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Colloid Titration Behavior of the Maleic Acid–Methyl Vinyl Ether Copolymer

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Synopsis. The colloid titration of the maleic acid–methyl vinyl ether (MA–MVE) copolymer with trimethylammonium glycol chitosan iodide (MGCH) was carried out at various pH values. The mechanism of the formation of the polyion complex between the MA–MVE copolymer and the MGCH ions was discussed.

The colloid titration, which was originated by Terayama,[1] is based on the stoichiometric complex formation between polyacidic and polybasic titrants. Strong polyelectrolytes, such as potassium poly(vinyl alcohol) sulfate (PVSK),[1] trimethylammonium glycol chitosan iodide (MGCH),[1] and poly(diallyldimethylammonium chloride),[2] are frequently used as standard titrants.

In previous studies,[3,4] the effects of the pH on the dissociation of the above-mentioned three polyelectrolytes were investigated by using colloid titration and electrophoresis. From the results obtained, the mechanism of the formation of the polyion complex between polyacidic and polybasic titrants was discussed.

In the present study, the colloid titration with MGCH was carried out for the maleic acid–methyl vinyl ether (MA–MVE) copolymer, which is a representative polydibasic acid. The colloid titration curves were compared with the results of electrophoresis and potentiometric titration reported previously,[5] and the mechanism of the formation of the polyion complex between the MA–MVE copolymer and the MGCH ions was discussed.

Experimental

Materials. The MA–MVE copolymer and the sodium salt of the copolymer (NaMA–MVE copolymer) used were prepared in the manner described in previous paper.[5] The MA–MVE copolymer was prepared by the hydrolysis of the maleic anhydride–MVE copolymer manufactured by the General Aniline & Film Co. On the other hand, the NaMA–MVE copolymer was prepared by the neutralization of the MA–MVE copolymer with sodium hydroxide. The molecular weight of the repeating unit for the MA–MVE copolymer, as estimated by elemental analysis and by potentiometric titration, was 176. This value agrees with that calculated on the assumption that this copolymer is an alternating copolymer. The intrinsic viscosity of the NaMA–MVE copolymer was 1.57 dl/g, as established by viscometric measurement in a 1M NaCl solution at 25 °C. The PVSK and MGCH were obtained from Wako Pure Chemical Industries, Ltd. These properties were characterized in previous papers.[3,4]

Colloid Titration. The sample solution (0.005 N) was titrated indirectly with MGCH (0.005 N) by the method of Terayama.[1] An excess of MGCH was added to the sample solution to precipitate a polyion complex, and then the excess of MGCH was back-titrated with PVSK (0.0025 N). A blank titration was also carried out. The titrant volume was determined by means of the difference in these titration results. The end point was indicated by the metachromatic color change of toluidine blue[1] and the turbidity measurements. The pH of the titration system was adjusted with 0.1—1M HCl, NaOH, $Ba(OH)_2$, and tetrabutylammonium hydroxide (TBAH).

Results and Discussion

The colloid titration curve was obtained by plotting the reciprocal of the equivalent weight (E_w) of the sample copolymer against the pH. A titration curve of the NaMA–MVE copolymer is shown in Fig. 1. In contrast to the results for poly(sodium acrylate) (NaPAA) and carboxymethylcellulose (CMC),[2] the titration curve shows an inflection point at about pH 6.5. From this result, it can be estimated that one of the two carboxylic groups in a monomer residue of the copolymer dissociates at first in the pH region below the inflection point, while the other dissociates in the pH region above the inflection point. This agrees with the result of the potentiometric titration.[5] The values of E_w (219) and pH (*ca.* 6.5) at the inflection point are equal to the molecular weight of the repeating unit for the NaMA–MVE copolymer and to the pH value at a half-neutralization point of the potentiometric titration curve, respectively. Therefore, this inflection point can be considered to be the half-neutralization point.

