Preparation of Nano- and Microparticles through Self-Assembly of Azobenzene-Pendent Ionomers

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ABSTRACT: The particle formation of azobenzene-containing ionomers, through self-assembly, in aqueous media (THF/H_2O solvent) was studied. The ionomers were synthesized by copolymerization between azobenzene-pendent methacrylate and methacrylic acid. It was revealed by UV–vis spectra and light scattering measurements that the extent of H-aggregation of the azobenzene units first decreased, and then increased with increasing volume fraction of H_2O of the solvent. The H_2O fraction at which the extent of H-aggregation began to increase became lower, when the copolymers contained more azobenzene units. Colloidal particles were prepared by slow addition of various concentrations of aqueous NaOH to the copolymer THF solutions. The hydrodynamic diameters of the particles obtained by the procedures were several hundreds of nanometer. When the azobenzene unit content in the copolymer was smaller, the diameters of the particles became smaller. When the colloidal particles dispersions were cast on a carbon sheet and dried, the particles aggregated and formed larger spherical particles, with diameters of several micrometers. The size of the particles obtained by the drying process became smaller, when higher concentrations of aqueous NaOH solutions were used. Therefore, the particle sizes were controlled by the azobenzene units content in the copolymers and the concentration of aqueous NaOH solutions. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3913–3918, 2006

**Key words:** azo polymer; colloids; micelles; NLO; self-assembly

INTRODUCTION

Recently, it has received a great deal of attention that amphiphilic copolymers, such as block[1–3] and graft[4–8] copolymers and ionomers,[9–11] form particles in the size range from nanometer to micrometer, in polar media. The obtained particles are composed of a core of hydrophobic monomeric units and a shell of hydrophilic ones, and their dispersions are stable. The particle size can be controlled easily by changing the preparation conditions, such as solvents, polymer concentrations, and temperatures.[1]

Generally, the size distributions of the particles formed from the ionomers are not as narrow as those of the block copolymer particles. However, the syntheses of the ionomers are simple, compared with block and graft copolymers. So far, the particle preparation from some kinds of ionomers has been reported. For example, randomly carboxylated polystyrene[9] and lightly sulfonated poly(phyenylene oxide)[10] formed the colloidal particles, with diameters from 10–100 nm, when solvents are exchanged with selective solvents. On the other hand, thermosensitive ionomers reversibly formed particles in responding to the temperature stimuli.[12–14]

Azobenzene derivatives have two important properties, i.e., a nonlinear optical property and photoresponsive isomerization.[15–17] Many research groups have studied the thin film preparation from azobenzene-containing polymers and their application to the optical devices.[18–20] However, to our knowledge, only Wang's group reported the preliminary particle preparation from azobenzene-containing ionomers.[21,22] Recently, the optical devices using dielectric microparticles, i.e., microresonator, microswitching devices, and so on, have been the subject of intense study, because their volume is expected to become much smaller than that for the conventional optical devices.[23–25] These functions of the particles can be controlled by their dielectric properties, sizes, and morphologies.[26,27] Thus, the particle preparation from azobenzene-containing ionomers will be interesting, because of their relatively large third-order nonlinear optical constants.
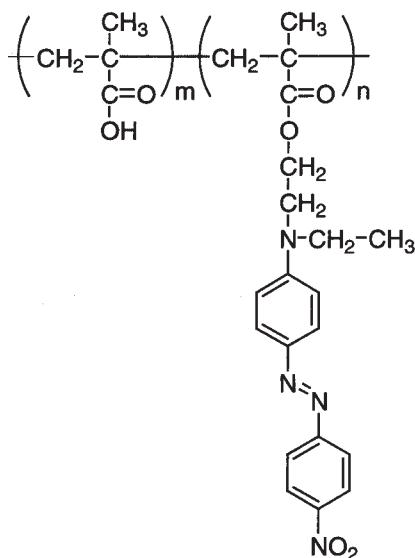
Scheme 1 Chemical structure of copolymer.

In this report, we studied the particle preparation from azobenzene-containing ionomers in aqueous media, and revealed the effect of the preparation conditions, such as kinds of solvents, azobenzene contents in the ionomers, and the evaporation of the solvents on the particle sizes. The chemical structure of the ionomer used in this study is shown in Scheme 1.

EXPERIMENTAL

Materials

4′-[(2-Methacryloyloxy)ethyl]ethylamino]-4-nitroazobenzene (MR2) was synthesized according to the literature.[28] Methacrylic acid (MA) (Kanto Kgaku) was purified by distillation. 2,2′-Azobisisobutyronitrile (AIBN) (Kanto Kgaku) was recrystallized from methanol. Other reagents were used as received.

