

The potentiometric behaviour of copolymers of methacrylic acid in water-ethanol solutions

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Summary

The synthesis is reported of copolymers of styrene with methacrylic acid and of methyl methacrylate with methacrylic acid by radical copolymerization, of copolymers of methyl methacrylate with methacrylic acid by partial alkaline hydrolysis of poly(methyl methacrylate), and of block copolymers of styrene with methacrylic acid. Modified titration curves of all these copolymers were recorded in water and water-ethanol solutions. In a solution containing 50 mass.% ethanol, only small differences could be observed between the potentiometric behaviour of the individual copolymers and polymethacrylic acid. Also, there were no essential differences in any of the solvents used between the potentiometric behaviour of block copolymers of styrene with methacrylic acid, on the one hand, and polymethacrylic acid, on the other. On the contrary, maxima and minima were always observed on the modified titration curves of statistical copolymers with a higher content of the hydrophobic comonomer in solutions with a high water content. Thus, using the modified titration curves, it is possible to decide whether a given copolymer is of the block or statistical type.

Introduction

In an earlier paper (1) we described the different potentiometric properties of statistical and block copolymers of 2-dimethylaminoethyl methacrylate (DMAEMA). The modified titration curves, i.e. the dependences of the apparent dissociation constant (pK_{app}) on the degree of neutralization (α) differed considerably: the modified titration curve of a copolymer prepared by partial quaternization of poly(2-dimethylaminoethyl methacrylate) pDMAEMA with methyl iodide in water-ethanol medium was very similar to that of the homopolymer of pDMAEMA and completely different from that of a copolymer prepared by the copolymerization of DMAEMA and methacryloyloxyethyltrimethylammonium methyl sulfate (MOETA⁺MS⁻). The NMR spectra of the copolymers also differed considerably (2). Hence, using the recorded modified titration curves, it was possible to decide whether the copolymer was a statistical or predominantly a block one.

We were interested to find out if the potentiometric properties differed also for statistical and block copolymers containing carboxylic groups, and if their different structures could also be discerned potentiometrically. We chose copolymers of methacrylic acid (MAA), the titration curves of which had been satisfactorily interpreted in the literature (3). The titration curves of copolymers of MAA with styrene (St) and methyl methacrylate (MMA) in water and in a water-dioxan solution are also known (4,5), in connection with the investigation of their conformational transitions. The titration curves of copolymers MMA-MAA, St-MAA and of polymethacrylic acid (pMAA) also differed from each other due to strong

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hydrophobic interactions. On the other hand, the potentiometric behaviour of statistical copolymers of 2-hydroxyethyl methacrylate (HEMA) with MAA (MAA content above 48 mol.%) in water-ethanol solution (16.5 mass % ethanol) differed only little from the behaviour of pMMA (6). Also, the titration curves of various copolymers of acrylamide with MAA do not differ too much from each other (7). Hence we know, that hydrophilic comonomers do not affect the potentiometric behaviour of copolymers of MAA as much as hydrophobic comonomers. Furthermore, analysis of the titration curves shows (8) that the neutralization of polymer acids is accompanied by the conformational transition compact-swollen random coil. The transition is the more pronounced, the more hydrophobic component (e.g., styrene structural units (5)) there is in the macromolecule, i.e., with increasing St content in the copolymer the negative Gibbs free energy of transition also increases. On the contrary, addition of the organic solvent (dioxan (5) or methanol (9)) to the titration mixture brings about a decrease in the negative Gibbs energy. A similar effect of an organic solvent has also been observed with other copolymers (10).

Experimental

Materials

Statistical copolymers St-MAA were prepared by radical copolymerization in ethanol with benzoyl peroxide at 60°C up to a conversion of about 7 mass %. The concentration of the monomers was 10 mass %, that of MAA in the mixture of monomers was 67 and 80 mass %. The resulting MAA content in the copolymers determined titrimetrically, was 60 and 76 mass %, respectively. The stock solution for titration in 50% ethanol was obtained by directly dissolving 1 g of the copolymer in 50 g of the water-ethanol mixture. Solutions in 20% ethanol were prepared by adequate dilution of the stock solution with water with intensive stirring. The solution of the copolymer in water was prepared by slow evaporation of the ethanolic stock solution to half its original volume, diluting with water to the original volume, and evaporating to half the volume once again.

