

Effect of substituents on the composition and dissociation behaviour of some four component phenolic copolymers

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Some random four component phenolic copolymers have been prepared by condensing formaldehyde with *p*-chlorophenol, *p*-aminophenol, *p*-toluidine, and *p*-cresol. The compositions of the copolymers have been determined by electrometric titration in a non-aqueous solvent, and halogen estimation. Several samples of the copolymers have been obtained by changing the feed composition. Composition of the copolymer has been correlated with the reactivity of the four monomeric units. Hyperacidity of some of the functional groups in the copolymer chain is interpreted in terms of intramolecular hydrogen bonding.

Keywords Dissociation; phenolic copolymers; electrometric titration; halogen estimation

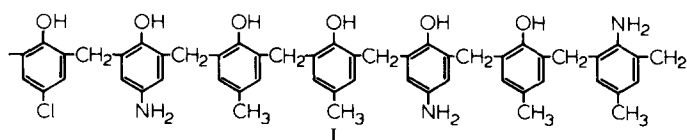
INTRODUCTION

Simultaneous copolymerization of two or more monomeric species leads to the formation of copolymers, which may have, in addition to heterogeneity in molecular weight, macromolecules of heterogeneous composition. The heterogeneity in copolymer composition is expected to be more complex as the number of components used to form the copolymer increases. Preliminary investigations on some two and three component phenolic systems revealed that electrometric titration techniques in non-aqueous media may provide valuable information regarding the structure, composition, and acidic or basic character of the copolymers¹⁻³. Thus, it was considered of interest to see whether this simple technique could be extended to a more complex system, e.g. four component copolymers. The ultimate object of this study was to correlate reactivity of monomers (in terms of its substituents) with the composition of the copolymer. Copolymers obtained by the condensation of formaldehyde with *p*-aminophenol, *p*-toluidine, *p*-cresol and *p*-chlorophenol have been chosen for the present investigation. This system is interesting in view of the fact that each unit has a functional group which can be estimated and the composition of the copolymer

established from their electrometric titration curves in non-aqueous media. An attempt has been made here to correlate hyperacidity of some of the functional groups in the copolymer chain, with intramolecular hydrogen bonding, and the composition with the reactivity of monomers.

EXPERIMENTAL

p-Chlorophenol (pClP), *p*-amino phenol (pAP), *p*-toluidine (pT), *p*-cresol (pC), formaldehyde random copolymer (I), was prepared by refluxing the monomers in definite molecular proportions with 10N HCl (2 ml) as catalyst for 4 h at 100°C.



The reaction mixture was poured into ice-cold water and washed several times with distilled water to remove any unreacted monomers. The polymer yield was around 75%. Several samples of the above copolymer were prepared by changing the feed compositions (see Table 1). The

Table 1 Feed composition and composition of copolymers I-VI

Copolymer No.	Feed composition					Composition of copolymer*			
	pClP	(moles (M) of various components)				(moles of different monomer units per unit wt. of copolymer)			
		pAP	pT	pC	HCHO	pClP	pAP	pT	pC
I	0.1 M	0.2 M	0.1 M	0.6 M	1.0 M	0.0012	0.0037	0.0008	0.0023
II	0.1 M	0.4 M	0.1 M	0.4 M	1.0 M	0.0019	0.0037	0.0005	0.0019
III	0.1 M	0.6 M	0.1 M	0.2 M	1.0 M	0.0026	0.0022	0.0015	0.0017
IV	0.2 M	0.1 M	0.6 M	0.1 M	1.0 M	0.0016	0.0021	0.0039	0.0004
V	0.25 M	0.25 M	0.25 M	0.25 M	1.0 M	0.0025	0.0008	0.0025	0.0022
VI	0.6 M	0.1 M	0.2 M	0.1 M	1.0 M	0.0033	0.0039	0.0005	0.0003

* Moles per unit wt. of copolymer

RESULTS AND DISCUSSION

Figures 1 to 6 show the potentiometric and conductometric titration curves of the copolymers I to VI. Phenolic OH groups have been estimated by titrating against sodium methoxide with pyridine as the medium of titration, whereas amino groups have been titrated in a

