Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Correlation of Composition and DP of Some ThreeComponent Phenolic Block Copolymers with Their Titration Curves in Nonaqueous Media

S. K. Chatterjee[a]; R. L. Pandith[a]; L. S. Pachauri[a]
[a] Department of Chemistry, University of Delhi, Delhi, India

To cite this Article Chatterjee, S. K. , Pandith, R. L. and Pachauri, L. S.(1981) 'Correlation of Composition and DP of Some ThreeComponent Phenolic Block Copolymers with Their Titration Curves in Nonaqueous Media', Journal of Macromolecular Science, Part A, 16: 3, 717 — 727

To link to this Article: DOI: 10.1080/00222338108056818

URL: http://dx.doi.org/10.1080/00222338108056818

J. MACROMOL. SCI.–CHEM., A16(3), pp. 717-727 (1981)

Correlation of Composition and DP of Some Three-Component Phenolic Block Copolymers with Their Titration Curves in Nonaqueous Media

S. K. CHATTERJEE, R. L. PANDITH, and L. S. PACHAURI

Department of Chemistry
University of Delhi
Delhi 110007, India

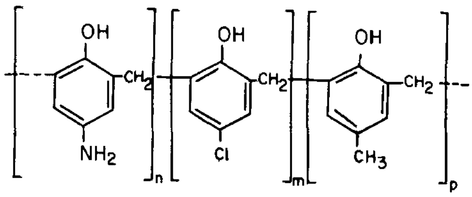
ABSTRACT

Some three-component phenolic block copolymers have been prepared from the following three monomeric units: p-aminophenol, p-chlorophenol, and p-cresol. Homopolymerization of these monomers has been done with formaldehyde in the presence of acid catalyst. The homopolymer samples were then condensed together with stoichiometric quantities of formaldehyde and acid catalyst. Several samples of the copolymers were also prepared by changing the composition of the feed during homopolymerization. Composition, DP, and the average number of a particular monomeric unit in a block of a copolymer chain has been deduced from electrometric titration curves of the copolymers in nonaqueous media.

Simultaneous copolymerization of three different monomer species may give rise to a copolymer whose composition will depend on the relative reactivity of the monomers. In normal copolymerization the different monomers alternate in the chain either in a more or less regular or in a completely random manner. Some preliminary investigations on a few three-component random phenolic copolymers revealed that composition, DP, and dissociation behavior of such systems could be evaluated by electrometric titration techniques in nonaqueous media [1]. Since three-component copolymers as such are quite complex, it was therefore considered of interest to see whether such simple techniques could be used for getting information about these copolymers prepared under various conditions. Keeping this fact in view, block copolymers involving the following three monomeric units have been prepared: p-aminophenol (PAP), p-chlorophenol (PClP), and p-cresol (PC). Block copolymers have been prepared by combining the homopolymer chains of the three monomers with the aid of functional groups and formaldehyde. The feed composition of the homopolymers has also been varied to change the size of the blocks. The characteristic feature of these three-component copolymers is the presence of a phenolic OH group in each of its repeating units and the presence of $-NH_2$ and Cl groups as structural substituents in some of the repeating units. One can thus deduce the composition of the copolymers from the quantitative estimation of Cl and $-NH_2$ groups. An attempt has been made in this paper to correlate composition, DP, size of some of the blocks in the copolymer chains, intramolecular hydrogen bonding, etc. with the features of electrometric titration curves of the copolymers in nonaqueous media.

EXPERIMENTAL

Homopolymer chains of the three monomers PAP, PClP, and PC have been prepared by refluxing the respective monomers with formaldehyde in the presence of 2 mL of 10 N HCl as catalyst for 1 h at 130°C. The three homopolymer samples were then mixed together with stoichiometric quantities of formaldehyde and HCl catalyst and further refluxed for $1\frac{1}{2}$ h at 130°C. The reaction mixture was then poured into ice-cold water and washed several times with distilled water to remove unreacted monomers.



n = 1,2,3,4 etc.; m = 1,2,3,4 etc.; p = 1,2,3,4 etc.

