

Template-free Formation of Microspheres Based on Poly(*N*-methylaniline)

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Polyaniline and polypyrrole are the most widely studied conducting polymers and are often synthesized by a simple oxidative polymerization method in a bulk solution. The resulting polymers show either granular or fibrillar morphology, depending on experimental conditions.^{1–3} Some groups have also reported that spherical polymers are formed by using steric stabilizers^{4–6} or by synthesizing polymers by microemulsion process.^{7,8} In addition, inorganic and organic materials⁹ like silica, salicylic acid,¹⁰ and β -naphthalene sulfonic acid¹¹ are employed for preparing polyaniline particles of different shapes. Microspheres comprising conducting polymers may probably be well suited for certain specific applications such as conducting paints and antistatic agents. They have been also applied to conducting fillers in transparent conducting thin films.¹² In particular, microspheres having a smooth surface are expected to form easily two- or three-dimensional periodic lattices possessing photonic band gap, which will lead to novel optical properties.^{13,14} However, a fine tuning of the morphology and the size of conducting polymer spheres still needs some improvement.

Up to the present time, several reports have described morphological studies of polyaniline and its ring substituted derivatives generated by electrochemical means. The synthesized polymer films showed either fibrillar or granular morphology just like those formed in solutions.^{15,16} We have recently reported the formation of microspheres based on electrochemical oxidation of *N*-methylaniline (NMA) in acid solutions, although the resulting poly(*N*-methylaniline) (PNMA) microspheres were fused in part to the electrode surface and were hard to be isolated.^{17,18} However, this self-assembling nature of NMA to form spherical par-

ticles hints us the possibility for the formation of PNMA microspheres by chemical oxidation of NMA in a solution.

The present communication describes a template-free formation of PNMA microspheres based on a simple chemical polymerization method using monomer, acid, and oxidant.

EXPERIMENTAL

N-Methylaniline (NMA), aniline, *o*-toluidine and *o*-anisidine used as monomer were distilled under reduced pressure. Adipic acid, HClO₄, HBF₄, H₂SO₄, HCl, HNO₃, (NH₄)₂S₂O₈ (APS), FeCl₃, and K₂Cr₂O₇ were used as received. Appropriate quantities of monomer and acid were dissolved in deionized water. An oxidant solution was added to the solution and the reaction was maintained for a given period of time until adding an excess amount of ethanol to the solution for stopping the polymerization. The resulting solution was centrifuged, and the precipitate was washed repeatedly with water and alcohol several times. Finally, the product was dried in vacuum for 24 h at room temperature.

The morphology and size of PNMA microspheres were measured with a JEOL JSM-6320F field-emission scanning electron microscope (SEM). A 20 nm Pt layer was sputtered on the sample prior to SEM measurements.

RESULTS AND DISCUSSION

Figure 1 shows SEM images of PNMA polymerized at 25 °C by oxidizing 0.025 M NMA in different concentrations of adipic acid solutions with 0.025 M

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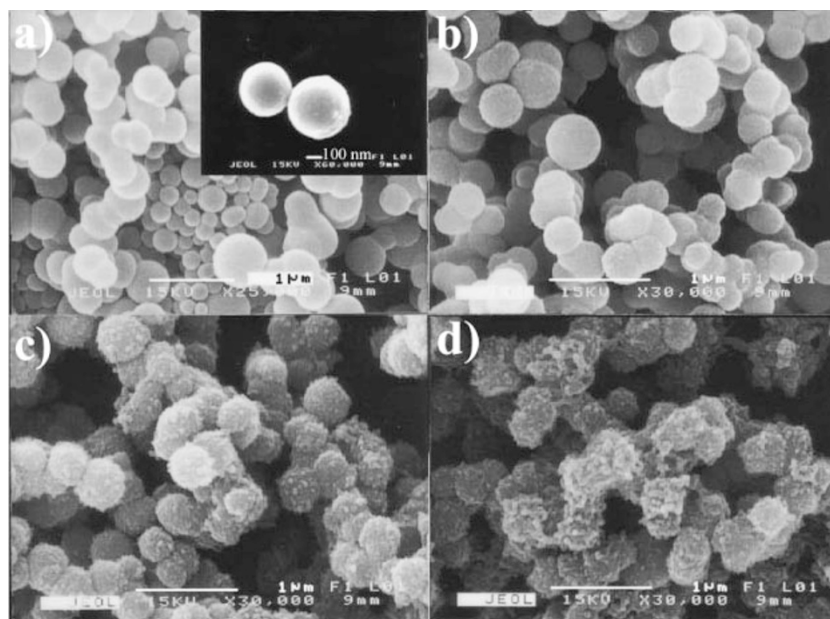


Figure 1. SEM images of PNMA prepared in adipic acid solutions at concentrations of a) 0.025, b) 0.050, c) 0.10, and d) 0.20 M. Other conditions: [NMA] = [APS] = 0.025 M; 24 h; 25 °C.

