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S. K. Chatterjee<sup>a</sup>; Anita Katyal<sup>a</sup>; L. S. Pachauri<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Delhi, Delhi, India

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## **Influence of Monomer Reactivity on the Composition of Some Four-Component Phenolic Copolymers**

S. K. CHATTERJEE, ANITA KATYAL, and L. S. PACHAURI

Department of Chemistry  
University of Delhi  
Delhi 110007, India

### **ABSTRACT**

Some four-component random phenolic copolymers were prepared from four typical phenolic monomers; for example, p-nitrophenol, p-chlorophenol, p-aminobenzoic acid, and p-hydroxybenzoic acid. Several samples of the copolymer were prepared by changing the feed composition, and the composition of the copolymers was established by estimating  $-NH_2$  and  $-OH$  groups by electrometric titration technique in nonaqueous media. Halogen was estimated by Volhard's method. The composition of the copolymers could be accounted for on the basis of the structure of the monomeric species. Hyperacidity of some of the functional groups in the copolymer chain is interpreted in terms of intramolecular hydrogen bonding.

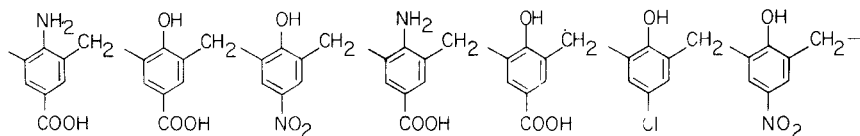
### **INTRODUCTION**

Joint copolymerization of several monomeric species may lead to the formation of copolymers which may have different sequence combinations of monomer units in the copolymer chain. In fact, combinations of various monomeric units and the actual composition of the copolymer depend on the reactivities of the monomers. Some earlier in-

vestigations from this laboratory indicated that electrometric titration techniques in nonaqueous media may provide valuable information regarding the structure, composition, and acid or basic character of two- and three-component phenolic copolymers [1-3]. The main objective of this investigation was to use this simple technique to derive the composition of a complex four-component phenolic copolymer, and also to account for the actual compositions of the copolymers in terms of the reactivities of the different monomers used for copolymerization. Copolymers obtained by the condensation of formaldehyde with p-chlorophenol (pCIP), p-hydroxybenzoic acid (pHB), p-aminobenzoic acid (pAB), and p-nitrophenol (pNP) were chosen for the present study. From the estimation of halogen content, acidic, and basic functional groups in a given weight of the product, the compositions of the copolymers could be established. An attempt has been made in this paper to correlate composition with monomer reactivity, and hyperacidity of some of the functional groups in the copolymer chain with intramolecular hydrogen bonding.

### EXPERIMENTAL

pCIP, pNP, pHB, pAB, and formaldehyde random copolymer (1) were prepared by refluxing the monomers in definite molecular proportions with 10 N HCl (2 mL) as the catalyst for 4 h at 100°C.



(1)

The reaction product was poured in ice-cold water and washed several times with distilled water to remove unreacted monomers. Several samples of the above copolymer were prepared by changing the feed compositions (see Table 1). The polymer yield varied from 50 to 60%. The halogen content of the copolymers was estimated using standard methods [4].

A Radiometer pH meter (model pH M 26 C) with a glass (G 202 B) and a calomel electrode (K 401) as reference was used for pH titrations. A Leeds and Northrup (4959) electrolytic conductance bridge was used for conductometric titrations. The details of the titration procedure have been reported elsewhere [3].