Five samples of the above three-component block copolymers have been prepared by choosing the following feed compositions:

Copolymer I: 0.1m PClP + 0.1m PC + 0.8m PAP
Copolymer II: 0.2m PClP + 0.2m PC + 0.6m PAP
Copolymer III: 0.3m PClP + 0.3m PC + 0.4m PAP
Copolymer IV: 0.33m PClP + 0.33m PC + 0.33m PAP
Copolymer V: 0.4m PClP + 0.4m PC + 0.2m PAP

Different feed compositions have been used during homopolymerization so as to obtain different size blocks. The copolymer yield in all cases was from 70-75%. The halogen content of each of the five samples has been determined by treating the copolymer with sodium metal, and the resultant sodium chloride was estimated by Volhard's method [2].

A Radiometer pH meter (pHM 26c) with glass (G 202B) and calomel (K 401) electrodes as reference was used for pH titrations, and a Leeds and Northrup conductance bridge (4959) was used for conductometric titrations. The details of the titration procedure have been described elsewhere [3]. For acidic functional groups, pyridine was used as the medium of titration and sodium methoxide as the titrant base. Estimation of basic functional groups has been done in glacial acetic acid medium with perchloric acid in methanol as the titrant acid. The copolymer concentration used was around 1.5 g/L. The reproducibility of each titration curve has been checked and found to be within ±2-3%.

RESULTS AND DISCUSSION

Figure 1 shows the conductometric and potentiometric titration curves of Copolymer I in pyridine and glacial acetic acid media. The titrant base and acid used were sodium methoxide and perchloric acid, respectively. The conductometric curves of Copolymer I in glacial acetic acid medium (Curve B of Fig. 1) showed three distinct breaks, and the final break naturally indicates the complete neutralization of $-NH_2$ groups per 100 g of the copolymer. From this value and the Cl content of Copolymer I (cf. Table 1), one can derive the composition of the copolymer. On the basis of these observations, the composition of Copolymer I found to be 0.11m PClP + 0.04m PC + 0.85m PAP, with the average molecular weight of the repeating unit involving the three monomers in the above ratio coming to 125.1. Thus one can calculate on the basis of average molecular weight of this repeating unit the total amount of OH groups per 100 g of copolymer. The final break in the conductometric curve (e.g., Curve A of Fig. 1) of Copolymer I in pyridine with sodium methoxide as titrant coincided within experimental error with the calculated value of total OH groups (cf. Table 2). Apart from the final break, the conductometric curve in pyridine (Curve A of Fig. 1) showed a series of additional breaks. The smallest interval between any two consecutive breaks was found to be about 45 mEq/100 g of copolymer, and the