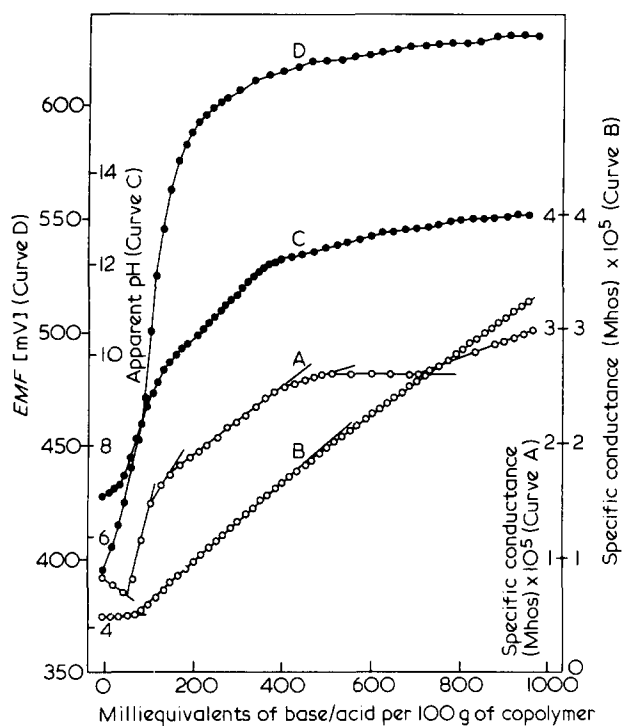


Figure 1 Titration curves of copolymer I. Conductometric curves: (A) in pyridine with sodium methoxide; (B) in glacial acetic acid with perchloric acid. Potentiometric curves: (C) in pyridine with sodium methoxide; (D) in glacial acetic acid with perchloric acid

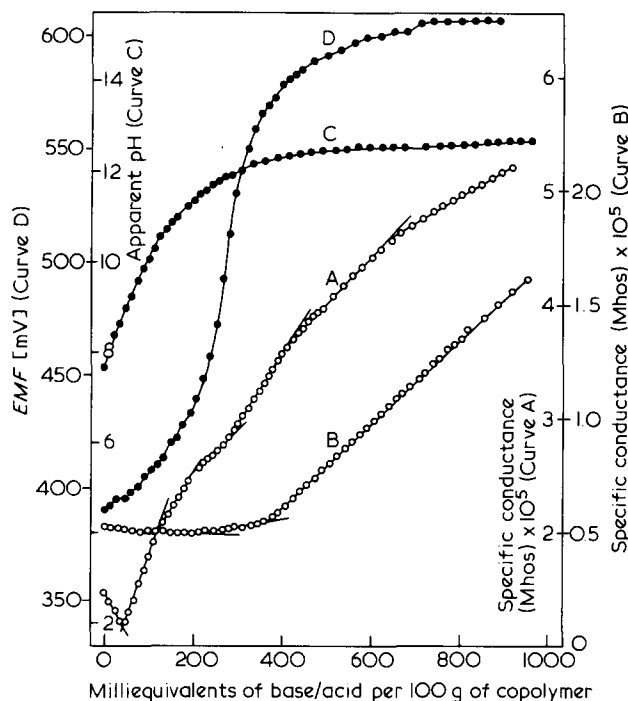


Figure 3 Titration curves of copolymer III. Conductometric curves: (A) in pyridine with sodium methoxide; (B) in glacial acetic acid with perchloric acid. Potentiometric curves: (C) in pyridine with sodium methoxide; (D) in glacial acetic acid with perchloric acid

