Conductometric Tiration Curves of Some Synthetic Copolymers in Relation to Their Structure

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ABSTRACT

Two copolymers of p-aminobenzoic acid, p-hydroxybenzoic acid, and formaldehyde were prepared with different feed compositions. The copolymers were fractionated and their conductometric titrations carried out in nonaqueous solvent. The features of the titration curves have been interpreted in terms of DP, composition, and structure of the copolymers.

The composition of copolymers depends on a variety of factors such as degree of conversion, reactivity ratio of the monomeric units, and initial feed composition. Some preliminary work on the nonaqueous titration of some synthetic copolymers having acidic and basic functional groups revealed that the composition of the co-polymer and its dependence on the feed could be evaluated from such studies [1]. p-Aminobenzoic acid (AB), p-hydroxybenzoic acid (HB), and formaldehyde have been condensed in the presence of acid catalyst to obt .in the copolymers. Since the monomers differ in their tendency to enter into copolymers, it was therefore considered of interest to prepare two copolymers of extreme feed

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compositions, e.g., 0.1 m (AB):0.9 m (HB), and 0.9 m (AB):0.1 m (HB), respectively. Fractionation of the above copolymers revealed that the composition among the fractions differed markedly. These copolymers are interesting in view of the fact that the repeating unit of each one of them contains a COOH group and a OH or NH_2 group. Thus the various fractions may have copolymer chains having different numbers of NH_2 and OH groups. One can say from the probable structure of the co-polymer that on an average the total number of COOH groups should be equal to the sum of NH_2 and OH groups in a given weight of the co-polymer. Thus from the total number of observed acidic groups (COOH and OH), one can obtain the number of NH_2 groups by the method of difference. Conductometric titration curves of the various fractions of the copolymers, in nonaqueous solvents showed some interesting features. A large number of additional breaks, which occur in simple multiples of a smallest interval, have been observed for each of the fractions. This smallest interval, of course, was found to be different for each of the fractions. An attempt has been made in this paper to correlate these observations with the composition of the copolymer, the degree of polymerization (DP), intramolecular hydrogen bond formation, and homoconjugation.

EXPERIMENTAL

p-Aminobenzoic acid—formaldehyde—p-hydroxybenzoic acid random Copolymer I was prepared by refluxing the components in the
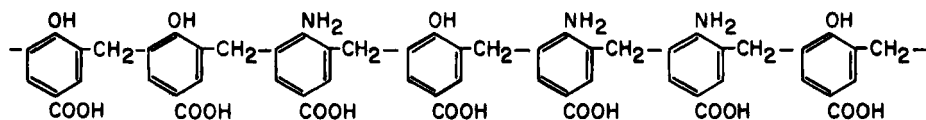
I

molar proportions given in Table 1 in the presence of 2 cc of 10 $\underline{N}$ HCl as catalyst for $2\frac{1}{2}$ hr at 120°C.

The reaction mixture was poured in ice-cold water and washed several times with water to remove unreacted monomers. It was then filtered, dried, and powdered. The polymer yield was about 75%. The copolymer thus obtained was then fractionated by dissolving a known weight of the copolymer in methanol, and various fractions were separated by adding water as the nonsolvent. The quantity of each co-polymer taken and the amount of various fractions separated at each stage of precipitation are given in Table 2.

A Leeds and Northrup 4959 Electrolytic Conductance Bridge was

TABLE 1

Copolymer	AB ($\underline{M}$)	HB ($\underline{M}$)	HCHO ($\underline{M}$)
I	0.1	0.9	1.0
II	0.9	0.1	1.0

TABLE 2

| Copolymer (g) | Fractions (g) | | | | |
	1	2	3	4	5
I 7.0	3.09	1.30	0.86	1.3	0.45
II 3.0	0.33	0.25	1.01	0.63	0.74

used for conductometric titrations. The titration vessel was stirred with a magnetic stirrer which was switched off during each measurement. The titrations were performed at room temperature, and 2 to 3 min was used after each addition of titrant to obtain equilibrium readings. Approximately 0.05 g of the copolymer was taken. Pyridine was used as a medium for the titration and sodium methoxide as the titrant base. The above solvent and titrant have been found to be most suitable for the resolution of the polybasic acids. The reproducibility of each titration curve has been checked and found to be within ±2 to 3%.

