pH-Responsive Swelling of the Ultrafine Microsphere

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Introduction

The volume change of polymer gels caused by pH, temperature, and electric field has obtained strong interest from the viewpoint of high-technology materials such as optoelectronic, mechanochemical, and biomedical materials. Rapid response is strongly needed in these materials, and, therefore, miniaturization of polymer gel is one of the approaches toward the development of polymer devices. The volume change of polymer gel is proportional to the square of the gel size. Tanaka et al. showed the response of a micron-sized gel particle could be within millisecond range.[1] The temperature-dependent phase transition of *N*-isopropylacrylamide gels having diameters from 0.2 to 1.0 μm was described by Hirose et al.[2] To our knowledge, however, no paper has ever reported on pH response of submicron gels. Our interest lies in applications of pH-sensitive microspheres as optoelectronic devices. In this line of research we have recently developed an electrical pH modulator made of a polyaniline-coated electrode.[3]

Poly(acrylamide–acrylic acid) copolymer and poly(vinyl alcohol–acrylic acid) copolymer are the well-known examples of pH-responsive gels; however, the preparation of these polymer microspheres having a diameter below 0.1 μm is difficult.

In this report, we describe the pH-dependent swelling of methyl methacrylate–acrylic acid copolymer microspheres having a diameter of tens of nanometers.

Experimental Section

Methyl methacrylate, acrylic acid, and water were distilled, and other reagent-grade chemicals were used without further purification. Microspheres were prepared by emulsion polymerization, whose detailed conditions are described in Table I. Every polymerization was performed in a 0.5-L separation flask. Surfactants used for emulsion polymerization were anionic Emal 2F and nonionic Emanon 3199 from Kao-Atlas Co. Ethylene glycol dimethacrylate was used for cross-linking. Polymerized samples were dialyzed against deionized water to remove decomposed initiating agents and excess surfactant.

For the measurement of the microsphere size a dynamic light scattering system DLS 7000 (Otsuka Electronics Co.) was employed. The mean diameter of microspheres and the decay rate of the light intensity correlation function were determined by applying the analysis software provided as the standard function of the DLS system.

The pH of the distilled water treated with 50-nm Millipore filters was adjusted by mixing with a solutioin of either HCl or NaOH. The sample was added dropwise to the pH-adjusted solution. Once mixed, the resulting pH was not adjusted further. The resulting pH value was measured in the optical measuring cell by using a miniaturized ISFET pH sensor (pH 2135, Kurare Co., Ltd.), which would minimize mechanical disturbances and any possible contaminations into a small amount of sample solutions. New samples and solutions were used for each pH. All the measurements were carried out at 25 °C.

Table I
Polymerization Recipe and the Resulting Diameter of Microspheres[a]

sample	monomer, g MMA	AA	EDG	surfactant, g	diameter, nm shrinked	swollen
T1	50	1	0	4 (Emal)	75	85
T2	50	2.5	0	4 (Emal)	90	140
T3	50	5	0	4 (Emal)	85	180
T4	50	5	1.5	4 (Emal)	80	140
T5	50	7	0	4 (Emanon)	140	255

[a] Emulsion polymerization was carried out in a dispersed medium of 200 mL of water at ca. 65 °C in a nitrogen atmosphere. The medium was stirred at 300 rpm with a 6-cm semicircular paddle, and the reaction was completed in 40 min. The redox system consisting of 0.16 g of $K_2S_2O_8$ and 0.15 g of $Na_2S_2O_3$ was employed as initiating agents: MMA, methyl methacrylate; AA, acrylic acid; EGD, ethylene glycol dimethacrylate.