Statistical copolymers MMA-MAA were prepared by radical copolymerization in hexane with benzoyl peroxide at 60°C up to a conversion of about 4 mass %. The MAA concentration in the mixture of monomers was 67 and 80 mass %, its content in the copolymers was 61 and 80 mass %. Stock solutions used in the titrations were obtained by dissolving 0.1 g of copolymer in 15 g ethanol and diluting with water to the desired ethanol content, 20 or 50 mass %. The aqueous solutions were prepared similarly to the statistical copolymer St-MAA.

Poly(methyl methacrylate) (pMMA) was obtained by the radical polymerization of the monomer with benzoyl peroxide in hexane, at 60°C for 8 h.

Poly(methacrylic acid)-block-poly(styrene)-block-poly(methacrylic acid) was synthesized in two stages. In the first stage a block BAB copolymer poly(methyl methacrylate)-block-poly(styrene)-block-poly(methyl methacrylate) was prepared by anionic copolymerization. The required amount of styrene was added dropwise into an intensively stirred solution of sodium dihydronaphthylide in tetrahydrofuran at room temperature during ten minutes. The mixture was cooled to 195 K, and after 15 min. MMA was added at once. After 45 min the reaction was terminated with methanol. All materials used were purified and dried by standard procedures, cf., e. g. (12). All operations were performed in dry argon. The resulting copolymer was precipitated into methanol and dried. The conversion varied about 95 %.

In the second stage, MMA units in this copolymer were transformed to MAA units by alkaline hydrolysis. To an intensively stirred hot 10 mass %

solution of the copolymer in dimethylsulfoxide (DMSO), a hot aqueous solution of KOH was added (volume ratio DMSO:H₂O = 8:1, molar ratio KOH:MAA = 5:1). The mixture was then heated to the boil (415 K). After several minutes the hydrolyzed product began to precipitate from solution; it was insoluble in DMSO, and eventually formed an independent phase - the gel. The hydrolysis proceeded with boiling and stirring for 1 h. On completion of the reaction, the mixture was cooled, DMSO was removed and replaced by water in which the copolymer dissolved. From this solution the copolymer was precipitated by dropwise addition of conc. HCl in excess. The precipitate was washed on a glass filter with c. 20% HCl, which helped to remove KCl. After that, it was washed several times with boiling water in which the copolymer in its acid form does not dissolve, in order to remove most of HCl and the remaining KCl. The mixture was then dried in vacuo. The last operation was a 24 hour extraction with hot chloroform, by which the homopolymer of styrene and the copolymer with a low MAA content were removed from the block copolymer. According to the IR spectra of neutralized samples and to potentiometric titrations, the degree of hydrolysis varied about 0.95. The stock solution of the copolymer with 63 mass % MAA in water was obtained by dissolving 1 g of the copolymer in 60 g of a tetrahydrofuran-water mixture (4:1 by vol.), after which 30 g water was added with intensive stirring, and tetrahydrofuran was evaporated. The other stock solutions for titration were obtained by diluting this solution with ethanol.

Measurement

The methods of potentiometric measurements have been described earlier (11). The concentration of methacrylic acid structural units was about 0.007 mol dm⁻³. The rate of titration (in the range 8.3x10⁻³ to 5.2x10⁻⁴ cm³ s⁻¹) did not affect the shape of the titration curves.

Results and Discussion

According to the copolymerization parameters (13) the copolymers St-MAA and MMA-MAA prepared by copolymerization to low conversion are statistical. This is also indicated by the similar MAA content in the mixture of monomers and in the copolymer (cf. Experimental).

Fig. 1 shows the modified titration curves of two statistical copolymers, St-MAA and pMAA, in two water-ethanol solutions and in pure water. In 50% aqueous ethanol the potentiometric properties of copolymers St-MAA and pMAA do not differ too much, while in other media maxima appear in the modified titration curves at the degrees of neutralization in the range $\alpha = 0.2-0.5$. These maxima are more pronounced with copolymers having a higher content of the hydrophobic St. Similar titration curves have been recorded with copolymers MMA-MAA (Fig. 2), with the only difference that pronounced maxima in the pK_{app} vs. α curve appeared only in the aqueous medium. The difference between the statistical copolymers St-MAA and MMA-MAA is attributed to the higher polarity ("hydrophilicity") of MMA compared with St; its conformational transition is therefore not so sharp as in the case of the more hydrophobic copolymer St-MAA. This is also corroborated by the fact that the St-MAA copolymers (with the exception of 50% aqueous ethanol) showed milky turbidity at the beginning of the titration; the turbidity disappeared in those regions of α , which correspond to a maximum on the modified titration curves. On the contrary, solutions of the copolymers MMA-MAA remained clear in all the cases investigated in this study, which indicates their higher hydrophilicity compared with the copolymers St-MAA.