### RESULTS AND DISCUSSION

Copolymers I to IX, obtained by condensation of formaldehyde with pCIP, pAB, pNP, and pHB, can be represented by the general formula

TABLE 1

Copolymer no.	Feed composition <sup>a</sup> (moles of different monomers per unit weight of reactants)				Copolymer composition <sup>b</sup> (moles of different monomer units per unit weight of copolymer)				
	pCIP	pNP	pHB	pAB	HCHO	pCIP	pNP	pHB	pAB
I	0.00152	0.00152	0.00152	0.00152	0.0061	0.0006	0.00395	0.00010	0.00275
II	0.0152	0.00244	0.00061	0.00152	0.0061	0.0004	0.00180	0.00050	0.00450
III	0.00152	0.00061	0.00244	0.00152	0.0061	0.0003	0.00215	0.00065	0.00390
IV	0.00246	0.00153	0.00153	0.00061	0.0061	0.0004	0.00335	0.00045	0.00300
V	0.00060	0.00151	0.00151	0.00242	0.0061	0.0002	0.00376	0.00040	0.00270
VI	0.00060	0.00242	0.00151	0.00151	0.0061	0.0002	0.00360	0.00050	0.00270
VII	0.00246	0.00061	0.001542	0.00154	0.0061	0.0004	0.00230	0.00080	0.00370
VIII	0.00152	0.00152	0.00244	0.00061	0.0061	0.0004	0.00050	0.00080	0.00550
IX	0.00152	0.00152	0.000611	0.00244	0.0061	0.0004	0.00125	0.00080	0.00475

<sup>a</sup>Moles per unit weight of reactants.

<sup>b</sup>Moles per unit weight of copolymer.

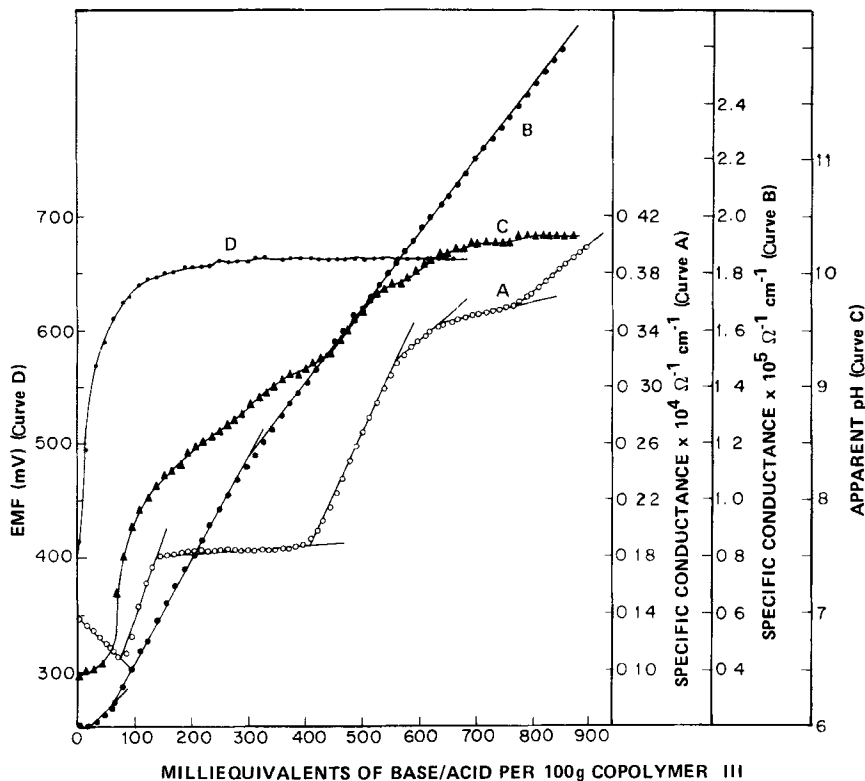


FIG. 1. Titration curves of Copolymer III. Conductometric curves: (A) in pyridine with sodium methoxide, (B) in glacial acetic acid with perchloric acid. Potentiometric curves: (C) in pyridine with sodium methoxide, (D) in glacial acetic acid with perchloric acid.