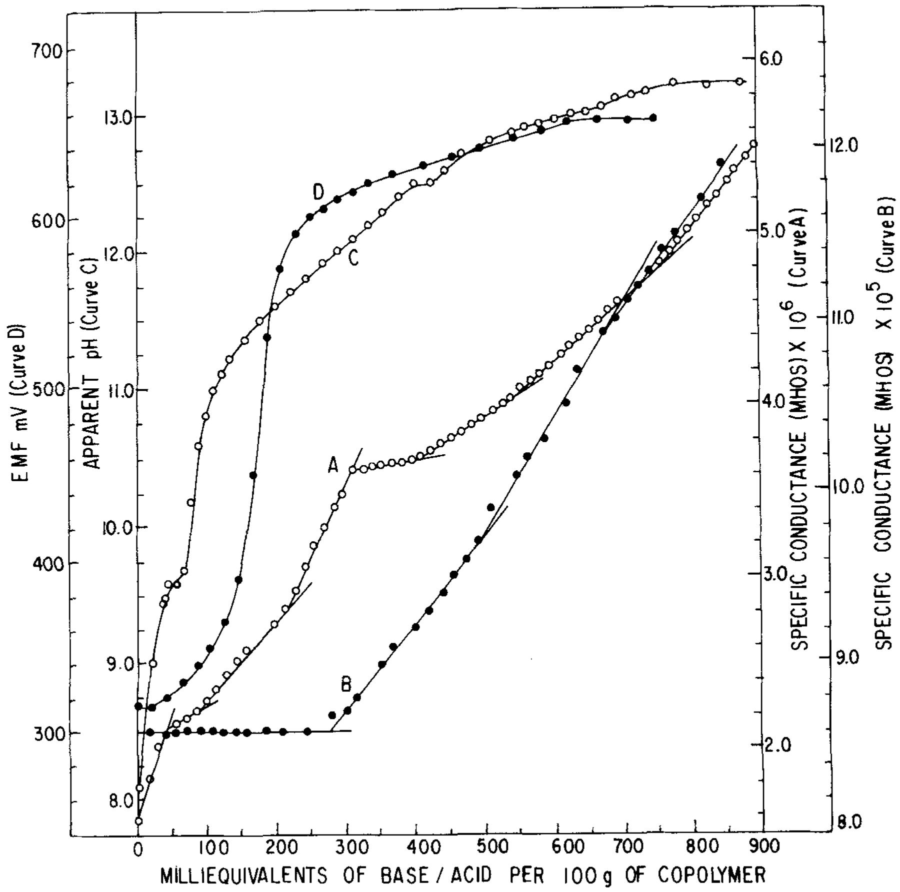


FIG. 1. Titration curves of Copolymer I. Conductometric curves: (A) in pyridine with sodium methoxide, (B) in glacial acetic acid with perchloric acid. Potentiometric curves: (C) in pyridine with sodium methoxide, (D) in glacial acetic acid with perchloric acid.

remaining breaks were found to occur in simple multiples of this smallest interval. The corresponding potentiometric curve in pyridine (e.g., Curve C of Fig. 1) showed a very sharp inflection followed by two weak inflections. The sharp and the weak inflections occur in simple multiples of the smallest interval. The potentiometric curve in glacial acetic acid medium (e.g., Curve D of Fig. 1) also showed a sharp and a weak inflection which occurred in simple multiples of the smallest interval.

Figures 2 to 5 show the potentiometric and conductometric curves

TABLE 1. Composition of Copolymers I to V

Copolymer	Cl (%)	Copolymer composition[a]			Smallest interval (mEq/100 g of copolymer)	DP	Average molecular weight of repeating unit
		PClP	PAP	PC			
I	2.74	0.11m	0.85m	0.04m	45	17.9	125.1
II	3.80	0.15m	0.65m	0.20m	45	17.7	125.8
III	6.52	0.26m	0.54m	0.20m	52	15.1	127.6
IV	8.10	0.33m	0.24m	0.43m	47	16.5	128.9
V	10.55	0.42m	0.17m	0.41m	62	11.7	130.8

[a] Compositions are expressed in mole (m) ratios.

TABLE 2. Amount of OH and NH_2 Groups in Copolymers I to V

Copolymer	Total NH_2 groups (mEq/100 g of copolymer) (obs)	Total OH groups (mEq/100 of copolymer) (calc)[a]	Total OH groups (mEq/100 of copolymer) (obs)
I	690	799.3	755
II	525	795.0	790
III	415	785.9	785
IV	195	775.7	780
V	135	764.2	750

[a] On the basis of halogen and amino group estimations.

of Copolymers II to V, respectively, in pyridine and glacial acetic acid media. The conductometric curves of these copolymers in pyridine (e.g., Curve A of Figs. 2-5) also showed a final break which coincided with the calculated amount of OH groups for the respective copolymers. The calculated and observed values of OH groups, the average molecular weight of the repeating units corresponding to the various compositions of the copolymers, and the smallest interval for each copolymer are shown in Tables 1 and 2. The basic differences between these titration curves (e.g., Figs. 2-5) and the titration curves of Copolymer I (e.g., Fig. 1), may be summarized as follows: (1) The potentiometric curves in pyridine (Curves C of Figs. 2-5) showed a correspondingly larger number of sharp inflections, (2) a fall in conductance was observed in all the conductometric curves in pyridine (Curves A of Figs. 2-5) at certain stages of neutralization, and (3) no sharp inflection was observed in the potentiometric curves in glacial acetic acid medium (e.g., curves D of Figs. 2-5). The most significant fact observed in the conductometric curves of Copolymers I to V in glacial acetic acid medium (e.g., Curves B of Figs. 1-5) is that the intervals at which breaks are observed decreases as the molar proportion of p-amino phenol (PAP) in the copolymer decreases (i.e., from Copolymer I to V).

