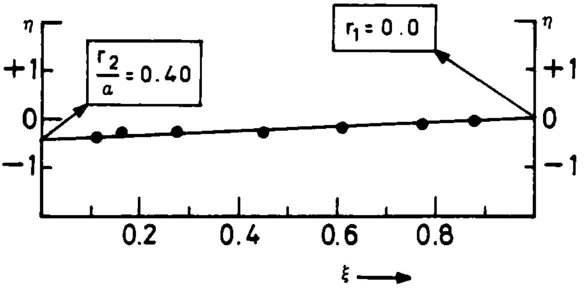


FIG. 6. Kelen-Tüdös plot for copolymerization of p-aminobenzoic acid and p-iodophenol.

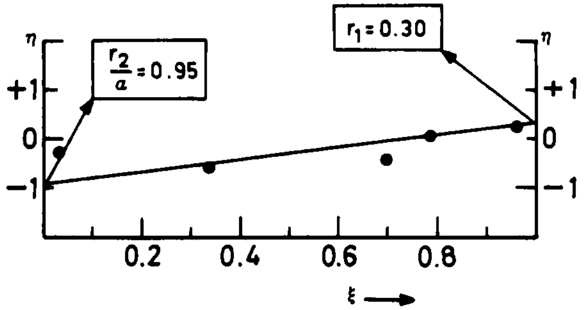


FIG. 7. Kelen-Tüdős plot for copolymerization of p-aminophenol and p-chlorophenol.

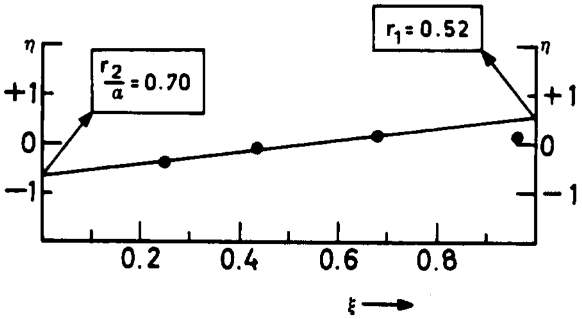


FIG. 8. Kelen-Tüdős plot for copolymerization of p-aminophenol and p-bromophenol.

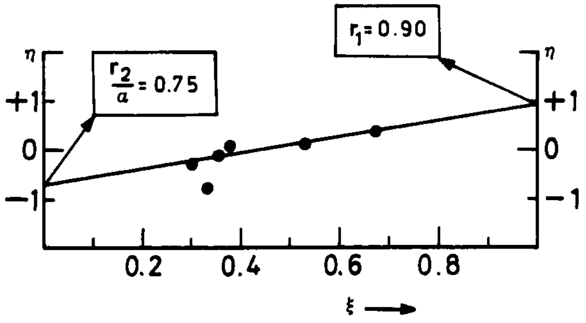


FIG. 9. Kelen-Tüdős plot for copolymerization of p-aminophenol and p-iodophenol.

TABLE 4. Reactivity Ratios for Copolymerization Systems (I to IX)[a]

No.	Comonomer	r_1	r_2	$1/r_1$	$1/r_2$
	Sulfanilic acid (M_2)				
I	p-Chlorophenol (M_1)	0.075	1.0353	13.3333	0.9661
II	p-Bromophenol (M_1)	0.08	1.4022	12.5000	0.7131
III	p-Iodophenol (M_1)	0.2	4.0698	5.0000	0.2457
	p-Aminobenzoic acid (M_2)				
I	p-Chlorophenol (M_1)	0.20	1.4763	5.0000	0.6773
II	p-Bromophenol (M_1)	0.12	1.0795	8.3333	0.9263
III	p-Iodophenol (M_1)	0.00	1.4892	-	0.6715
	p-Aminophenol (M_2)				
I	p-Chlorophenol (M_1)	0.30	1.2026	3.3333	0.8315
II	p-Bromophenol (M_1)	0.52	1.2445	1.9231	0.8035
III	p-Iodophenol (M_1)	0.90	1.3344	1.1111	0.7494

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

The general observations from Table 4 may be summarized as follows. Since the reciprocal of a reactivity ratio gives the relative reactivity of monomers with a given comonomer, one can write the following relative order of reactivity of halogen-substituted phenolic monomers when they are copolymerized with SA, PAB, and PAP, respectively (see Table 4).

p-Chlorophenol ($1/r_1$) > p-bromophenol ($1/r_1$) > p-iodophenol ($1/r_1$) (comonomer: SA)

p-Iodophenol ($1/r_1$) > p-bromophenol ($1/r_1$) > p-chlorophenol ($1/r_1$) (comonomer: PAB)

p-Chlorophenol ($1/r_1$) > p-bromophenol ($1/r_1$) > p-iodophenol ($1/r_1$) (comonomer: PAP)

However, on comparing the reciprocal of r_2 for the monomers SA, PAB, and PAP, the following order has been obtained (cf. Table 4):

SA ($1/r_2$) > PAP ($1/r_2$) > PAB ($1/r_2$) (comonomer: p-chloropheno

PAB ($1/r_2$) > PAP ($1/r_2$) > SA ($1/r_2$) (comonomer: p-bromophen

PAP ($1/r_2$) > PAB ($1/r_2$) > SA ($1/r_2$) (comonomer: p-iodophenol)

When SA is copolymerized with p-chlorophenol, p-bromophenol, an p-iodophenol, respectively, its reactivity (i.e., $1/r_2$) decreases in the order of electronegativity of the halogen substituent in the comonomer Similar observations have been made in the case of PAP. However, th reactivity ($1/r_2$) of PAB on copolymerization with either p-chlorophen and p-iodophenol is almost identical, and it is slightly higher with p-bromophenol as the comonomer (see Table 4).

Some of these interesting observations may be explained on the bas of the following factors: 1) different degrees of resonance stabilizatio of the monomers, and 2) the opposite polarization caused by the electr donating or electron-withdrawing substituents present in the monomer Because of the presence of a COOH group, p-aminobenzoic acid (PAB expected to have a higher degree of resonance stabilization compared SA and PAP. As a result of resonance stabilization and polarization due to the presence of a COOH group, the PAB molecule would prefer to add monomers with an electron-donating group. Since iodine is les electronegative compared to bromine and chlorine, p-iodophenol react more readily with PAB compared to p-bromo- or p-chlorophenol. Thi was actually the sequence of reactivity obtained when these halogen-substituted phenolic monomers were copolymerized with PAB (cf. Table 4).

On copolymerization with p-chlorophenol, the observed sequence of reactivity (i.e., $1/r_2$) of the monomers SA, PAP, and PAB can also be explained on the basis of the relatively lower degree of polarization of SA compared to PAP and PAB. With p-bromophenol or p-iodophenol as the comonomer, the sequence of reactivity of the above three monomers again changes. This obviously indicates that the reactivity of these monomers depends to a large extent on the electronegativity of the halogen substituents present in the phenolic comonomer. In general, it may be stated that a growing chain end with a structural unit containing an electron-donating substituent (i.e., which, as a result of polarization, carrys a negative overcharge) prefers to add a monomer with an electron-attracting substituent. The opposite effect is also expected to hold good.

In conclusion, the rate of addition of monomers in a copolymerization reaction depends not only on the opposite polarization caused by electrophilic or neucleophilic substituents but also on the magnitude of resonance stabilization of the monomers. In fact, the overlapping of these two effects probably influences the rate of addition of the two monomeric species in a copolymerization reaction.

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