(1). The various monomeric units in the copolymer chain have acidic or basic functional groups, and some of the units have halogen (Cl) as a structural substituent. Potentiometric and conductometric titrations in nonaqueous solvents were carried out with each of the Copolymers I to IX. Some representative titration curves of the Copolymers III, VII, and VIII are shown in Figs. 1 to 3, respectively. Phenolic OH groups were estimated by titrating against sodium methoxide with pyridine as the medium of titration, whereas amino groups were titrated in glacial acetic acid medium with perchloric acid as the titrant acid. The general features of the titration curves can be summarized as follows: Conductometric curves in pyridine for all the copolymers (e.g., Curve A of Figs. 1 to 3) showed several distinct breaks before complete neutralization of all the phenolic OH groups in a given weight of the

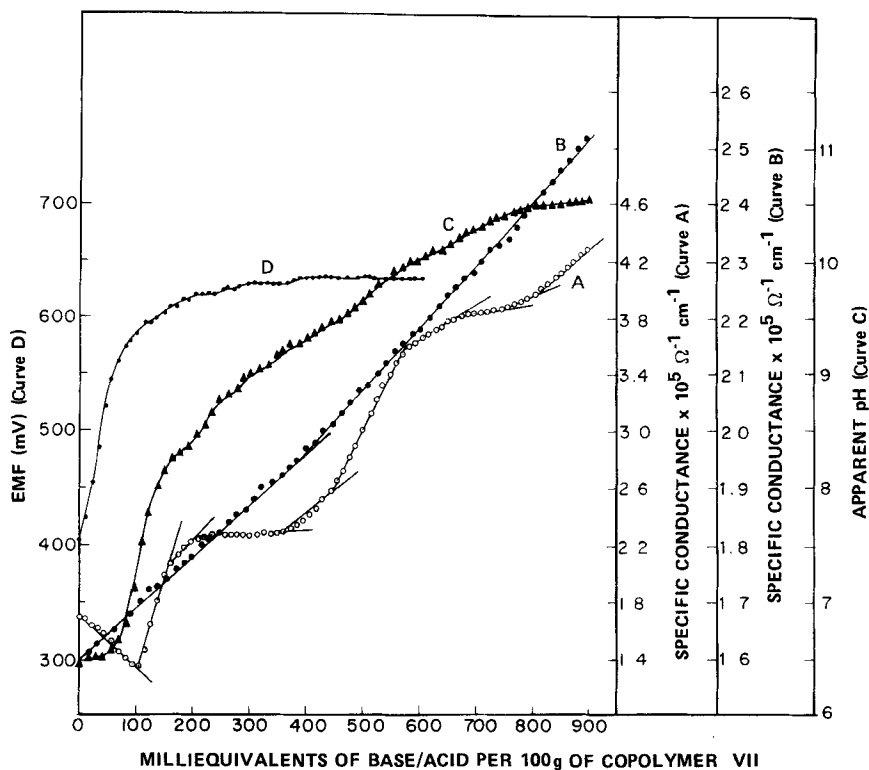


FIG. 2. Titration curves of Copolymer VII. Conductometric curves: (A) in pyridine with sodium methoxide, (B) in glacial acetic acid with perchloric acid. Potentiometric curves: (C) in pyridine with sodium methoxide, (D) in glacial acetic acid with perchloric acid.

copolymer. The corresponding conductometric curves in glacial acetic acid medium (e.g., Curve B of Figs. 1-3), did not show as many breaks, and more often neutralization of  $\text{NH}_2$  groups was found to be merged. The potentiometric curves of the copolymers in the pyridine medium (e.g., Curve C of Figs. 1 to 3), showed only one or two sharp inflections which invariably coincided with the strong acid portion (e.g., fall in conductance) of the conductometric curves. Similar correlations could also be seen between potentiometric and conductometric curves in the glacial acetic acid medium.

The composition of Copolymers I to IX could be derived as follows from the titration curves and the halogen content of each copolymer. The relative proportion of pCIP units in the copolymer chain can be obtained from the percentage of halogen present in the copolymer. Let