Syntheses of copolymers

The two monomers were copolymerized at 60°C in a thermostatic bath, using AIBN as a free radical initiator, as follows. The DMF solution containing both the monomers (total monomers concentration = 1.0M; feed ratio of MR2 = 25, and 50 mol %) and the initiator (10 mM) was placed in a round bottom flask. The solution was bubbled with N_2 for 1 h and then sealed. The polymerization was conducted for 24 h at 60°C. The obtained copolymer was precipitated into an excess amount of petroleum ether. The precipitate was filtrated and washed with petroleum ether and chloroform, and dried at reduced pressure at 70°C. The MR2 contents of the copolymers were determined by ^{1}H NMR to be 15 and 37 mol %. Hereafter, these copolymers were called M-15 and -37, respectively.

The yields of the copolymers were 41 (M-15) and 64% (M-36), respectively.

Particle preparation and scanning electron microscopy observation

The NaOH solution and THF, used for the particle preparation, were filtrated (Millipore, 0.45 μm). The copolymers were dissolved in THF (concentration: 1.0, 5.0, and 10 g/L). To the solution, NaOH solution (0, 1, 5, and 10 mM) was added dropwise, with vigorous stirring, until the solution became turbid. A few drops of the particle dispersion were cast onto a carbon sheet and dried *in vacuo*. The scanning electron microscopy (SEM) observation was performed on a Hitachi S-4700 electron microscope, operated at 15 kV.

Measurements

^{1}H NMR spectra were recorded on a JEOL-GX400 spectrometer at 70°C, using d_6-DMSO as a solvent. Dynamic light scattering (DLS) measurements of the colloidal particles were conducted with an Otsuka electronics DLS-7000HL, at a detection angle of 90° at 25°C, according to the previous paper.[14] The light source was He-Ne laser (633 nm). UV–vis spectra measurements of the copolymer dispersions were recorded with a Hitachi U-3210 spectrophotometer.

RESULTS AND DISCUSSION

UV–vis spectra of copolymer solutions

The extent of the aggregation of the copolymers, with varying the aqueous NaOH fractions of their solvents (THF/aqueous NaOH), was probed by the UV–vis spectral change, resulting from the MR2 units. THF is good solvent for MR2 units[29] and nonsolvent for MA units,[30] whereas aqueous NaOH is good one for MA[30] and nonsolvent for MR2. Figure 1 shows the results of M-37. λ_{max} (around 500 nm) resulting from π–π* transition first red-shifted and then blue-shifted, with increasing volume fractions of aqueous NaOH. The solvent composition dependences of λ_{max} and the maximum absorbance were summarized in Figure 2. Both λ_{max} and the maximum absorbance increased and then decreased, with increasing fraction of aqueous NaOH, in both the copolymers. These changes reflected the extent of the H-aggregation of the azobenzene units; the extent of the H-aggregation increased and then decreased, with increasing fraction of aqueous NaOH. The critical aqueous NaOH fractions at which the maximum absorbance and λ_{max} began to decrease were 60 and 30 vol % for M-15 and -37, respectively. It should be noted that the extent of H-aggregation was high at the higher THF volume fraction, though THF is good solvent for MR2 units. This phenomenon is
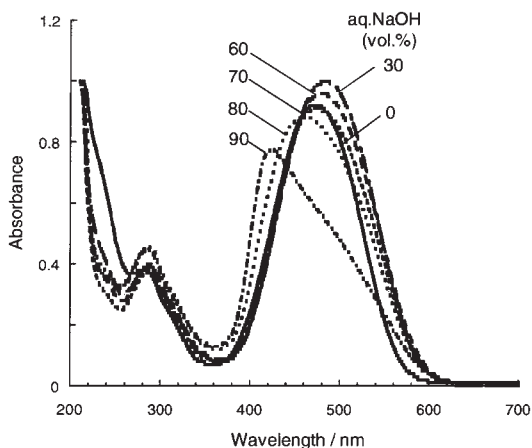
Figure 1 UV–vis absorption spectra of M-37 solutions, with varying volume fractions of aq. NaOH (M-37 conc. = 0.2 g/L; conc. of aq. NaOH = 10 mM).

