A Nonaqueous Potentiometric Titration Study of the Dissociation of *t*-Butyl Methacrylate-Methacrylic Acid Copolymers

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The dissociation of *t*-butyl methacrylate-methacrylic acid copolymers in dimethyl sulfoxide was analyzed by a nonaqueous potentiometric titration technique. The negative logarithm of the dissociation constant of the monomer unit of a methacrylic acid (MAA) monotonously increased with the increasing degree of dissociation corresponding to the titrant/MAA amount ratio, and was highly influenced by the copolymerization ratio. The results are discussed in terms of the suppression of the dissociation of MAA by a neighboring charged methacrylate anion unit.

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Introduction

Studying the dissociation of a polymer is significant for understanding the dissolution behavior of resist materials, proteins, membranes, synthetic colloids, and so forth. The dissociation behavior of various water-soluble polymers has been both experimentally and theoretically reported.¹⁻⁸ For a resist resolution in photolithography, acid dissociation of the resist polymers is one of the important factors. Although potentiometric titration is useful as a quantitative analysis of acid dissociation, direct measurements of the acidity of resist polymers cannot be performed by aqueous potentiometric titration since the polymers do not dissolve in water. If nonaqueous potentiometric titration can be applied to resist polymers, the relationship between the dissolution in a developing alkaline solution and the acidity of the polymers can be analyzed in detail. Nonetheless, nonaqueous potentiometric titration has rarely been applied to resist polymers so far, except for a few preliminary reports.^{9,10} In this study, nonaqueous potentiometric titration was demonstrated for *t*-butyl methacrylate-methacrylic acid copolymers (Poly-(BuMA_{1-x}MAA_x), *x*; copolymerization ratio), which are typical polymers and are also used as a model of resist polymers. The copolymerization ratio dependence of the acid dissociation of Poly(BuMA_{1-x}MAA_x) is discussed in detail.

Experimental

As a sample solution, dimethyl sulfoxide (DMSO) containing Poly(BuMA_{1-x}MAA_x) (*x* = 0.33, 0.40, 0.46, 0.60, and 0.80) with a molecular weight of 5000 – 6000 was used. A methanol solution of tetrabutylammonium hydroxide (Wako Pure

Chemical Industries, for non-aqueous titration) (0.2 M, 1 M = 1 mol/dm³) was injected into a stirred sample solution (10 cm³) using a syringe pump (kdScientific, Model 100) at a flow rate of 2 cm³/h; the potential difference between a glass electrode (Horiba, 1076A-10C) and an Ag/Ag⁺ electrode (BAS, RE-5) was measured by an electrometer (Keithley, 6517 Electrometer) with time. Prior to the titration of Poly(BuMA_{1-x}MAA_x), salicylic acid (12.5 mM) in DMSO was titrated with a tetrabutylammonium hydroxide solution using this experimental setup. The pH value calculated from the potential difference was calibrated using a dissociation constant of salicylic acid in DMSO (*K*_a, 10^{-6.7}).¹¹ All measurements were performed at room temperature (293 – 295 K).

Results and Discussion

As an organic solvent of nonaqueous potentiometric titration, methyl isobutyl ketone, DMSO, acetonitrile, and so forth are frequently used. However, the solubility of Poly-(BuMA_{1-x}MAA_x) for methyl isobutyl ketone or acetonitrile was very low. For an *x* range of 0.33 – 0.80, Poly(BuMA_{1-x}MAA_x) was only dissolved in DMSO; therefore, the solvent was used in the present study. Potentiometric titration curves at a concentration of 12.5 mM, as the total concentration of the monomer unit (*C*_M) of methacrylic acid (MAA) and *t*-butyl methacrylate (BuMA), are shown in Fig. 1. The equivalent values for *x* = 0.46 and 0.80 are estimated to be 0.27 and 0.47 cm³ as the titrant volumes, respectively. Indeed, the pH was jumped close to the titrant volumes (Fig. 1). For a polyacid with a high molecular weight, the time required to form a stable conformation has been reported to be long.¹² In the present polymers, however, the time to a stable conformation is expected to be short due to the relatively small polymers (molecular weight; 5000 – 6000). Actually, the titration curves at a titrant injection rate of 2 cm³/h were in good agreement with those of 0.8 cm³/h. The pH was saturated at 16 – 17 due to autoprotolysis in the DMSO/methanol system although the autoprotolysis constant of DMSO has been reported to be

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Fig. 1 Potentiometric titration curves of Poly(BuMA_{1-x}MAA_x) in DMSO at $C_M = 12.5$ mM for $x = 0.46$ (a) and 0.80 (b).

10^{-30} .¹¹ When an isopropanol solution of tetrabutylammonium hydroxide was used, the pH was saturated around 22.¹¹ Because the titration curve for an isopropanol solution of tetrabutylammonium hydroxide was in good agreement with that for the methanol solution at pH values smaller than 16, a methanol solution of tetrabutylammonium hydroxide was used in the present study. If potentiometric titration is performed for weaker polyacids, isopropanol or DMSO as a titrant solvent should be used instead of methanol. The detection limit for the potentiometric titration was ~ 5 mM as the acid concentration, namely, a C_M of ~ 6 mM for $x = 0.8$.