RESULTS AND DISCUSSIONS

Figures 1 and 2 present the conductometric titration curves of the various fractions separated from Copolymers I and II in pyridine with sodium methoxide as the titrant base. Several sharp and distinct breaks have been observed in each of the titration curves. The titration curves also indicated steep rises and falls in conductance during the various stages of neutralization of the copolymer. The "smallest interval" between any two consecutive breaks in the titration curves is found to be different for the various fractions separated from a copolymer. For a given fraction, the remaining breaks occur in simple multiples of its "smallest interval." Since each repeating unit
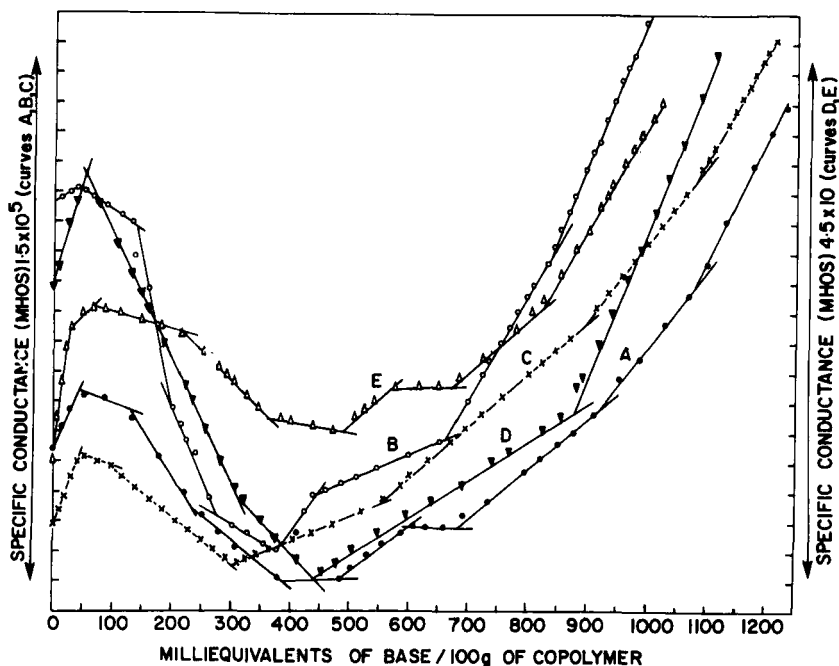
FIG. 1. Conductometric titration curves of fractions separated
from copolymer I in pyridine with sodium methoxide: Fraction 1
(Curve A), Fraction 2 (Curve B), Fraction 3 (Curve C), Fraction 4
(Curve D), and Fraction 5 (Curve E).

of the copolymers contains a COOH group, the total quantity of COOH
groups in 100 g of the copolymer can be calculated, which in this
particular case was found to be about 666 meq/100 g of copolymer.
The final break in each of the conductometric titration curves is found
to be quite sharp and indicates the neutralization of total quantity of
COOH and OH groups per 100 g of the copolymer. Therefore, by
substracting the calculated amount of COOH groups per 100 g of co-
polymer from this total quantity, the amount of OH can be obtained and,
consequently, the amount of NH_2 groups in the same quantity of the
copolymer. The distinct stepwise neutralization of the polymeric
compounds may be interpreted in terms of ion association. In a medium
of low dielectric constant, such as pyridine, various types of acid-
anion complexes may be formed, and perhaps the degree of dissociation
of such complexes may be different. Kolthoff and co-workers [2-4]
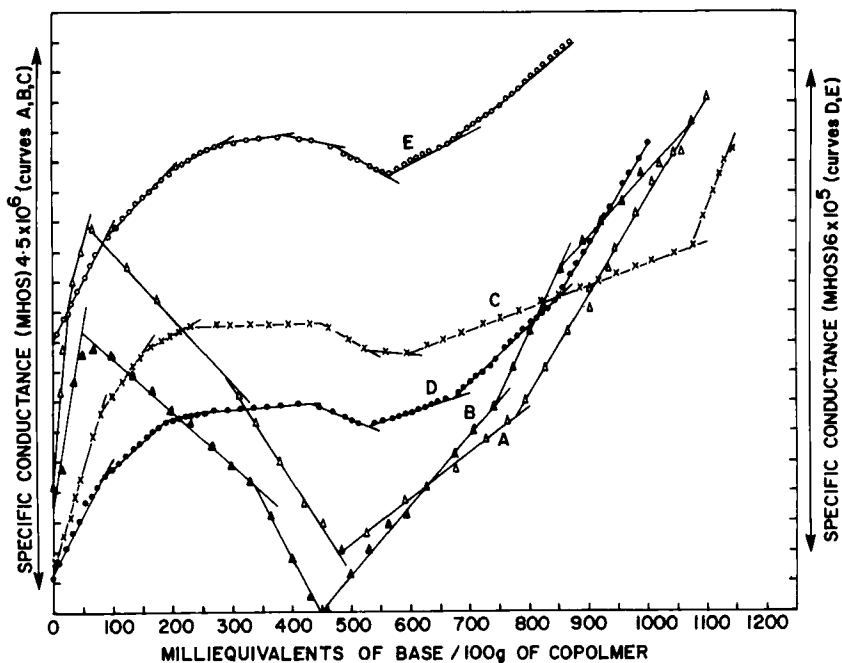have explained the peculiar nature of the titration curves of weak acids