APS. Microspheres having an average diameter of 0.38 μm were obtained when the concentration of adipic acid is 0.025 M (Figure 1a), indicating a successful formation of conducting microspheres in the absence of any template. Surfaces of the microspheres were smooth like those obtained by electrochemistry.^{17,18} The morphology of microspheres could be controlled only by changing acid concentration. The microsphere surfaces became coarse by increasing the concentration of adipic acid as shown in Figures 1b–d, although the acid concentration had no considerable influence on the size of microspheres. The surface of spheres generated at higher concentrations of adipic acid seemed to be covered with smaller particles of about several tens nanometers. On the other hand, the concentration of APS higher than 0.025 M was almost independent of the size and morphology of PNMA microspheres. The sizes of microspheres were 0.38, 0.34, and 0.35 μm for the APS concentrations of 0.025, 0.050, and 0.10 M, respectively.

Besides the concentration of acid, its sort was crucial for the formation of PNMA microspheres. Figure 2 shows SEM pictures of PNMA polymerized with 0.025 M of APS and NMA in different acid solutions of the common concentration at 0.025 M. When HClO_4 and HBF_4 as well as adipic acid were used, microspheres with smooth surfaces were formed. In acid solutions such as HNO_3 , HCl and H_2SO_4 , on the other hand, morphologies of PNMA were not spherical, but granular or fibrous. Dependence of morphology of PNMA particles on the sort of acid was consistent with the result of electrochemical polymerization of NMA in different acid solutions as report-

ed.¹⁵ It is noted that the difference between electrochemical and chemical polymerization is found in the size of PNMA spheres: 0.7 to 4.3 μm for the former compared with 0.38 μm for the latter technique. It is likely that the difference in size of PNMA spheres may be related to that in concentration of NMA. Actually, the average diameters of PNMA microspheres obtained by electrochemical polymerization were 1.9, 1.7, and 0.95 μm for the monomer concentration of 0.8, 0.4, and 0.2 M, respectively, under the same potential-scan rate and cycle number. Higher concentrations of NMA were also examined in the chemical polymerization process with HClO_4 as acid and APS as oxidant. When the NMA concentration was kept at 0.2 M, PNMA particles with a morphology like Figure 1c were formed in solutions with HClO_4 at concentrations of 0.2 to 1 M. With 0.1 M or lower concentrations of HClO_4 , solubility of NMA was poor. After sonication of the phase-separated solutions, however, they gave emulsions and, interestingly, the oxidation by APS yielded smooth-surfaced microspheres of ca. 0.7 μm in diameter. According to the findings described above, it is reasonable to presume that polymerization of NMA occurs not in emulsions, but in dilute HClO_4 solutions saturated with NMA.

Some other results are tabulated in Table I. With APS as an oxidant, the size of PNMA microspheres depended greatly on the reaction temperature (samples 1-3). As the temperature is increased, the average diameter of microspheres decreased from 0.54 μm at 0 °C to 0.27 μm at 50 °C. It has been reported that chemical polymerization of aniline derivatives at higher temperatures leads to the formation of lower

