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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Chatterjee, S. K. and Pachauri, L. S.(1978) 'Effect of Structure on Titration Curves of p-Bromoaniline-Formaldehyde-p-Cresol Copolymers in Nonaqueous Media', *Journal of Macromolecular Science, Part A*, 12: 1, 17 – 34

To link to this Article: DOI: 10.1080/00222337808081019

URL: <http://dx.doi.org/10.1080/00222337808081019>

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Effect of Structure on Titration Curves of p-Bromoaniline-Formaldehyde-p-Cresol Copolymers in Nonaqueous Media

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ABSTRACT

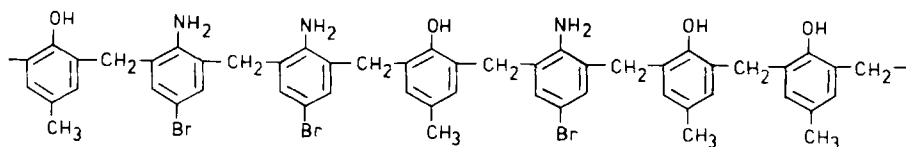
Copolymers obtained by the condensation of p-bromoaniline, formaldehyde, and p-cresol have been separated into five fractions by a fractional precipitation method. Some of these copolymers showed characteristic titration curves in non-aqueous media. The titration curves indicated a series of breaks which bear integral relations to each other. These features have been interpreted in terms of homoconjugation, intramolecular hydrogen bonding, and composition of the copolymers.

Joint polymerization of monomeric species having acidic and basic functional groups leads to the formation of copolymers which may have different sequence combinations of the functional groups in the copolymer chain. The reactivity of some of these functional groups may be influenced by such structural factors as intramolecular hydrogen bonding between neighboring groups. Some of these influences could be reflected in the titration curves of these copolymers. In fact, some preliminary investigations on nonaqueous titration

curves of some copolymers revealed that DP and total acidity or basicity of the copolymers could be estimated conveniently [1, 2]. The copolymer obtained by the condensation of p-bromoaniline, formaldehyde, and p-cresol has been chosen for this investigation. This system is interesting in view of the fact that each repeating unit of the copolymer contains an OH or NH₂ group, and the total amount of NH₂ groups could be calculated from its Br content, which in turn could be estimated by chemical analysis. The titration curves in nonaqueous media of the various fractions separated from the copolymer showed some interesting features. In general, the composition of the various fractions were found to be different from the copolymer and the feed. A large number of additional breaks and inflections have been observed before the complete neutralization of the functional groups. An attempt has been made in this paper to correlate the various observations with intramolecular hydrogen bonding, homoconjugation, and ion association in a medium of low dielectric constant.

EXPERIMENTAL

p-Bromoaniline (PBA)-formaldehyde-p-cresol (PC) random copolymer (I) was prepared by refluxing a mixture of p-bromoaniline



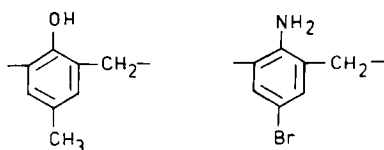
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(0.5 mole), p-cresol (0.5 mole), and formaldehyde (1.0 mole) in the presence of 2 ml of 10 N HCl as catalyst for 3 hr at 130°C. The reaction mixture was poured into ice-cold water and washed several times with distilled water to remove the unreacted monomers. The polymers yield was about 80%. The copolymer thus obtained was then fractionated by dissolving about 12.0 g of the product in methanol, the higher molecular weight fractions being separated by addition of water as nonsolvent. Approximately, 1.6, 3.2, 4.1, 1.4, and 0.7 g of the copolymers separated at five consecutive stages of precipitation. The Br content of the conglomerate and the five fractions were found by treating the copolymer with sodium metal, and the resultant sodium bromide was estimated by Volhard's method [3].

A Radiometer pH meter (model PHM 26c) with glass electrode (G202 B) and a calomel electrode (K401) 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 [1].

RESULTS AND DISCUSSIONS

Figures 1-6 show the potentiometric and conductometric titration curves of the copolymer (I) and the five fractions separated from it. The titrations were carried out in pyridine with sodium methoxide as titrant base. The conductometric titration curves (curves A of Figs. 1-6), showed a distinct final break, which represents the neutralization of total amount of OH groups per 100 g of the copolymer. The values obtained at the final break tallied with calculated values obtained on the basis of Br estimation of the samples. The copolymer chains contain two types of distinct repeating units; these may be linked in a completely random manner, or there may be a small block of one type of repeating unit followed by another block of the other repeating unit.



On the basis of the Br estimation of the conglomerate and each of the fractions, one can calculate the total amount of OH/NH₂ groups per 100 g of the copolymer. If the mole fraction of each repeating unit of the copolymer is 0.5, then 304 g (total molecular weight of the repeating units), contain one equivalent each of OH and NH₂ groups, 100 g of the copolymer should contain 328 meq of OH and NH₂ groups each. Of course, if the mole-fraction of the components varies in the copolymer chain (as is actually found on the basis of Br estimation), then the amount of OH/NH₂ groups per 100 g of the copolymer will change, and this quantity can be calculated from the mole fraction of the components in the copolymer. Table 1 shows the Br content, mole fraction of the components, and calculated and observed amounts of total OH and NH₂ groups in the conglomerate and each of the fractions.