One can obtain the number-average DP of a copolymer by dividing the total amount of OH groups of the copolymer by its smallest interval. This is of course based on the assumption that each chain contributes only one OH group to its smallest interval. Since the average molecular weight of the repeating units in the various Copolymers I to V do not differ much (cf. Table 1), therefore the smallest interval could also be attributed to one p-amino phenol monomer unit in the copolymer chain. On the basis of these

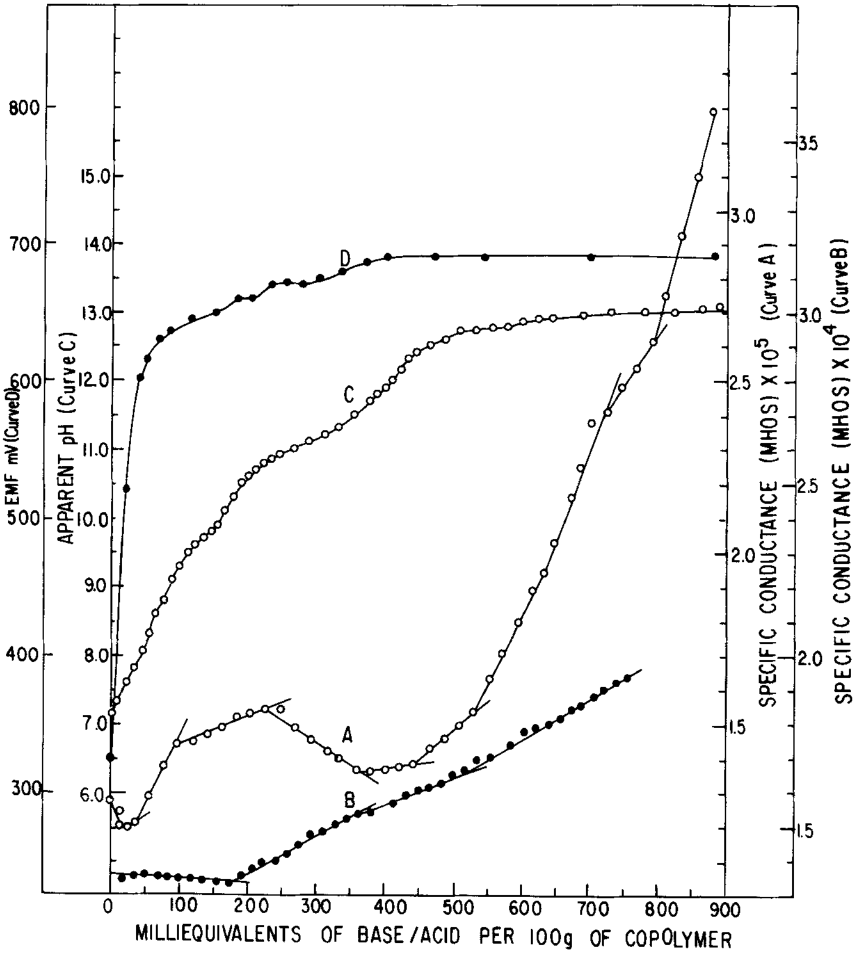


FIG. 2. Titration curves of Copolymer II. Conductometric curves: (A) in pyridine with sodium methoxide, (B) in glacial acetic acid with perchloric acid. Potentiometric curves: (C) in pyridine with sodium methoxide, (D) in glacial acetic acid with perchloric acid.

arguments, the average number of p-aminophenol monomer units present in the blocks of the copolymer chain is found to vary from six to two for Copolymers I to V, respectively, These values have been arrived at by dividing the various intervals (breaks) in the conductometric curves (e.g., Curves B of Figs. 1-5) by the respective smallest interval. This order is in complete conformity with the molar proportions of p-aminophenol present in the different copolymers.