On the other hand, it is observed from the colloid titration curve that E_w^{-1} reaches a constant value above pH 9. This suggests that the two carboxylic groups in a monomer residue are completely dissociated in this pH region. However, the value of E_w (145) is not equal to one-half of the molecular weight of the repeating unit for the NaMA–MVE copolymer. The electrophoretic studies of polycarboxylic acids in previous papers[5,6] showed that the binding effect of the counterion on the MA–MVE copolymer ion is larger than that of the counterion on the NaPAA and CMC ions in the pH region from 7 to 10. The disagreement mentioned above can be explained on the basis of the assumption that the complex formation of the MA–MVE copolymer with MGCH is not stoichiometric

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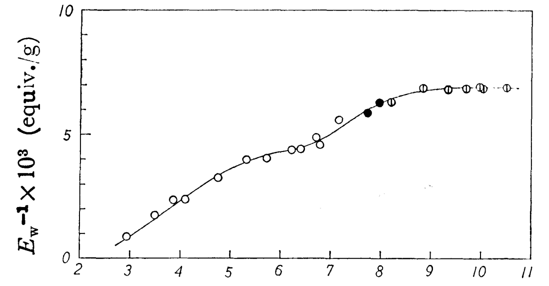

Fig. 1. Colloid titration curve of NaMA-MVE copolymer with MGCH.
pH-adjuster: ○, HCl; ⦶, NaOH; ●, non.

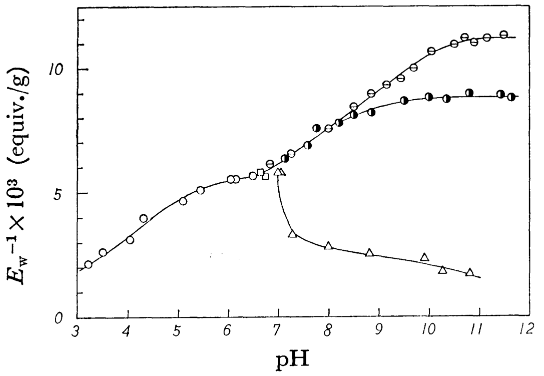

Fig. 2. Effects of pH-adjusters on the colloid titration curve of MA-MVE copolymer with MGCH.
pH-adjuster: ○, HCl; ⊖, TBAH; ◑, NaOH; △, $Ba(OH)_2$; □, non.

because of the inhibitory effect of the counterion.

In order to confirm this assumption, a colloid titration with MGCH was carried out for the MA–MVE copolymer, using NaOH, $Ba(OH)_2$, and TBAH as pH-adjusters. The results are shown in Fig. 2. When the sample solution was titrated in the absence of any pH-adjuster, the pH of the titration system at the end point was about 6.5. Hence, the titration was carried out with adjustment of the pH with HCl in the pH region below 7 and with the bases in the pH region above 7. It is generally believed that the binding effect of a counterion on a polyacidic ion does not need to be considered if the counterion is a tetraalkylammonium ion.[7] In the case of a bivalent metal ion such as the Ba^{2+} ion, however, this effect on a polydibasic acid seems to be important, since a stable ring structure will be formed between the metal cation and the two carboxylate ions in a monomer residue. In Fig. 2, from the titration curve for which the pH was adjusted with NaOH, it is observed that E_w^{-1} is independent of the pH in the pH region above 9. The value of E_w (115) in this pH region is not equal to one-half of the molecular weight of the repeating unit for the MA–MVE copolymer. In contrast to this result, in the case of the titration curve for which the pH was adjusted with TBAH, E_w^{-1} increases in the pH region from 7 to 10, and reaches a constant value above pH 10.5. In the pH region above 10.5, the value of E_w (89) is comparable with one-half of the molecular weight of the repeating unit for the MA–MVE copolymer. On the other hand, when the pH was adjusted with $Ba(OH)_2$, E_w^{-1} rapidly decreased with the increase in the pH, since Ba^{2+} ions are bound to the MA–MVE copolymer ion. From these facts, it may be concluded that the binding effect of the counterion on the MA–MVE copolymer ion plays an important role in the complex formation of this copolymer with MGCH.

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