The corresponding potentiometric curves of the conglomerate and each of the fractions (curves B of Figs. 1-6), showed only one sharp inflection followed by one or two weak inflections, whereas the

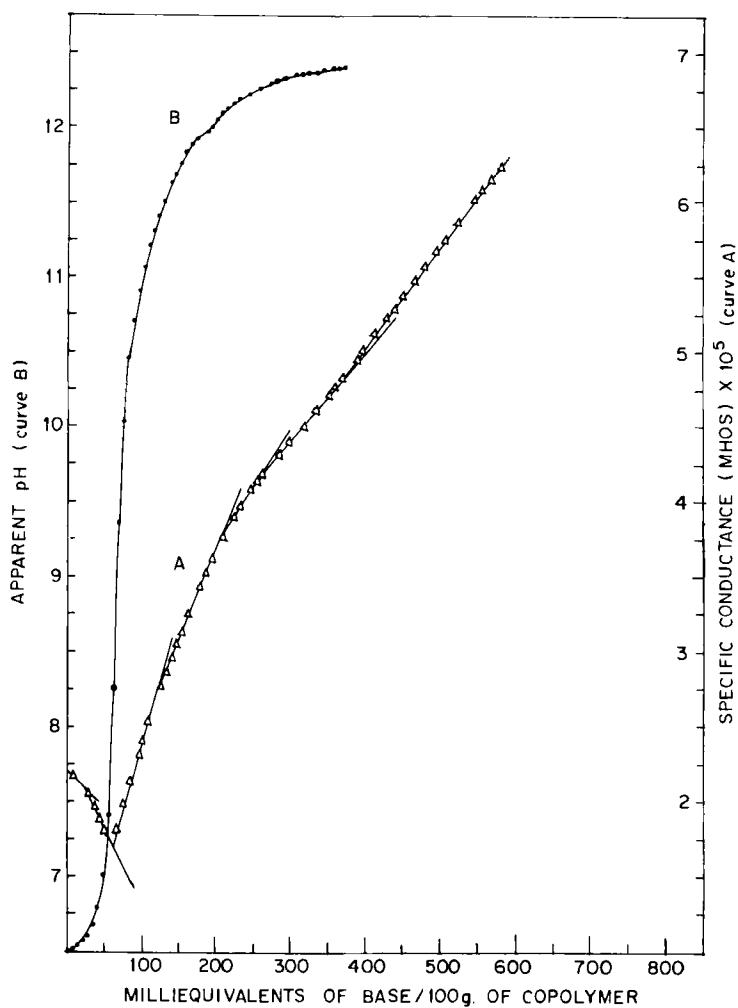


FIG. 1. Titration curves of conglomerate in pyridine with sodium methoxide: (A) conductometric curve, (B) potentiometric curve.

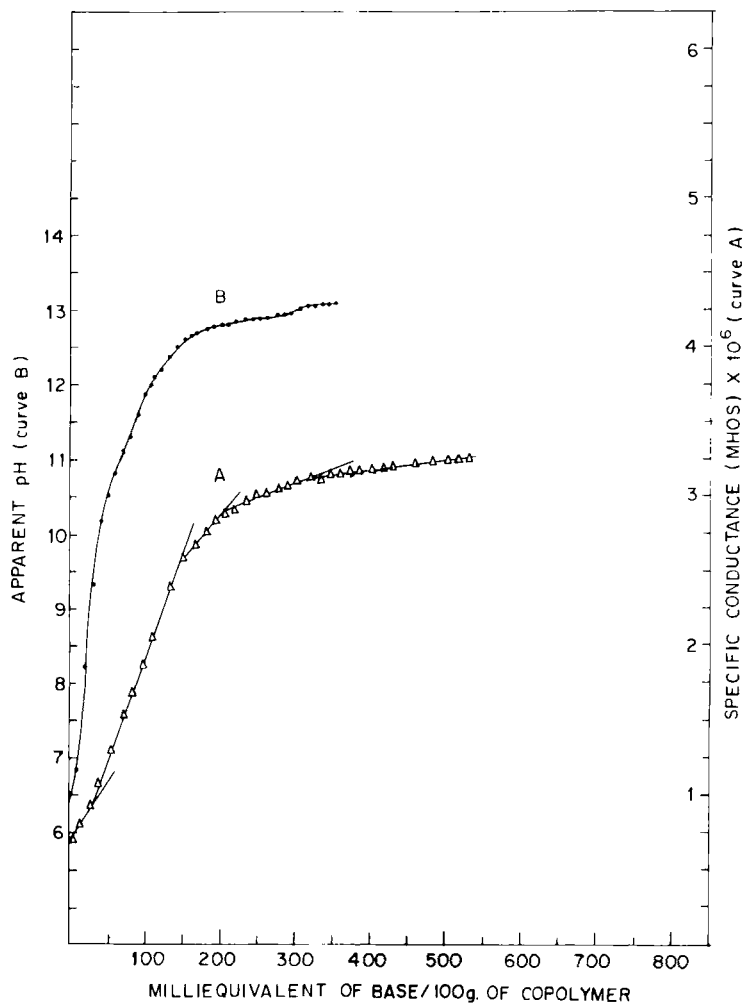


FIG. 2. Titration curves of fraction 1 in pyridine with sodium methoxide: (A) conductometric curve; (B) potentiometric curve.