Figure 3 H_2O volume fraction dependence of light scattering intensity of copolymer solutions (copolymer conc. = 5.0 g/L).

probably explained as follows: the polymer strand shrinks due to the insolubilization of MA units, so that the distance among the MR2 units becomes shorter. Thus, the MR2 units are easy to aggregate. The similar aggregation of an ionomer, resulting from the insolubilization of carboxylic unit in THF, is also reported in randomly carboxylated polystyrene.[9]

Light scattering measurements of copolymer solutions

The aggregation of the copolymers, with increasing H_2O content in the H_2O/THF solvent, was monitored by light scattering intensity of the solution. The copolymers were dissolved in 1.0 vol % THF-containing H_2O at a concentration of 5.0 g/L. Then, H_2O was added dropwise to the solution, with stirring, and the laser light scattering intensity (at 633 nm) was moni-
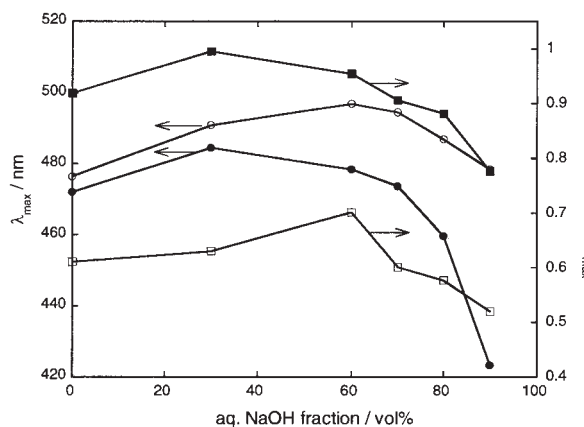

Figure 2 Aq. NaOH volume fraction dependences of λ_{max} and maximum absorbance of copolymer solutions (copolymer conc. = 0.2 g/L; conc. of aq. NaOH = 10 mM). Open and filled symbols are for M-15 and -37, respectively.
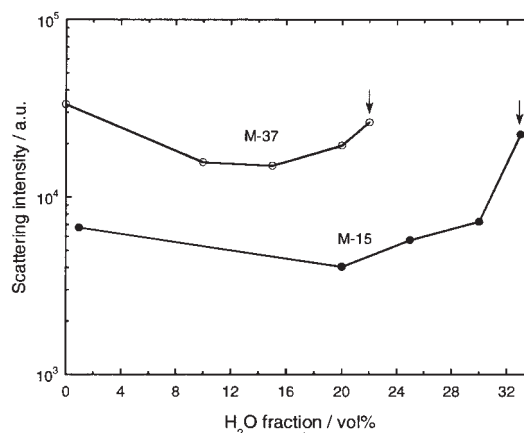
tored. As shown in Figure 3, the scattering intensity of both the copolymer solutions decreased at first and then increased, with increasing H_2O content. At the points indicated by the arrows, the solutions began to cloud. These critical points were 33 and 22 vol % for M-15 and -37, respectively. The change of the scattering intensity, depending on the H_2O contents, indicated that the extent of the aggregation of the copolymers became low and then high with increasing H_2O content. The increase in the aggregation extent of M-15 began at higher H_2O content than M-37. These results were consistent with those obtained by the UV–vis spectra measurements. The clouding phenomena were not observed, when 10 mM aq. NaOH was used instead of pure H_2O. Thus, the ionization of MA unit by NaOH addition enhanced the solubility of the copolymers.

The hydrodynamic diameter distributions of the colloidal particles obtained from the copolymers were determined by DLS method. The DLS measurements were conducted just above the critical H_2O content. The results were shown in Figure 4. The size distributions were relatively narrow in both the copolymers and the size rages were 80–400 and 100–600 nm for M-15 and -37, respectively. The hydrodynamic diameter of M-37 was larger than that of M-15. This indicated the smaller association number of M-15 copolymer in one colloidal particle. These results would be explained as follows: the particle has core–shell structure and the ionic MA units surround the hydrophobic MR2 core, to stabilize the particle. Thus, the larger MA unit content in the copolymer leads to a decrease in the particle size to raise the specific surface area, i.e., ratio of particle surface area and its volume. Similar dependence of particle sizes on ionic group content was also reported in other ionomers.[9,12,14]
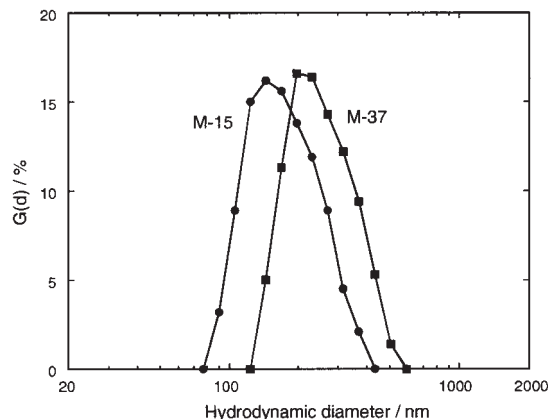
Figure 4　Z-weighted hydrodynamic diameter distributions of colloidal particles formed from copolymers in THF/H$_2$O mixtures at 25°C. Initial copolymer concentration (THF solution) was 5.0 g/L. Volume fractions of H$_2$O were 33 and 22 vol % for M-15 and -37, respectively.