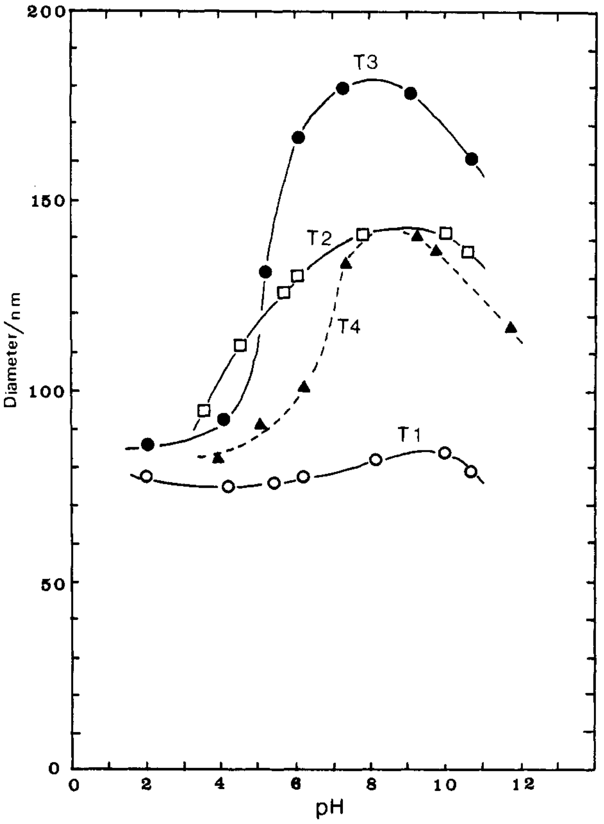

Figure 1. Swelling of the microspheres of the MMA/AA copolymer in solutions of varying pH. The weight ratio is in Table I.

Results and Discussion

Figure 1 shows the swelling curves of microsphere samples (T_1, T_2, T_3, and T_4) suspended separately in solutions of varying pH. The swelling curves of the microsphere demonstrated the characteristics of bulk gels having the ionizable group of acrylic acid. For homogeneous bulk gels a theory based on Donnan equilibrium has proven applicable to the experimental results.[4] In this case, a steep increase in swelling is expected at pH 7 and is observed in experiments on bulk gels. By contrast, the microsphere prepared by emulsion polymerization shows a gradual increase in swelling near pH 7. This unexpected behavior is attributed to an inhomogeneous distribution of ionizable groups.

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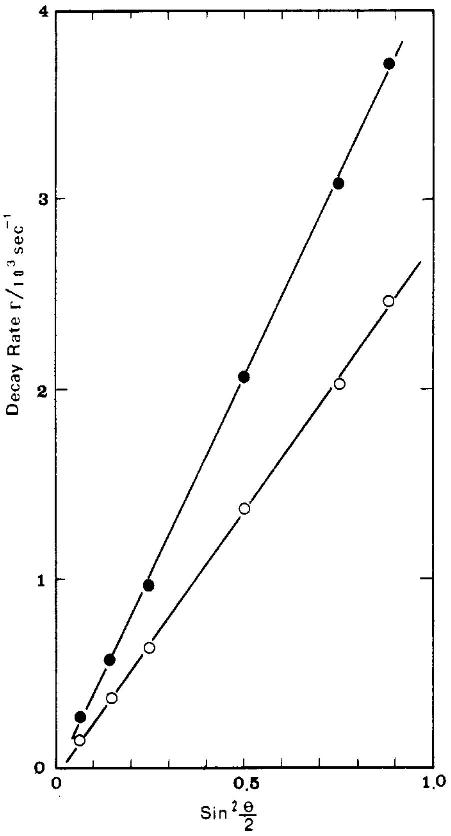

Figure 2. Angular dependence of decay rate Γ of the autocorrelation function. θ is a scattering angle. Sample T_3 is employed. -○-: pH = 9.2. -●-: pH = 3.9.

The experiment shows that the extent of apparent swelling of the cross-linked gel (T_4) is much less than that of the non-cross-linked gel (T_3). We presume that neither one of them would be likely to aggregate more than the other; i.e., aggregation will show no difference in the apparent swelling between the cross-linked and the non-cross-linked. On the other hand, one can expect a smaller extent of swelling in the case of cross-linked gels. On the basis of Flory theory, swelling volume is related to cross-linking density.