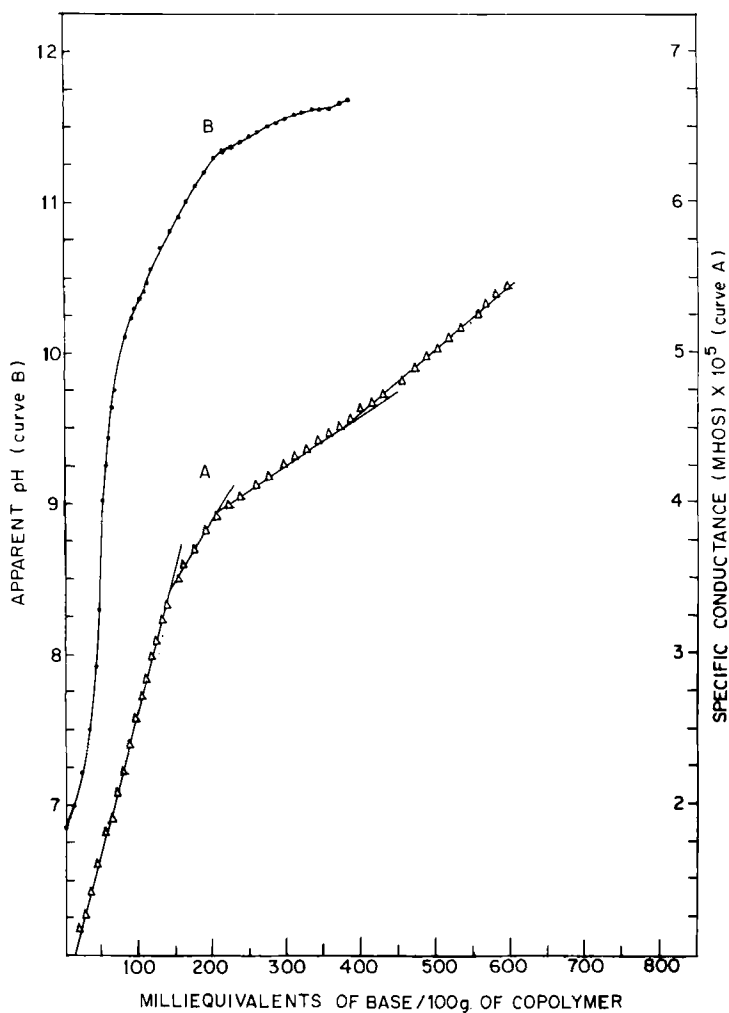


FIG. 3. Titration curves of fraction 2 in pyridine with sodium methoxide: (A) conductometric curve; (B) potentiometric curve.