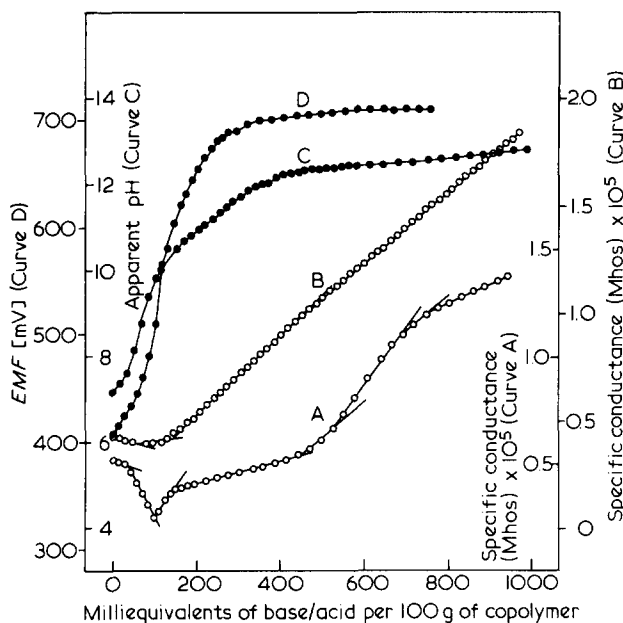


Figure 2 Titration curves of copolymer II. Conductometric curves: (A) in pyridine with sodium methoxide; (B) in glacial acetic acid with perchloric acid. Potentiometric curves: (C) in pyridine with sodium methoxide, (D) in glacial acetic acid with perchloric acid

halogen content of the copolymer was estimated by treating the copolymer with sodium metal, and the resultant sodium chloride was titrated by Volhard's method⁴.

A Radiometer pH meter (model PHM 26C) with a glass electrode (G 202B) and a calomel electrode (K 410) as reference, was used for pH titrations. A Leeds and Northrup 4959 electrolytic conductance bridge was used for the conductometric titrations. The details of the titration procedure have been reported elsewhere⁵.

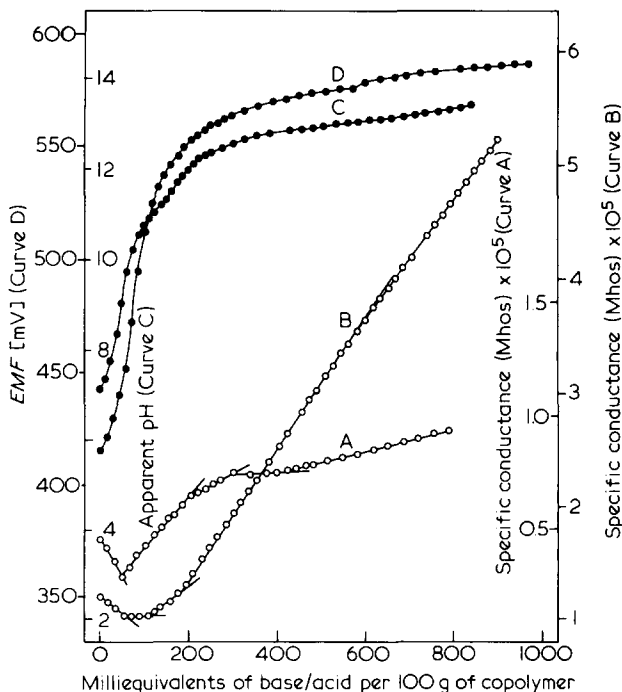


Figure 4 Titration curves of copolymer IV. Conductometric curves: (A) in pyridine with sodium methoxide; (B) in glacial acetic acid with perchloric acid. Potentiometric curves: (C) in pyridine with sodium methoxide; (D) in glacial acetic acid with perchloric acid

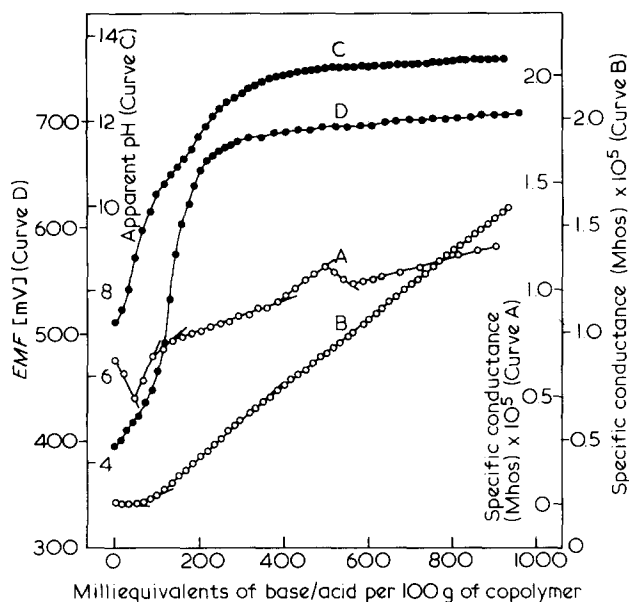


Figure 5 Titration curves of copolymer V. Conductometric curves: (A) in pyridine with sodium methoxide; (B) in glacial acetic acid with perchloric acid. Potentiometric curves: (C) in pyridine with sodium methoxide; (D) in glacial acetic acid with perchloric acid