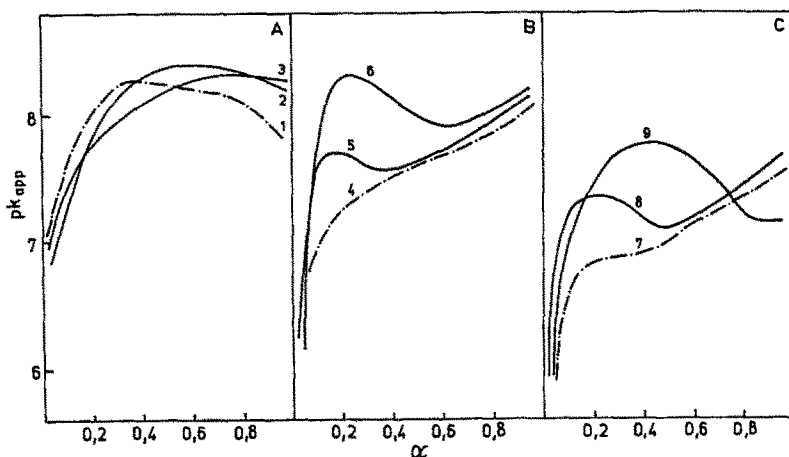


Fig. 1. Modified titration curves of statistical copolymers St-MAA and pMAA (curves 1,4,7) in mixtures water-ethanol (A-50%, B-20% of ethanol) and water (C), MAA content in the copolymers was 76% (2,5,8) and 60% (3,6,9). All per cent values are mass per cent.

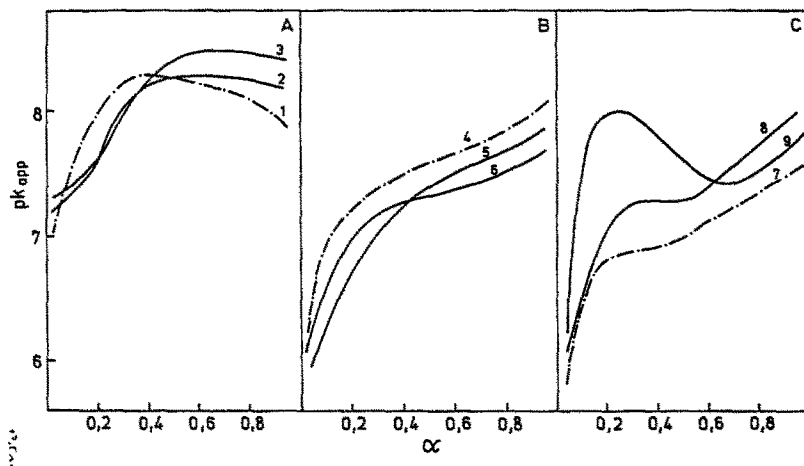


Fig. 2. Modified titration curves of statistical copolymers MMA-MAA and pMAA (1,4,7) in water-ethanol mixtures (same as in Fig.1). MAA content in the copolymers was 80% (2,5,8) and 61% (3,6,9).

Another series of MMA-MAA copolymers was obtained by partial hydrolysis of pMMA. The modified titration curves of these copolymers can be seen in Fig. 3. The titration curves of these copolymers in a solution with 50% ethanol also have a similar character, while in a solution with 20% ethanol some differences were perceived with copolymers containing 57 and 46 mass % MAA. Since the copolymers MMA-MAA prepared by partial hydrolysis of pMMA approach statistical MMA-MAA copolymers obtained by copolymerization in their potentiometric behaviour, it may be inferred that their structure is also statistical, i.e. that the hydrolysis of pMMA (under conditions