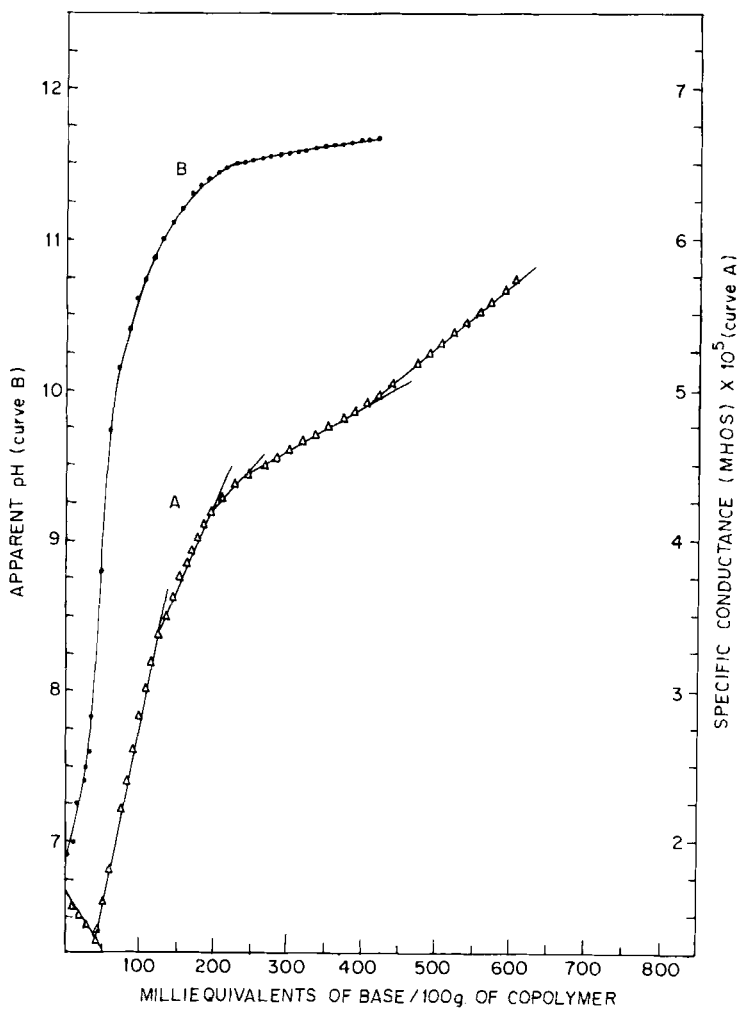


FIG. 4. Titration curves of fraction 3 in pyridine with sodium methoxide: (A) conductometric curve; (B) potentiometric curve.

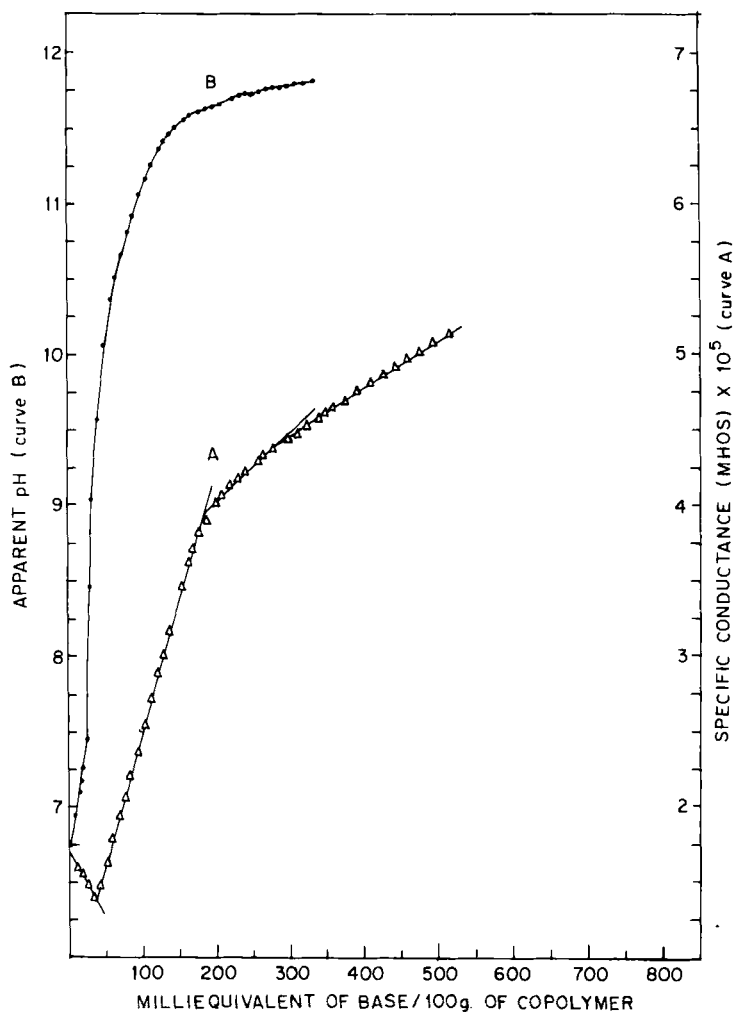


FIG. 5. Titration curves of fraction 4 in pyridine with sodium methoxide: (A) conductometric curve; (B) potentiometric curve.