The dynamic light scattering theory states that the autocorrelation function of scattered light intensity for the motion of a spherical particle will show an exponential form and will yield a linear plot of decay rate Γ with $\sin^2(\theta/2)$, where θ is a scattering angle. When aggregation occurs, shapes of most particles will be nonspherical and deviations from the linear plot will appear at large angles. The angular dependence of decay rate Γ is shown in Figure 2. In the plot for swollen gels (pH 9.2), the departure from linearity can hardly be recognized.

On the basis of the Donnan theory on the polymer swelling, one can expect that the swelling is dependent on salt concentration. Our experimental results are consistent with this idea as shown in Figure 3.

The reversible volume change of the microsphere by successive change of solution pH was confirmed. pH adjustment was performed by means of alternative addition of HCl and NaOH solution. As shown in Figure 4, the microspheres demonstrated a pseudoreversibility when they were suspended in a series of solutions of different pH. The deviation from perfect reversibility is probably due to the formation of NaCl in the course of pH alteration. The (pseudo)reversible change in microsphere diameter seems to be another explicit proof for pH-responsive swelling (not aggregation) of the polymer microspheres.

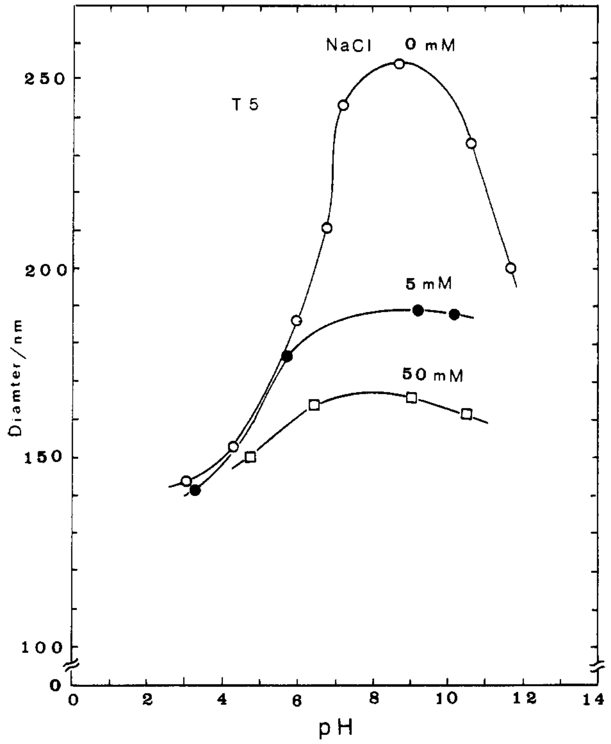

Figure 3. Swelling of the microspheres (sample T5) in the presence of NaCl. The NaCl concentration is in the figure.

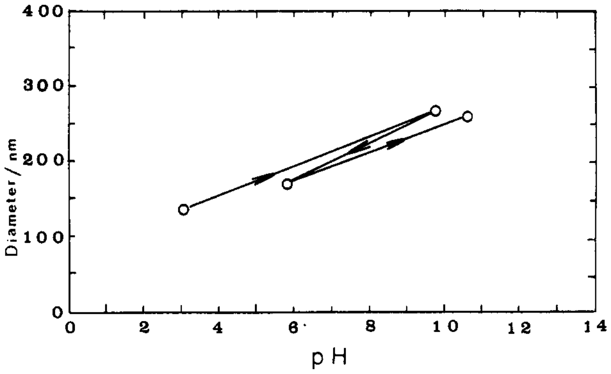

Figure 4. Reversible diameter changes of sample T5 upon successive pH changes of solution.

In conclusion, we have confirmed that the pH-dependent swelling of the microspheres having a diameter of tens of nanometers mirrors that of bulk gels with the exception that a less steep slope in pH swelling was observed in the case of the microspheres.

Since the response time of these sized gels is expected in the microseconds range,[1] the results obtained here encourage us to exploit the ultrafine pH-sensitive microsphere as a functional material with rapid response.

References and Notes

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