The potentiometric titration curves for weak polyacids have usually been analyzed by using $pK_a = pH - \log(\alpha/(1 - \alpha))$, where pK_a and α are the negative logarithm of the dissociation constant and the degree of dissociation corresponding to the ratio of tetrabutylammonium hydroxide to MAA before titration, respectively. The pK_a value for a small compound is constant, independent of α , while that for a polyacid depends on α .^{1,2} Figure 2 shows pK_a versus α plots for various x and C_M values. The pK_a value of Poly(BuMA_{1-x}MAA_x) increased with increasing α . The acid dissociation can be suppressed by strong electrostatic repulsions of the charged methacrylate anion unit (MA⁻), as reported concerning aqueous polyacid solution systems.⁴⁻⁶ On the other hand, pK_a increased with increasing x for the same α (Fig. 2a). These results indicate that the distance between MAA and MA⁻ is significant for acid dissociation. In resist polymers, carboxyl and hydroxyl groups are typical alkaline-soluble groups. When the pK_a at $\alpha = 0.5$ is defined as $pK_{a,1/2}$, this value for Poly(BuMA_{1-x}MAA_x) is similar to that for resist polymers possessing a hydroxylhexafluoroisopropyl or carboxylfluoromethylidene group as a monomer unit ($pK_{a,1/2} = 10 - 13$ in DMSO).⁹ The $pK_{a,1/2}$ value for Poly(BuMA_{1-x}MAA_x) is much greater than that of resist polymers having a 1-carboxyl-1,2,2,2-tetrafluoroethyl group as a monomer unit ($pK_{a,1/2} = 5 - 6$ in DMSO).⁹

At the same C_M , the total MAA and MA⁻ concentration (C_{MAA}) for $x = 0.8$ is 2-times that for $x = 0.4$. The $pK_{a,1/2}$ difference between $x = 0.8$ ($C_{MAA} = 10$ mM) and $x = 0.4$ ($C_{MAA} = 5$ mM) was 1.5 at $C_M = 12.5$ mM (Fig. 2a). On the other hand,

Fig. 2 pK_a values of Poly(BuMA_{1-x}MAA_x) as a function of α at $C_M = 12.5$ mM for $x = 0.33 - 0.80$ (a) and at $C_M = 6.3 - 25.0$ mM for $x = 0.8$ (b).

the $pK_{a,1/2}$ values at $C_M = 12.5$ mM ($C_{MAA} = 10$ mM) and 6.3 mM ($C_{MAA} = 5$ mM) for $x = 0.8$ were almost the same within the experimental error (Fig. 2b). Therefore, the polymer-polymer interaction is negligibly small at α values lower than ~ 0.5 , and the polymer will be dissolved as a compact conformation in DMSO. However, the pK_a versus α curve for $x = 0.8$ slightly increased with increasing C_M at α values greater than ~ 0.5 (Fig. 2b). Although the methacrylate polymers are expected to be hydrophobic, Poly(BuMA_{0.2}MAA_{0.8}) at higher α values possesses a high charge density in the single-polymer chains. The polymer chain is then expanded so that the polymer-polymer interaction will be slightly induced at a C_M value greater than 10^{-2} M. To discuss the neighboring effect of charged MA⁻, pK_a versus αx was plotted, as shown in Fig. 3; αx corresponds to the ratio of the MA⁻ concentration to C_M in the single-polymer chains. The pK_a versus αx plots fall almost on the same curve, indicating that the pK_a - αx curves are directly related by the amount of MA⁻ in the same polymer chain, independent of x . It is concluded that the suppression of MAA dissociation is governed by the neighboring charged MA⁻ in the individual polymer chains as the main component in the C_M range of $10^{-3} - 10^{-2}$ M.

The solubility of a polymer in an aqueous tetramethylammonium hydroxide solution (developer) is one of the important properties of resist materials in determining the resolution and sensitivity. It has been reported that although Poly(BuMA_{1-x}MAA_x) with a higher x is easily dissolved in the developer, a complicated swelling behavior is observed during the developing processes.⁹ As discussed above, the pK_a of the polymer will increase with the developing time. Furthermore, highly concentrated tetramethylammonium hydroxide is added to the polymer film surface so that α in the surface layer of the film alone will increase in the initial stage of the developing processes. Thus, the dissolution of the polymer will compete with the swelling of the polymer film.

Fig. 3 αx dependence of pK_a of Poly(BuMA_{1-x}MAA_x) at $C_M = 12.5$ mM for $x = 0.33, 0.60$ and 0.80 .

Conclusion

The pK_a values of Poly(BuMA_{1-x}MAA_x) were measured in DMSO by nonaqueous potentiometric titration. The copolymerization ratio dependence of the pK_a versus α curve of Poly(BuMA_{1-x}MAA_x) was successfully distinguishable by this technique so that the curves could be discussed in terms of a suppression of the dissociation of MAA by the neighboring MA⁻ effect in the single-polymer chains. We consider that

nonaqueous potentiometric titration is sufficient to analyze the dissociation and dissolution mechanisms of polyelectrolytes in organic solvents. In particular, valuable information regarding resist polymers can be obtained by the present technique.

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