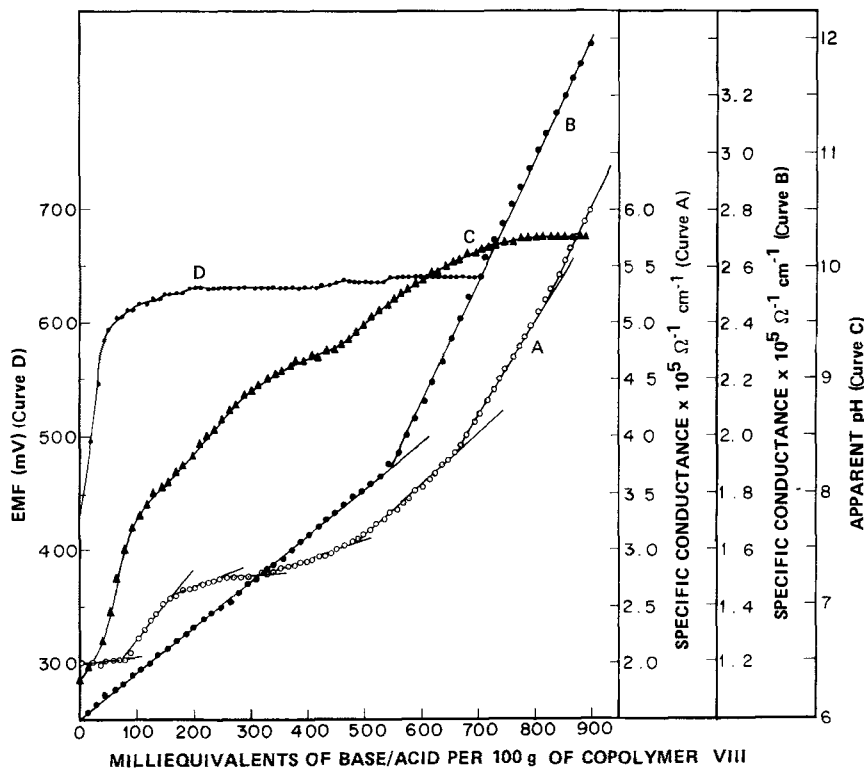


FIG. 3. Titration curves of Copolymer VIII. Conductometric curves: (A) in pyridine with sodium methoxide, (B) in glacial acetic acid with perchloric acid. Potentiometric curves: (C) in pyridine with sodium methoxide, (D) in glacial acetic acid with perchloric acid.

its value be  $X$  moles per gram of copolymer. Since the molecular weights of pAB, pHB, and pNP units in the copolymer chain are almost identical (i.e., around 150), and only pClP is slightly different, therefore, whatever may be the relative proportion of the four units, the weight of the sum of the four units will be around  $590.5 \text{ g} \pm 3\text{--}4\%$ . Thus, the total number of moles of pHB + pAB + pNP per unit weight of copolymer will be equal to  $[(4 - x)/590.5] = Y$ . Since pHB contains two equivalents of acidic functional groups, the total number of moles of acidic units (e.g., 2pHB + pAB + pClP + pNP) per unit weight of copolymer can be obtained from the final break of the conductometric curves (cf. Curve A of Figs. 1-3). Let it be equal to  $z$  moles. Similarly, the total number of basic units (e.g., pAB) can be obtained from the final break of the conductometric curve (cf. Curve B of Figs. 1-3). We will call this  $P$  moles per unit weight of copolymer. There-

TABLE 2. Observed Amount of  $\text{NH}_2$  and OH Groups in Copolymers I to IX

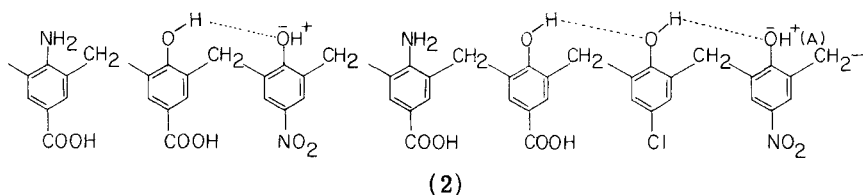
Copolymer	Cl(%)	Total $\text{NH}_2$ groups (meq/100 g of copolymer) observed	Total OH groups (meq/100 g of copolymer) observed
I	8	275	750
II	5.08	450	770
III	4.24	300	775
IV	6.30	300	765
V	2.45	270	740
VI	2.73	450	750
VII	6.38	370	800
VIII	4.97	550	800
IX	5.18	475	800

fore, the sum of pHB + pNP + pAB units will be equal to  $(Z - X) = Q$  moles. The amount of pHB units per unit weight of copolymer will be  $(Q - Y) = R$  moles and the amount of pNP units will be  $(Y - P + R) = S$  moles per unit weight of copolymer. On this basis, the number of moles of the four monomeric units per unit weight of Copolymers I to IX and the total amount of  $-\text{NH}_2$  and  $-\text{OH}$  groups per 100 g of Copolymers I to IX have been calculated and are shown in Tables 1 and 2, respectively.