Particles obtained by drying of dispersion

The colloidal particle dispersions (solvent: THF/H$_2$O) of the copolymers were dropped on a carbon sheet and dried *in vacuo*. The obtained samples were observed by SEM. Figure 5 shows the samples obtained from M-37 dispersions, with various H$_2$O contents. When the sample was obtained by the casting of the transparent solution [H$_2$O content = 20 vol %; Fig. 5(a)], the particles were fused with each other and the boundary among the particles was not clear. On the other hand, above the critical H$_2$O content [26 vol %; Fig. 5(b)] at which the solution became cloudy, the individual particles were clearly observed. Therefore, the segregation of core and shell of the particle in dispersion is the necessary condition to obtain individual particles after drying. In the following experiments, we added H$_2$O (or aq. NaOH) to THF solution of the polymer just above the critical content.

Figure 6(a) shows the SEM image of the particles obtained from M-15. The particle diameter was much larger than that of M-37 [Fig. 5(b)]. The size distributions of the particles of M-15 and 37 [Fig. 7(a,d)] were obtained

by analyzing the SEM images. The number average diameters (D_n) of the particles were 15 and 1.2 μm for M-15 and -37, respectively. The dried particle size (D_n) of M-15 was much larger than that in the dispersion (Fig. 4). This fact indicates that the reconstruction of the particle should proceed in M-15, during the drying process of the dispersion. Indeed, the magnified image of the particle of M-15 [Fig. 6(b,c)] revealed that the particle was formed by the aggregation of the small particles, with diameters less than 1 μm. On the other hand, the interparticle aggregation was not observed in the case of M-37. Because the aggregation was only observed in M-15, which contained more MA units than M-37, the MA units existing on the particle surface should play a crucial role in the particle aggregation process. Therefore, the probable interactions among the particles were (1) hydrogen bonding among the carboxyl groups and (2) the ion-pair interaction among the sodium carboxylate groups.

The effect of the aqueous NaOH concentration (0, 1.0, 5.0, and 10 mM) on the particle size was investigated. The results of M-15 were shown in Figure 7(a–c). The diameter decreased with increasing concentration of aqueous NaOH, and the particles were composed of small particles irrespective of the NaOH concentration. However, when the aqueous NaOH concentration was 10 mM, the solution did not become turbid by the addition of aqueous NaOH up to 90 vol %. When the resulting solution was cast on the carbon sheet, a film with smooth surface was observed by SEM (data not shown). The higher NaOH concentration led to a higher dissociation degree of MA units, so that the solubility of the polymer increased. Thus, the segregation of the core and shell did not proceed when 10 mM NaOH was used.

In the case of M-37, the film formation was observed when the NaOH concentration was more than 5.0 mM. When 1.0 mM NaOH was used [Fig. 7(d)], the particle size decreased compared with H$_2$O [Fig. 7(e)] but the interparticle aggregation was still not observed. Thus, the interparticle aggregation was the unique phenomenon for M-15 copolymer, which had more MA unit to assemble the particles by the interactions described earlier.
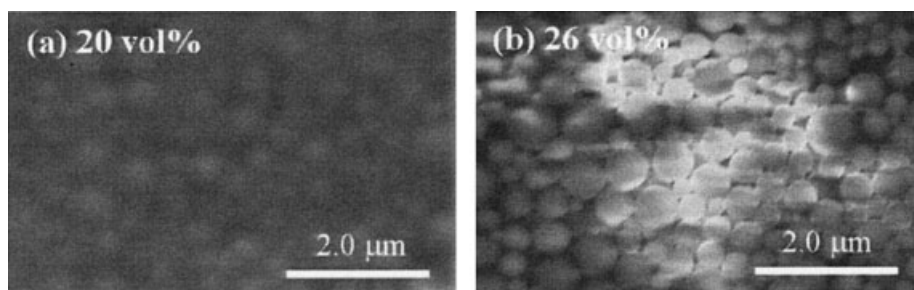