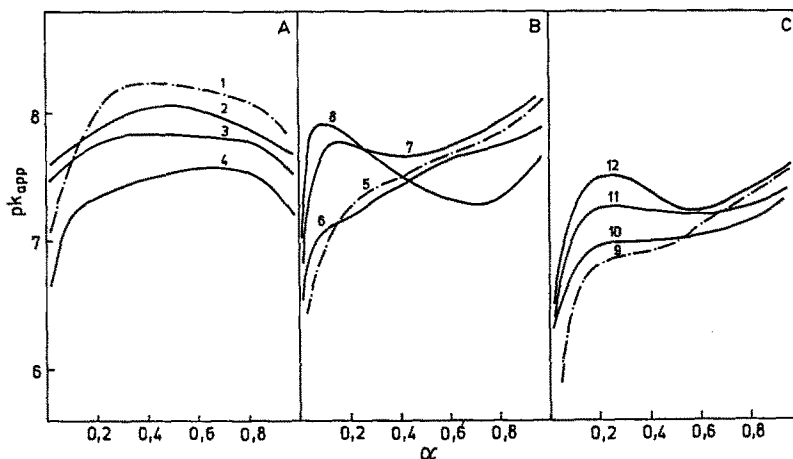


Fig. 3. Modified titration curves of pMAA (1,5,9) and of copolymers MMA-MAA obtained by partial hydrolysis of pMMA in water-ethanol mixtures (as in Fig.1). MAA content in the copolymers was 79% (2,6,10), 57% (3,7,11) and 46% (4,8,12).

outlined in the Experimental Part) proceeds at random. This random nature of the hydrolysis of pMMA has also been proved for other solvents by using kinetic methods (14).

Fig. 4 shows the modified titration curves of the block copolymer St-MAA of the type BAB and pMAA. In all the solvents used there is no difference between the characters of the curves. Consequently, the potentiometric behaviour of the MAA copolymers is sensitive - similarly to copolymers of 2-dimethylaminoethyl methacrylate (1) - to the distribution of

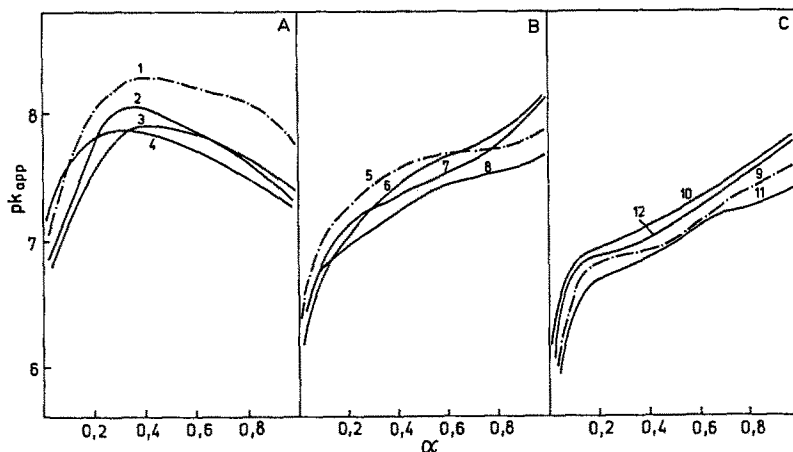


Fig. 4. Modified titration curves of block copolymers St-MAA and pMAA (1,5,9) in water-ethanol mixtures (as in Fig.1). MAA content in the copolymers was 80% (2,6,10), 74.5% (3,7,11) and 63% (4,8,12).

structural units containing a titratable functional group. In the case of block copolymers the potentiometric properties approach those of homopolymers, differing greatly from the properties of statistical copolymers. These differences (and particularly the occurrence of maxima and minima on the pK_{app} vs α curves) are the more pronounced, the higher the content of the hydrophobic comonomer in the copolymer and the more water there is in the mixed water-ethanol solvent. Maxima and minima appear in the modified titration curves of the St-MAA copolymers in water in those cases where there are about ten methacrylic acid units or less per styrene unit (5). With the copolymers MMA-MAA the corresponding ratio is about 1:4.6, and with the copolymer (6) HEMA-MAA it is 1:0.33 (here, of course, a water ethanol solution was used with 16.5 mass % ethanol).

Thus, by using the potentiometric titration described in this study, it is possible to decide whether the copolymers MMA-MAA, St-MAA and DMAEMA-MOETA⁺MS⁻ (cf. (1)) have a statistical or block structure.

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