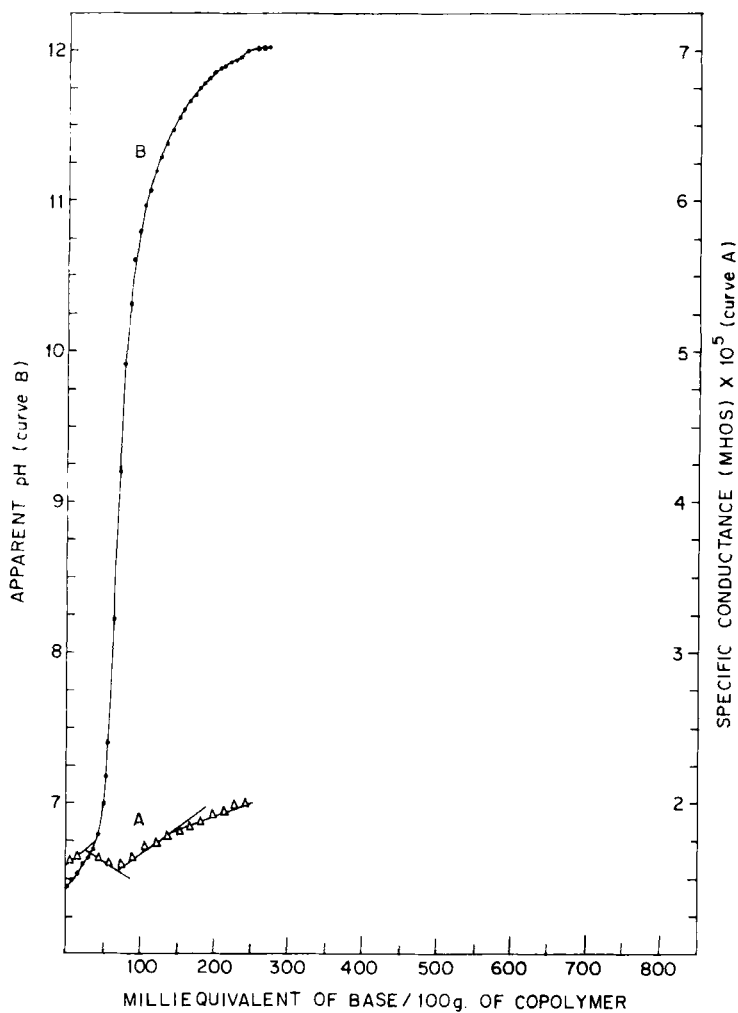


FIG. 6. Titration curves of fraction 5 in pyridine with sodium methoxide: (A) conductometric curve; (B) potentiometric curve.

TABLE 1. Observed Amounts of Acidic and Basic Groups in p-Bromoaniline-Formaldehyde-p-Cresol Copolymer (I)

Copolymer	Br (%)	Mole ratio PBA : PC	Smallest interval	Total NH ₂ groups (meq/100 g copolymer)		Total OH groups (meq/100 g copolymer)	
				Calcd ^a	Obsd	Calcd ^a	Obsd
Conglomerate	22.45	0.85:1.15	30	291	285	389	385
Fraction 1	25.25	0.96:1.04	35	305	290	345	330
Fraction 2	22.45	0.85:1.15	50	291	295	389	390
Fraction 3	19.74	0.75:1.25	40	260	270	434	415
Fraction 4	27.97	1.06:0.94	37	344	330	305	310
Fraction 5	37.41	1.41:0.59	25	424	445	179	145

^aOn the basis of Br estimation.

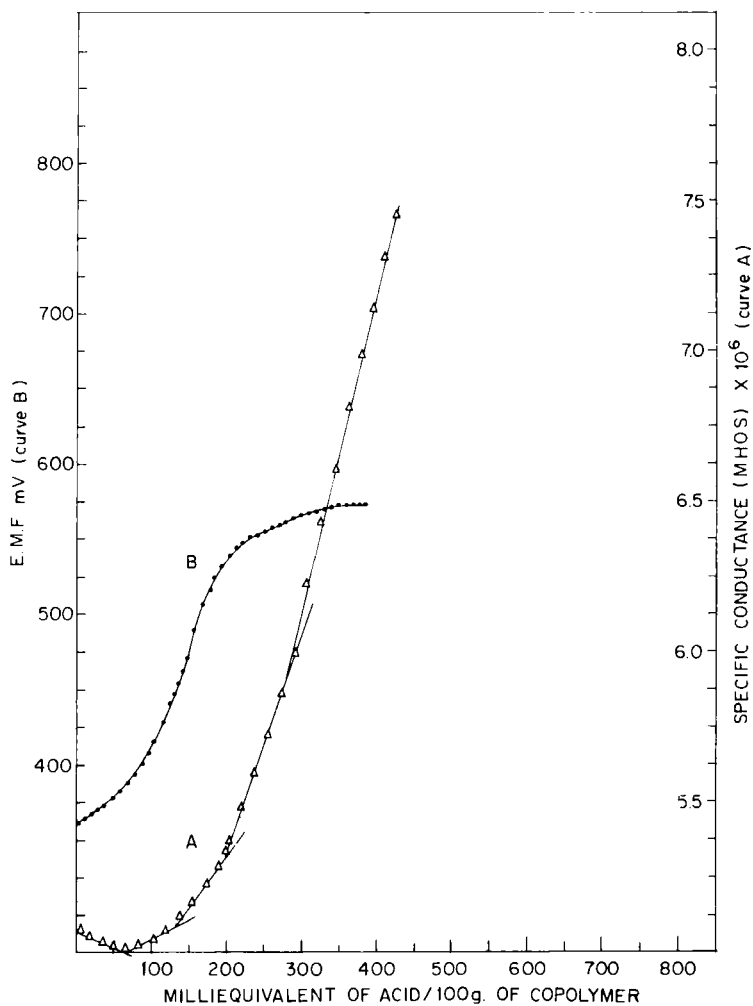


FIG. 7. Titration curves of conglomerate in glacial HAc with perchloric acid: (A) conductometric curve; (B) potentiometric curve.