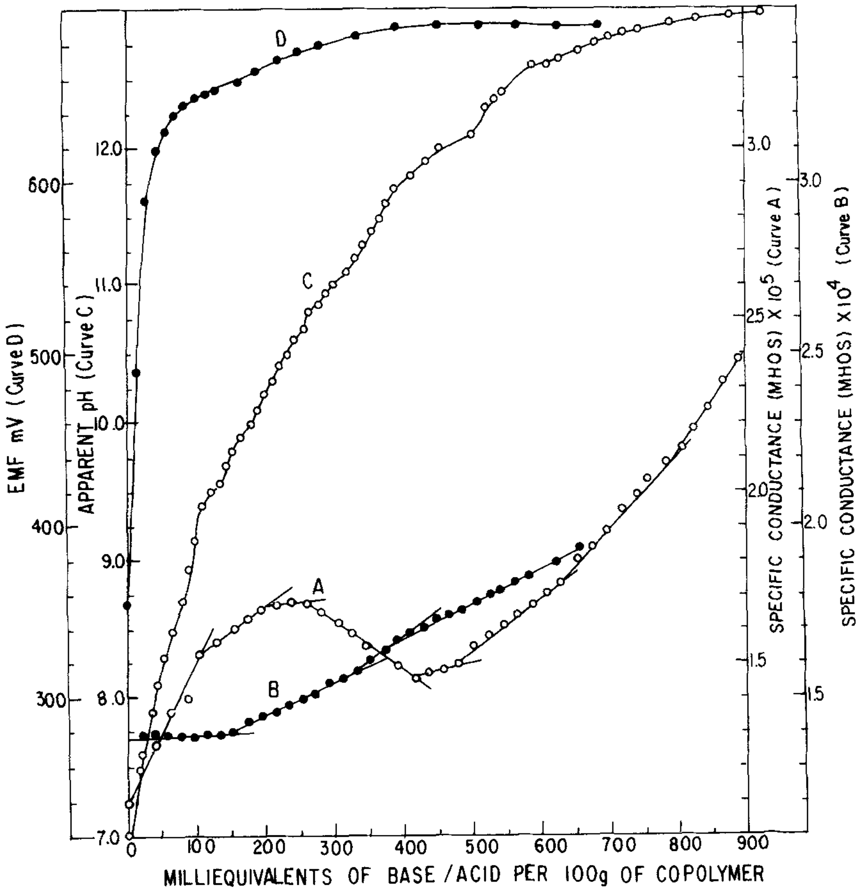


FIG. 3. Titration curves of Copolymer III. Conductometric curves: (A) in pyridine with sodium methoxide, (B) in glacial acetic acid with perchloric acid. Potentiometric curves: (C) in pyridine with sodium methoxide, (D) in glacial acetic acid with perchloric acid.

Some of the features of the titration curves of the copolymers may be summarized as follows: (1) Compared to potentiometric curves, conductometric curves showed a more distinct stepwise neutralization of the functional groups (in other words, for every break in the conductometric curve of a copolymer, its potentiometric curve did not show a corresponding inflection); (2) some of the conductometric curves (Curves A of Figs. 2-5) showed a fall in conductance during certain stages of neutralization; and (3) the number of distinct (sharp) inflections in the potentiometric curves (e.g., Curves C of Figs. 1-5) varied from copolymer to copolymer.