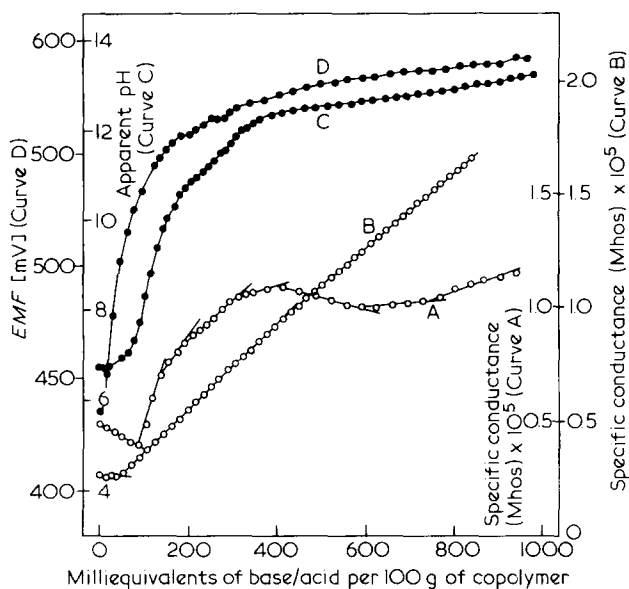
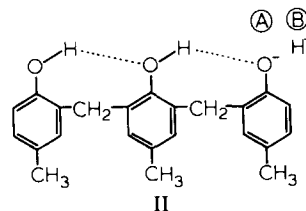


Figure 6 Titration curves of copolymer VI. Conductometric curves: (A) in pyridine with sodium methoxide; (B) in glacial acetic acid with perchloric acid. Potentiometric curves: (C) in pyridine with sodium methoxide; (D) in glacial acetic acid with perchloric acid

glacial acetic acid medium with perchloric acid as the titrant acid. Conductometric curves in pyridine for all the copolymers (e.g. curve A of Figures 1 to 6), showed several distinct breaks before complete neutralization of all the phenolic OH groups in a given weight of the copolymer. The corresponding conductometric curves in the glacial acetic acid medium (e.g. curve B of Figures 1 to 6), did not show as many breaks, and more often neutralization of NH_2 groups has been found to be merged. The potentiometric curves for copolymers I to VI in the pyridine medium (e.g. curve C of Figures 1 to 6), showed only one or two sharp inflections which invariably coincided with the strong acid portion (e.g. fall in conductance) of the conductometric curve. Similar

correlations could also be seen between potentiometric and conductometric curves in the glacial acetic acid medium.

The presence of intramolecular hydrogen bonding in phenolic oligomers and copolymers has been reported by several authors⁶⁻⁸. The hyperacidity of some of the OH groups in the copolymer chain could be attributed to intramolecular hydrogen bonding between neighbouring OH groups. For instance, as a result of intramolecular hydrogen bonding in the case of a phenolic oligomer (II), the -ve charge (A) gets delocalized, and consequently, the end proton (B) becomes more labile of hyperacidic⁶.



I.r. spectra of all the samples showed sharp absorptions in the range $3450\text{--}3600\text{ cm}^{-1}$, indicating that probable presence of $\text{O-H}\cdots\text{O}$ intramolecular hydrogen bonding. Both chemical and spectral evidence clearly shows the presence of intramolecular hydrogen bonding in these copolymers. Similar observations have also been made by other workers on phenolic oligomers and related copolymers⁶⁻⁸. However, one cannot rule out completely the possibility of intermolecular hydrogen bonding, in spite of the fact that we have studied the titration curves in very dilute solutions. The possibility of some intermolecular hydrogen bonding exists firstly, because one can expect strong association between the molecules in non-aqueous solvents, and secondly, the polymer molecules being sufficiently large, their segments are likely to interact.