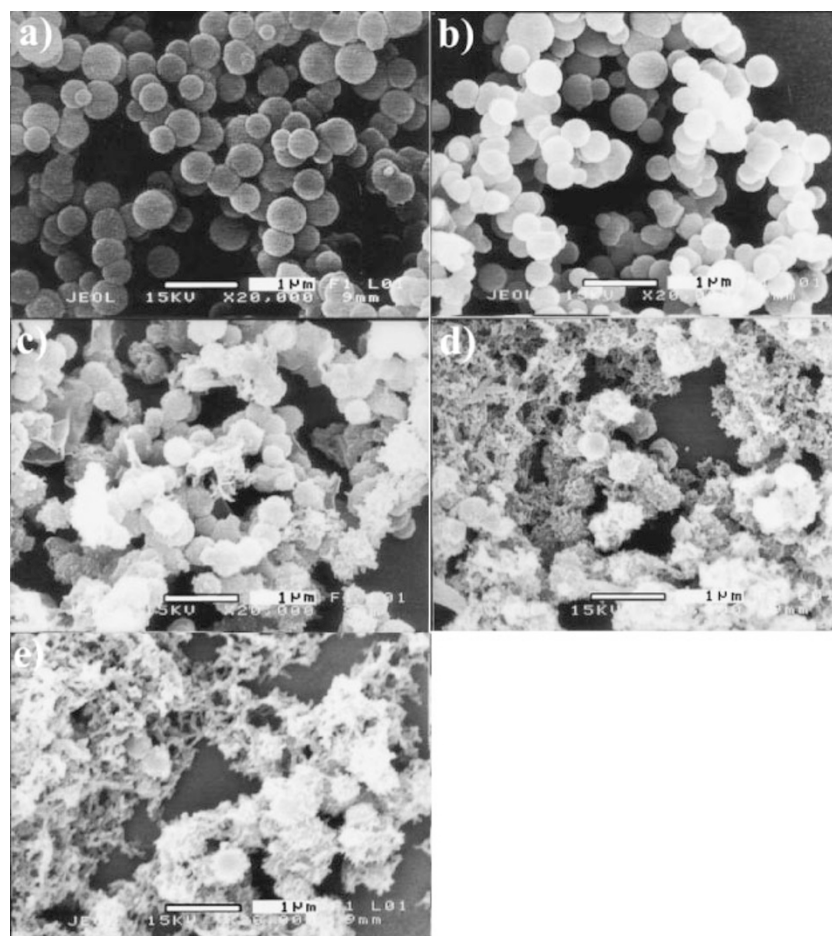


Figure 2. SEM images of PNMA polymerized from different acids: a) HClO_4 , b) HBF_4 , c) HNO_3 , d) HCl , e) H_2SO_4 . Other conditions: $[\text{NMA}] = [\text{acid}] = [\text{APS}] = 0.025 \text{ M}$; 24 h.; 25°C .

Table I. Shape and size of PNMA synthesized with some sorts of oxidants in 0.025 M adipic acid solutions at different temperatures

Sample number	Oxidant	Temperature / $^\circ\text{C}$	Shape	Average diameter/ μm
1	APS	0	sphere	0.54
2	APS	25	sphere	0.38
3	APS	50	sphere	0.27
4	$\text{K}_2\text{Cr}_2\text{O}_7$	25	granular	—
5	FeCl_3	25	not obtained	—

Other conditions: $[\text{NMA}] = [\text{oxidant}] = 0.025 \text{ M}$, reaction time = 24 h.

molecular weight polymers.^{19–21} At lower temperatures, the number of peroxy radicals available from the oxidant are limited and once the polymerization process is initiated further propagation continues systematically. This will result in the formation of longer chain polymers. At higher temperatures, on the contrary, the formation of peroxy initiator by cleavage of O–O bond is much more facile and as a result more number of peroxy radicals are available in the electro-

lyte solution. Owing to this, the process of termination of polymer chains becomes more favored than propagation. This will possibly restricts the size of microspheres during early stages of growth. When $\text{K}_2\text{Cr}_2\text{O}_7$ was used as an oxidant (sample 4), microspheres were not produced and the morphology of PNMA obtained was like aggregation of several nanometers particles. On the other hand, FeCl_3 gave no polymers, suggesting that this oxidizing agent is insufficient to oxidize NMA. Indeed, redox potentials of APS, $\text{K}_2\text{Cr}_2\text{O}_7$, and FeCl_3 are 2.05, 1.33, and 0.76 V compared with 0.96 V for NMA (vs. NHE).

Figure 3 shows average diameters of PNMA microspheres synthesized with APS and adipic acid as a function of the reaction time. The diameter of microspheres increases with time and reaches $0.38 \mu\text{m}$ at 60 min. Afterwards, no significant increase in diameter was observed even after 24 h. When the reaction time is shorter than 5 min, no deposit was found after centrifugation at 3,000 rpm. The resulting solution was filtrated with a filter of 20 nm in pore size, but no particles were detected on the filter, showing that the particles are smaller than the pore size of the filter