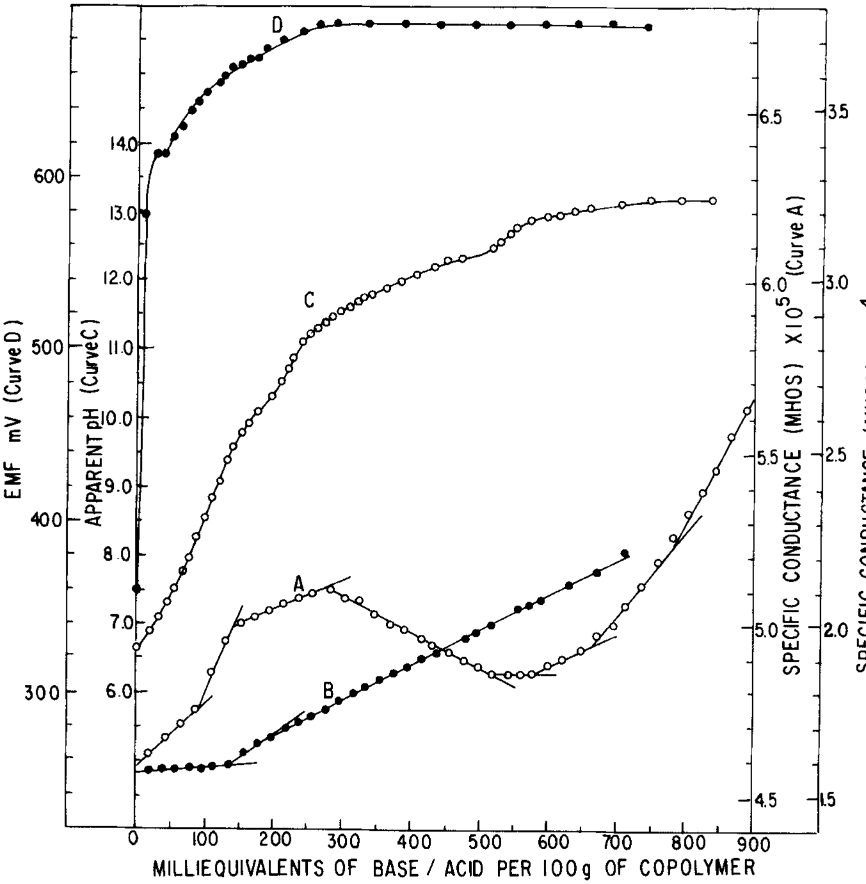


FIG. 4. Titration curves of Copolymer IV. Conductometric curves: (A) in pyridine with sodium methoxide, (B) in glacial acetic acid with perchloric acid. Potentiometric curves: (C) in pyridine with sodium methoxide, (D) in glacial acetic acid with perchloric acid.

The fact that OH groups in a copolymer chain are neutralized in distinct steps showed that some of them have acquired hyperacid character. This hyperacidity has been attributed to intramolecular hydrogen bonding between neighboring OH groups. IR [4], conformational [5], and electrometric titration studies [6-8] have unequivocally established the presence of intramolecular hydrogen bonding in such phenolic resins and oligomers. The IR spectra of all these copolymer samples showed sharp absorption in the region 3450-3600 cm^{-1}, indicating the presence of O–H. . .O bonding. The distinct