The composition of the copolymer is always different from its feed, obviously due to the difference in reactivity of the four monomers (cf. Table 1). It has been observed (cf. Table 1) that the proportion of pClP and pHB in the copolymers is always less compared to their amount in the corresponding feed. However, the same is not true in the case of the other two monomer units (pAB and pNP). In most of the copolymers the proportion of pNP units was found to be higher compared to its feed, whereas pAB units were always found to be present in greater proportion in the copolymer in relation to its feed. Obviously, the reactivity of the four monomeric units can be written in the order  $\text{pAB} > \text{pNP} > \text{pHB} > \text{pClP}$ . This trend in the reactivity of the monomers can be interpreted in terms of the following factors: (1) nature of functional groups and their influence on the polarization of the monomer molecules, (2) relative degree of resonance stabilization of the monomers, and (3) presence of acidic or basic functional groups in the monomers. Except in the case of pAB, each of the other three monomers (pClP, pHB, and pNP) contains substituents which are both electrophilic (e.g., Cl, OH, COOH,  $\text{NO}_2$ , etc.), whereas in the case of pAB there is a



nucleophilic ( $\text{NH}_2$ ) and an electrophilic substituent ( $\text{COOH}$ ). Thus the relative degree of polarization of pAB will be high compared to the other three monomers whereas the degree of resonance stabilization of these monomeric units is likely to be in the order  $\text{pNP} > \text{pHB} > \text{pClP}$ . Moreover, the presence of a basic functional group (e.g.,  $\text{NH}_2$ ) in pAB is likely to make it more susceptible to attack by the other three monomers ( $\text{pNP}$ ,  $\text{pHB}$ , and  $\text{pClP}$ ). On the basis of these arguments, one can account for the observed composition of Copolymers I to IX. It is well known in phenolic polymerization systems that chain growth proceeds by way of electrophilic attack of benzylic cations upon phenolic molecules [5]. One can expect two types of endgroups (e.g., benzylic cations) and the activation of the end ring (A) for further cationic attack due to intramolecular hydrogen bonding (2).



The observed order of reactivity of the four monomeric units  $\text{pAB} > \text{pNP} > \text{pHB} > \text{pClP}$  is thus expected. The four units are also expected to behave in an identical manner toward electrophilic attack by  $^+\text{CH}_2\text{OH}$  ion. Clearly, the relative degree of polarization and resonance stabilization are the more important factors which influence the addition of monomeric units to a growing polymer chain. The influence of reactivity of the units is actually reflected in the composition of the copolymers. The neutralization of acidic functional groups of the copolymer chain in several distinct steps (cf. Curve A of Figs. 1-3) indicates that some of them have acquired a hyperacid character. This has been attributed to intramolecular hydrogen bonding between neighboring OH groups [6].

The presence of intramolecular hydrogen bonding in such compounds has also been shown from conformational studies [7] and IR spectra [8]. The IR spectra of the copolymers studied indicate absorptions in the  $3450\text{-}3600\text{ cm}^{-1}$  range, showing the probable presence of  $\text{O-H}\cdots\text{O}$  intramolecular H-bonding.

In conclusion, it can be said that nonaqueous titration may provide a very versatile method for studying the dissociation behavior of functional groups in polymer molecules. Information concerning the composition and structure of complex polymeric systems, such as a four-component phenolic copolymer, could also be obtained from these studies. Composition of the copolymers could also be accounted for on the basis of reactivity of the monomeric species.

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