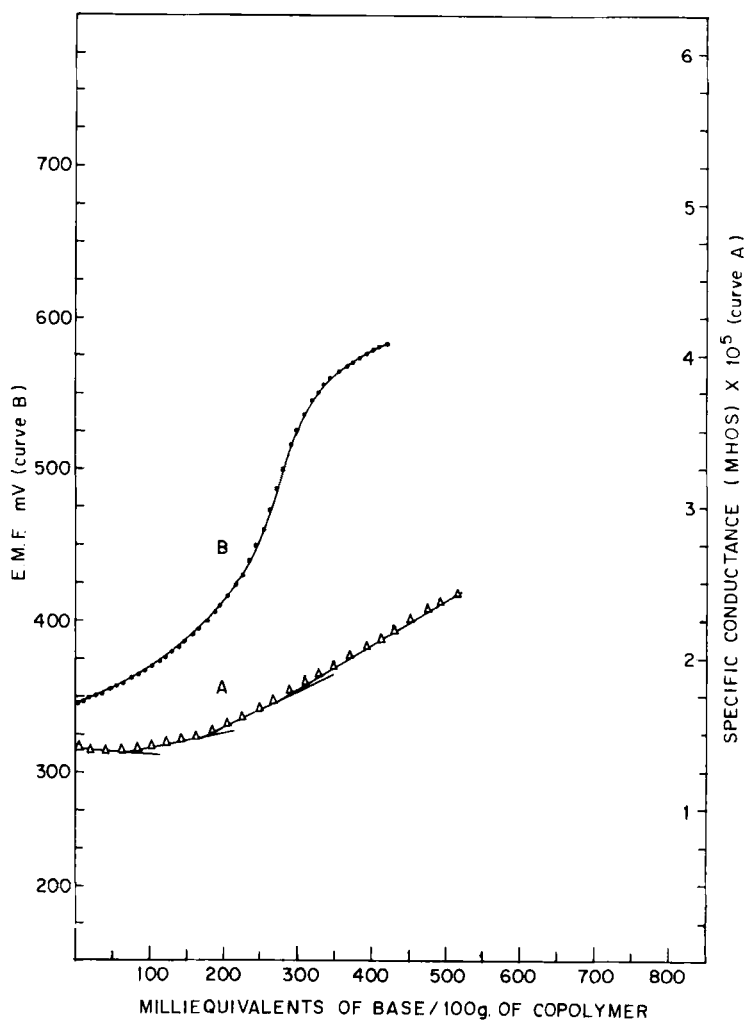


FIG. 8. Titration curves of fraction 1 in glacial HAc with perchloric acid: (A) conductometric curve; (B) potentiometric curve.

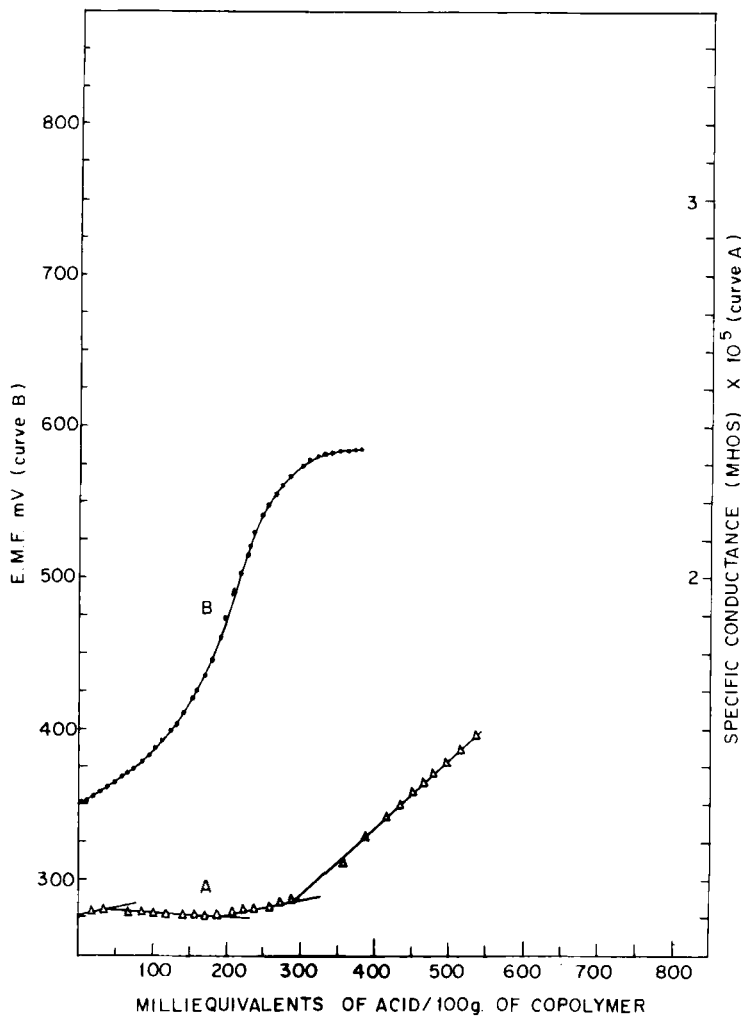


FIG. 9. Titration curves of fraction 2 in glacial HAc with perchloric acid: (A) conductometric curve; (B) potentiometric curve.