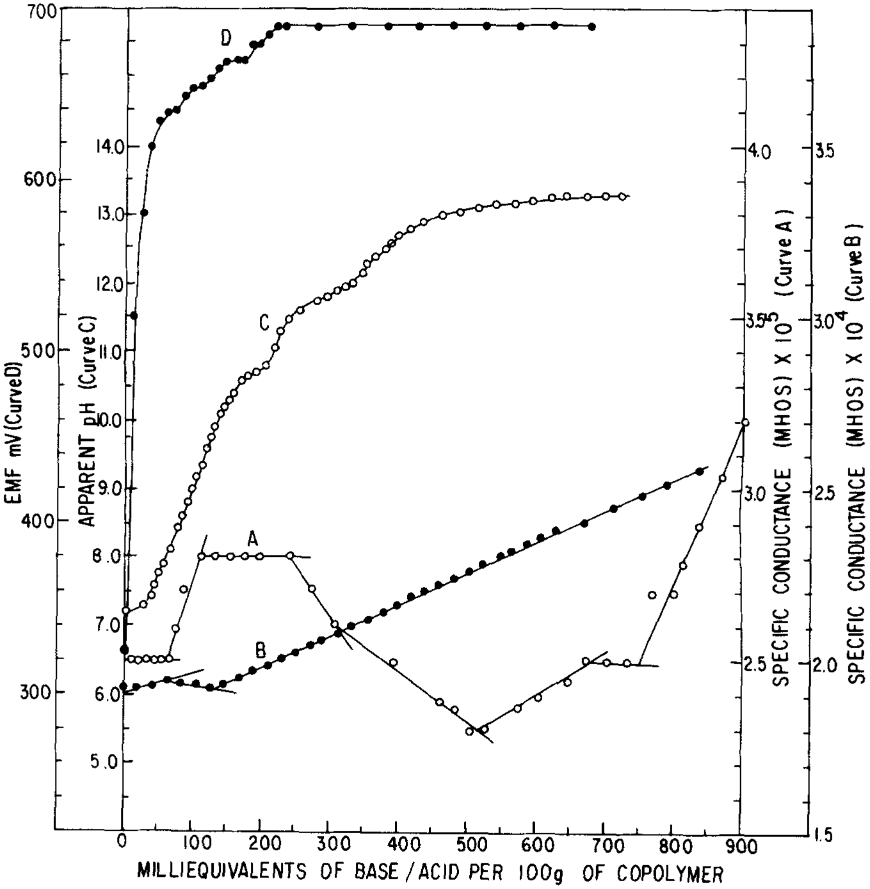


FIG. 5. Titration curves of Copolymer V. Conductometric curves: (A) in pyridine with sodium methoxide, (B) in glacial acetic acid with perchloric acid. Potentiometric curves: (C) in pyridine with sodium methoxide, (D) in glacial acetic acid with perchloric acid.

stepwise neutralization found in the conductometric curves can be interpreted in terms of the probable differences in the degree of dissociation of various acid-anion or base-cation complexes which are likely to be formed in a medium of low dielectric constant. These factors may not appreciably influence a potentiometric curve. The fall in conductance observed at certain stages of neutralization in the conductometric curves (e.g., Curves A of Figs. 2-5) may be attributed to ion association between the acid-anion with a comparatively high negative charge and the small metal cation (Na^+) of the titrant in a medium of low dielectric constant. The variation in the number of sharp inflections in the potentiometric curves in pyridine of the various copolymers may be attributed to different sequence combinations of the monomers present in a copolymer chain. The sequence combination of the monomers will be important because the acid character of the OH groups will be greatly influenced by the presence of electrophilic (Cl) or nucleophilic (CH_3, etc.) substituents present in the monomeric units.

Thus electrometric titration techniques in nonaqueous media may provide a very convenient and elegant method for determining the composition, DP, and probable number of monomeric units present in some of the blocks of three component copolymer chains having dissociable acidic and basic functional groups.

REFERENCES

[1] S. K. Chatterjee and L. S. Pachauri, Makromol. Chem., In Press.

[2] A. I. Vogel, Quantitative Organic Analysis, Longmans, Green, London, 1964.

[3] S. K. Chatterjee and N. Datta Gupta, J. Polym. Sci., Polym. Chem. Ed., 11, 1261 (1973).

[4] N. D. Coggesshall, J. Am. Chem. Soc., p. 5906 (1965).

[5] T. Cairns and G. Eglinton, J. Chem. Soc., p. 5906 (1965).

[6] G. R. Sprengling, J. Am. Chem. Soc., 76, 1190 (1954).

[7] S. K. Chatterjee and N. Datta Gupta, J. Macromol. Sci.–Chem., A8(2), 291 (1974).

[8] S. K. Chatterjee and L. S. Pachauri, Polymer, 19, 596 (1978).

Accepted by editor April 11, 1980
Received for publication April 22, 1980