FIG. 2. Conductometric titration curves of fractions separated from copolymer II in pyridine with sodium methoxide: Fraction 1 (Curve A), Fraction 2 (Curve B), Fraction 3 (Curve C), Fraction 4 (Curve D), and Fraction 5 (Curve E).

in terms of such homoconjugation. Apart from this, the fact that some of the COOH and OH groups are neutralized earlier than others in the same molecule indicates that they have a hyperacid character. Sprengling [5] explained such hyperacidity in the case of some o,o'-dihydroxy diphenyl methane type of compounds in terms of intra-molecular hydrogen bond formation between neighboring OH groups. The presence of intramolecular hydrogen bonding in such compounds has also been shown from conformational [6] and IR studies [7]. The IR spectra of almost all the copolymers studied indicated absorptions between the ranges 3450 to 3600 cm^{-1} and 3070 to 3350 cm^{-1}, showing the probable presence of O—H . . . O and N—H . . . N intramolecular hydrogen bonding.

Table 3 gives the total quantity of acidic groups (COOH and OH), number of OH groups, smallest interval, and mole fraction of p(OH) benzoic acid in each of the fractions separated from the two copolymers.

TABLE 3. Observed Amounts of Acidic Groups in p-Aminobenzoic Acid–Formaldehyde–p-Hydroxy-benzoic Acid Copolymer

Copolymer	Fraction	Total number of acidic groups (COOH + OH)	Number of[a] OH groups	Smallest interval	Av DP	Mole fraction of p(OH) benzoic acid
I	1	1080	(1080 - 666) = 314	40	16.6	0.29
	2	840	(840 - 666) = 174	45	14.8	0.20
	3	1090	(1090 - 666) = 324	50	13.3	0.29
	4	875	(875 - 666) = 209	55	12.1	0.24
	5	825	(825 - 666) = 159	75	8.8	0.19
II	1	850	(850 - 666) = 184	50	13.3	0.21
	2	775	(775 - 666) = 109	60	11.0	0.14
	3	1075	(1075 - 666) = 409	75	8.8	0.38
	4	900	(900 - 666) = 234	85	7.8	0.26
	5	690	(690 - 666) = 24	95	7.0	0.03

[a]Total number of observed acidic groups - calculated number of COOH groups.

In general, the mole fraction of p(OH) benzoic acid is found to be different for the various fractions, and in some fractions its mole fraction is negligibly small. This is to be expected, since the reactivity of the monomeric units are different. If it can be assumed that each chain contributes one COOH group during the smallest interval, then the degree of polymerization of the various fractions separated from the copolymer can be calculated as follows. Since each repeating unit of the copolymer contains a COOH group, and if we divide the calculated amount of base required to neutralize all the COOH groups in 100 g of copolymer by the amount required to neutralize one COOH group (smallest interval), the degree of polymerization of the copolymers can be calculated. The number-average DP calculated for the various fractions separated from the copolymers are indicated in Table 3. This method obviously suffers from a limitation if some of the chains do not contribute any COOH group and if some of the chains contribute more than one COOH group. However, some justification of calculating the number-average DP has been obtained from the study of titration curves of some o,o'-dihydroxy diphenyl methane type of compounds of known molecular weight and structure [8, 9].

It can thus be concluded that the average DP and the variation in compositions of the different fractions separated from a copolymer can be shown quite conveniently from their nonaqueous titration curves.

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