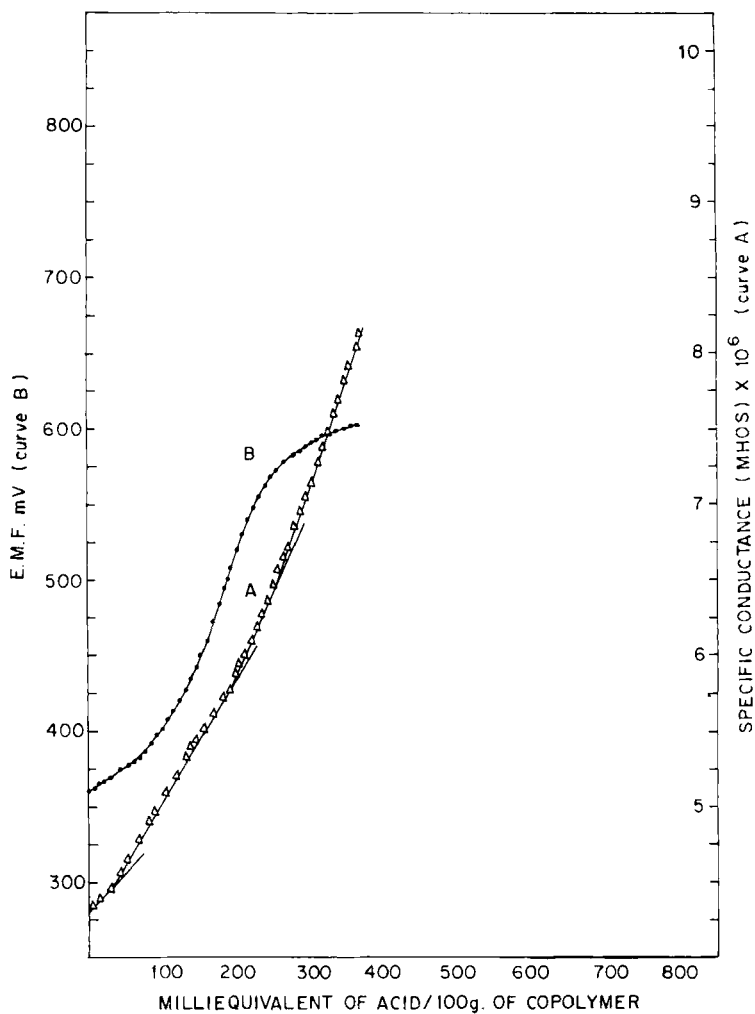


FIG. 10. Titration curves of fraction 3 in glacial HAc with perchloric acid. (A) conductometric curve; (B) potentiometric curve.

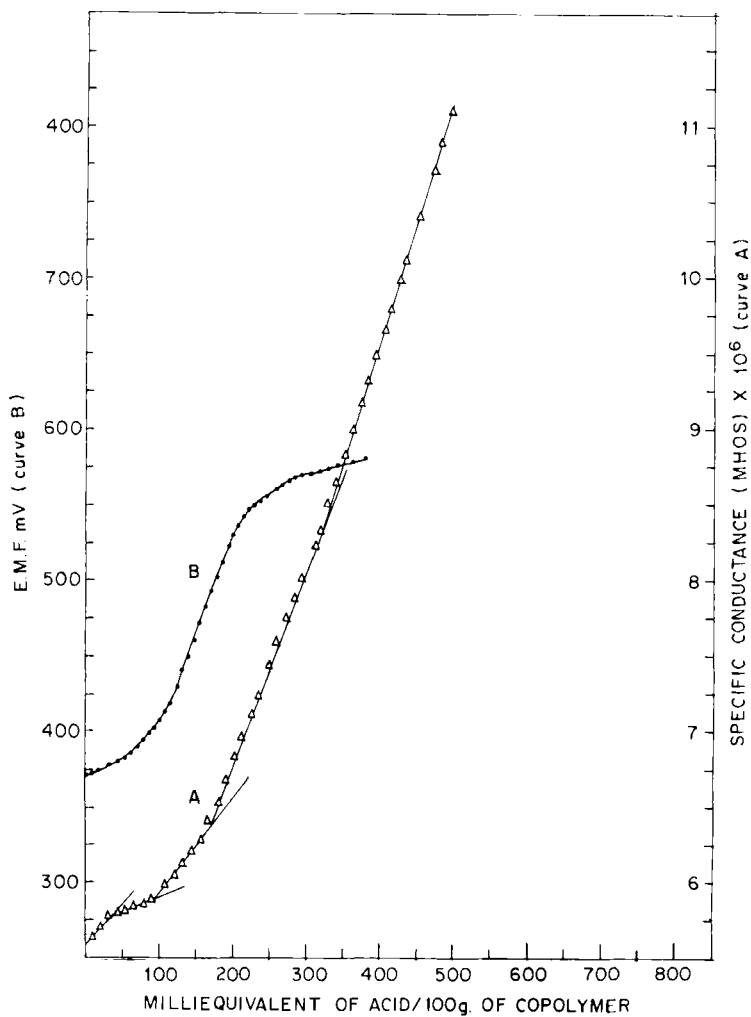


FIG. 11. Titration curves of fraction 4 in glacial HAC with perchloric acid: (A) conductometric curve; (B) potentiometric curve.