Figure 5　SEM images of particles obtained from THF/H$_2$O mixtures of M-37, with two different H$_2$O contents. Initial copolymer concentration was 10 g/L.
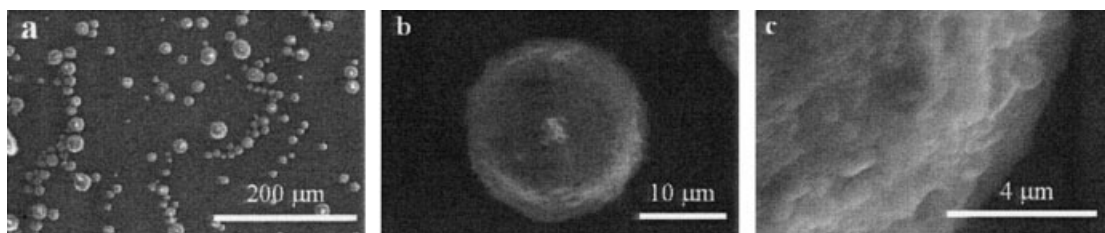
Figure 6 SEM images of particles obtained from THF/H$_2$O mixture of M-15. (b) and (c) are magnified image of (a). Initial copolymer concentration was 10 g/L.

CONCLUSIONS

The particle formation of azobenzene-containing ionomers through self-assembly in aqueous media was studied. The two copolymers with different azobenzene-unit content, M-15 and -37, were synthesized. Colloidal particles were prepared by addition of various concentrations of aq. NaOH to the copolymer THF solutions. The particle size depended on the azobenzene unit contents in the copolymer; the copolymer with smaller azobenzene content (M-15) formed larger particle. On the other hand, when the particle dispersions were dried, colloidal particles of M-15 aggregated to form larger particles. However, the interparticle aggregation was not observed in M-37 copolymer. The MA units probably play a crucial role in the interparticle aggregation process. The size of the particles obtained by drying became smaller, when the higher concentrations of aqueous NaOH solutions were used. Thus, the particle size can be controlled by the azobenzene unit content in the copolymers and the concentration of aqueous NaOH solutions. The obtained particles would be applicable for the optical devices, such as a resonator and a switch. These studies are now in progress in our group.
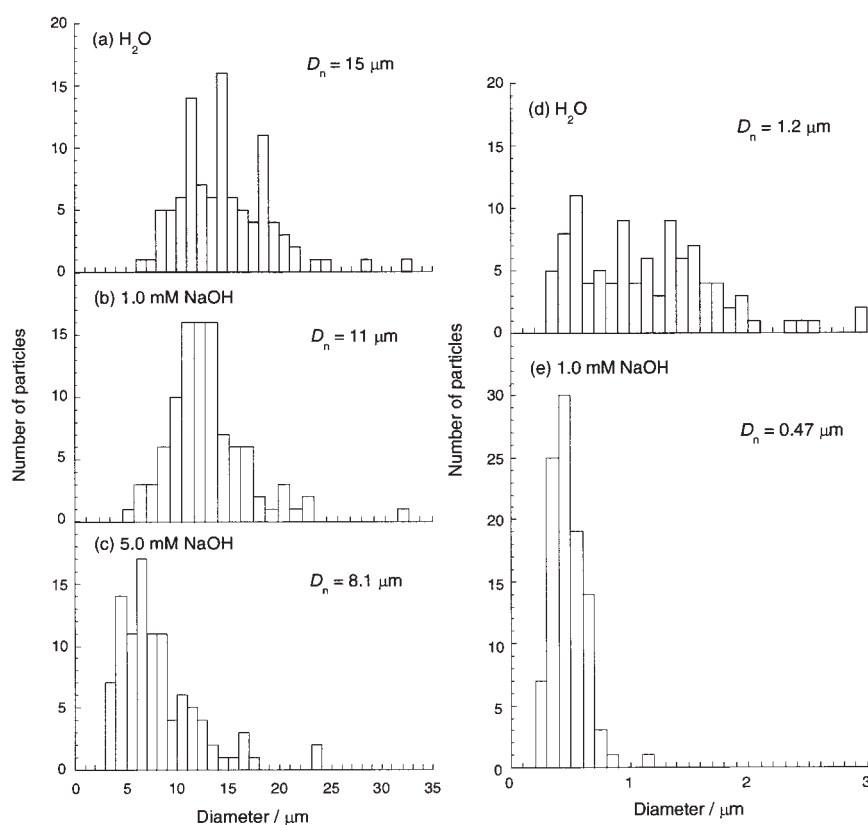
Figure 7 Size distributions of the particles obtained from M-15 (a–c) and -37 (d and e), by using aq. NaOH solutions, with different concentrations.

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