The composition of the copolymers could be derived as follows from the above titration curves and the halogen content of each copolymer. One can obtain, from the percentage of halogen present in the copolymer, the relative proportion of *p*-chlorophenol (pCIP) unit in the copolymer chain. Let its value be 'X' mole per g of copolymer. Since, the molecular weights of pAP, pC and pT units in the copolymer chain are almost identical (e.g. around 120), and pCIP is slightly different, therefore, whatever the relative proportion of the four units, the weight of the sum of four units will be around $500\text{ g} \pm 3\text{--}4\%$. Thus, the total number of moles of pT + pAP + pC per unit weight of copolymer will be equal to $\left(\frac{4-X}{500}\right) = Y$. The

total number of moles of acidic units (e.g. pCIP + pAP + pC) per unit weight of copolymer can be obtained from the final break of the conductometric curve (cf. curves A of Figures 1-6) and we will let it be equal to Z moles. Similarly, the total number of basic units (e.g. pAP + pT) can be obtained from the final break of the conductometric curve (cf. curves B of Figures 1-6) and we can call this P moles per unit weight of copolymer. Therefore, the number of moles of pC and pAP per unit weight of copolymer will be $(Y-P) = Q$ moles, and $[Z-(Q+X)] = R$ moles respectively. The number of moles of pT per unit weight of copolymer will be $[Y-(Q+R)] = S$ moles. On this basis, the number of moles of the four monomeric units per unit weight of the copolymers I to VI, and the amount NH_2 and OH groups

Table 2 Observed amount of NH₂ and OH groups in copolymers I to VI

Copolymer No.	Cl %	Total NH ₂ groups (meq/100 g of copolymer) obs.	Total OH groups (meq/100 g of copolymer) obs.
I	4.15	450	715
II	6.89	420	750
III	9.08	370	650
IV	5.54	600	410
V	8.70	325	560
VI	11.66	440	750

in copolymers I to IV have been calculated and shown in Table 1 and Table 2 respectively.

It can be seen from Table 1 that the composition of the copolymer is always different from that of its feed. This is expected in view of the difference in reactivity of the four monomers. The composition of the copolymer could be accounted for, to a large extent, on the basis of the following factors: (i) degree of resonance stabilization of the monomeric units, (ii) influence of electron attracting or electron donating groups present in the monomeric units, (iii) directive influence of substituents in the monomers, and (iv) polarization of the monomeric units.

It has been observed (see Table 1) that if the proportion of pCIP in the feed is large, then the copolymer contains a large proportion of pAP units, and relatively small proportions of pT and pC units. Because of the presence of excess pCIP in the feed, the growing polymer chain is expected to have this unit (e.g. pCIP) at the chain end. Cl being an electron attracting substituent causes the π electrons of the double bond to take part in the electronic system of the substituent. 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 such polarization takes place, then one can understand that a chain-end at which there happens to be a structural unit with an electron attracting substituent prefers a monomer with an electron donating substituent. Although the other two monomers, e.g. pT and pC also contain an electron donating group (e.g. CH₃), pAP is preferentially added due to two factors, e.g. the electron donating influence of NH₂ group, and the relatively high degree of resonance stabilization of pAP compared to pT and pC.

However, when the quantity of pAP is large in the feed, the relative proportion of all the three monomeric units, e.g. pCIP, pT and pC increases in the copolymer (see Table 1). With excess pAP in the feed, the growing polymer chain is expected to have a pAP unit at the chain-end. Because of the higher degree of resonance stabilization and polarization, pAP is likely to interact with all the remaining three monomeric units, e.g. pCIP, pT and pC. Moreover, it is well known that chain growth in phenolic polymerization proceeds by way of electrophilic attack of benzylic cations upon phenolic molecules⁹. One can expect two types of end groups, e.g. benzylic cations, and the activation of the end ring for further cationic attack due to intramolecular hydrogen bonding. The four monomeric units are expected to react in the order pAP > pCIP > pC > pT. One would also expect the same order of reactivity of the four units towards electrophilic attack by ⁺CH₂OH ion. Clearly, the degree of resonance stabilization of monomers and polarization are the more dominant factors which influence the addition of monomer units to a growing polymer chain. This trend in reactivity of the units is actually being reflected in the composition of the copolymers.

Thus, we can conclude that electrometric titration curves in non-aqueous solvents may provide valuable information concerning the composition and structure of complex polymeric systems such as a four component phenolic copolymer. Apart from this, the observed composition of the copolymers could also be accounted for on the basis of the structure of the monomeric species.

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