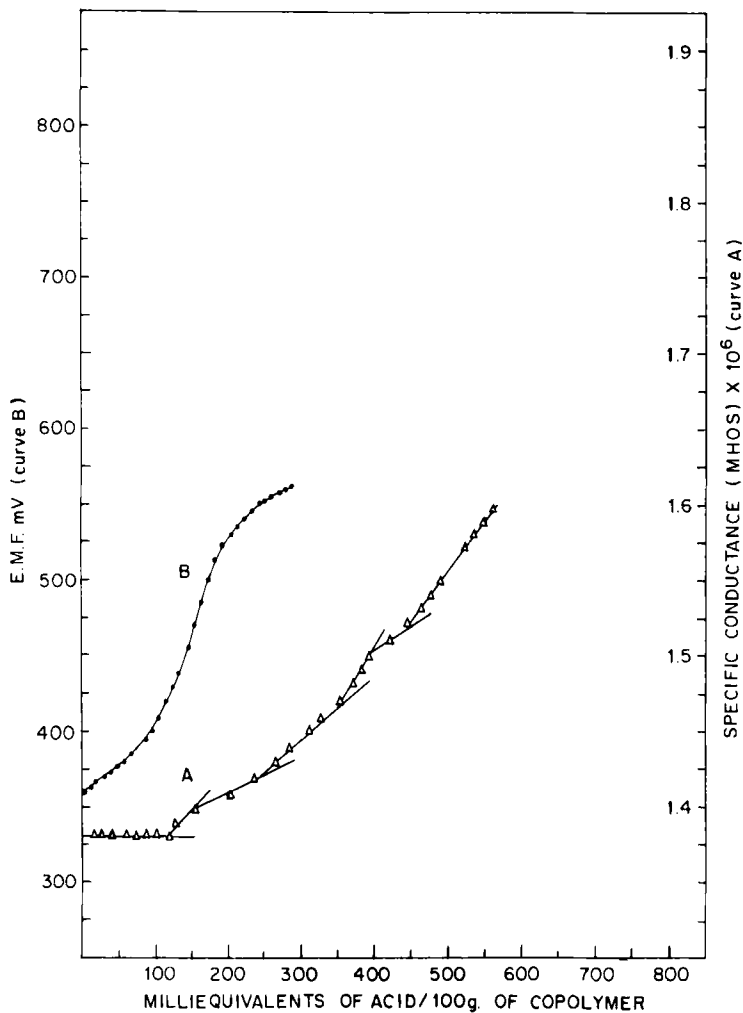


FIG. 12. Titration curves of fraction 5 in glacial HAc with perchloric acid: (A) conductometric curve; (B) potentiometric curve.

conductometric curves are characterized by the presence of a large number of additional breaks before the complete neutralization of acidic functional groups in a given weight of the copolymer. Such peculiar features of the conductometric titration curves of weak acids have been attributed by Kolthoff and co-workers to homoconjugation [4-6]. Figure 7-12 show the titration curves of the copolymer (I) and its five fractions in glacial acetic acid with perchloric acid as titrant acid. The final break of the conductometric curves (curves A of Figs. 7-12), invariably coincided with the total amount of NH_2 groups calculated as stated earlier. The main features of the titration curves with the acid are more or less identical to those with base. An important aspect which is worth consideration is that the amount of acid added for a particular fraction at the smallest interval between any two successive breaks coincides with the corresponding amount of base added at the smallest interval for the same fraction. This coincidence has been observed in the titration curves of all the fractions and the conglomerate. It is evident that the coincidence does not refer to the amount of acid or base added at first, second, or third break in the titration curves for a particular fraction. Coincidence of values at the various breaks is not expected, in view of the fact that the medium of titration was different in the two cases. The resolution of a polybasic acid depends on a number of factors, e. g., dielectric constant of the solvent, its solvating power, its acidic and basic character, the chain conformation of the polymer molecules in the solvent, and extent of ion pair formation. Thus, it is obvious that some functional groups may merge in one medium, whereas the same functional groups may neutralize independently in another medium. This was actually observed in the titration curves. The point of interest is that the smallest interval for a particular fraction is constant irrespective of whether it is titrated with acid or a base. All other breaks in the titration curves for a given fraction are simple multiples of this smallest interval. These observations are summarized in Table 1.

The hyperacid character of some of the OH groups in the copolymer chain can be attributed to intramolecular hydrogen bond formation between neighboring functional groups. Evidences of the presence of such hydrogen bonding in phenolic polymers have been reported from nonaqueous titrations [7], infrared [8], and conformational [9] studies. The IR of almost all the samples studied indicated absorptions in the range 3450-3600 and 3070-3350 cm^{-1} , showing the probable presence of O-H . . . O and N-H . . . N intramolecular hydrogen bonding.

An aspect of the study is that nonaqueous titrations may provide a fairly simple method of estimation of relative proportions of various repeating units present in a copolymer chain.

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Accepted by editor August 26, 1977

Received for publication September 12, 1977