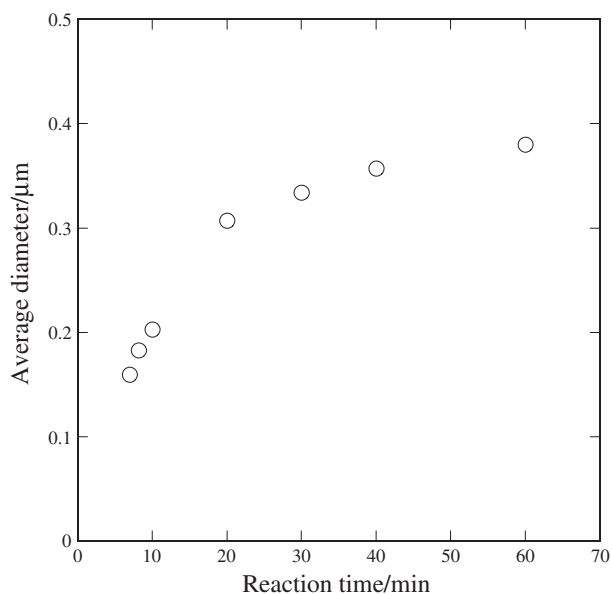


Figure 3. Dependence of average diameters of PNMA microspheres on the reaction time. Conditions: [NMA] = [adipic acid] = [APS] = 0.025 M; 25 °C.

or no particles are generated in the solution. According to our previous electrochemical study,¹⁶ mechanisms for the formation of PNMA microspheres are speculated as follows: 1) oxidation of monomers at electrode, 2) coupling of the resulting intermediate species (cation radicals) with monomers, 3) successive couplings of the oligomeric species in solution, and 4) precipitation of the oligomers as microspheres on the electrode surface. Kinetic analysis of the solution based on spectroscopy determined the lifetime of

the intermediate species to be *ca.* 2 min, much longer than a few seconds reported for the case of polyaniline. In view of this and lower concentrations of acid and monomer employed in this experiments, the reaction time shorter than 5 min appears to be insufficient to generate PNMA.

At present, it is difficult to elucidate exact mechanisms for the formation of PNMA microspheres. However, it should be stressed that microspheres are formed exclusively with NMA chemically as well as electrochemically without any templates. For a comparison purpose, SEM images of polyaniline, poly(*o*-toluidine), and poly(*o*-anisidine) synthesized with APS and adipic acid are depicted in Figure 4. Polyaniline, poly(*o*-toluidine), and poly(*o*-anisidine) were rock-like, granular of several tens nanometers, and a mixture of smooth and rough lumps, respectively. Even under the conditions which lead to the formation of PNMA microspheres, all of these monomers fail to generate microspheres with smooth surfaces. This implies that NMA has a competence to form microspheres, although the detailed mechanisms should be clarified in the future.

In summary, PNMA microspheres were successfully prepared through chemical polymerization of NMA with APS in acid solutions such as adipic acid, HClO₄, and HBF₄ without any templates. Surface morphologies and shape of microspheres could be changed by concentration and the sort of acid, respectively. The size of smooth microspheres was controlled to be 0.16–0.54 μm by changing the reaction time and temperature.

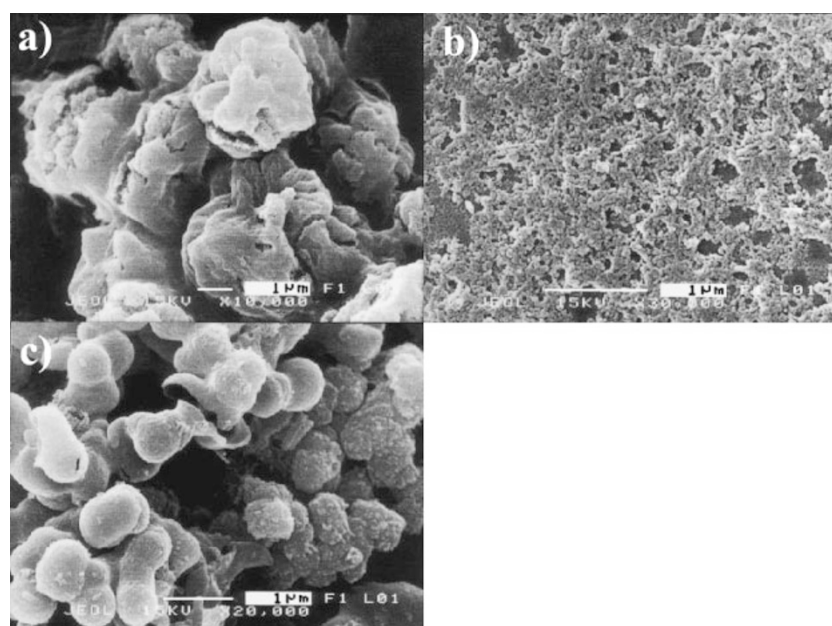


Figure 4. SEM images of a) polyaniline, b) poly(*o*-toluidine), and c) poly(*o*-anisidine) chemically polymerized with APS in adipic acid solutions. Other conditions: [monomer] = [acid] = [APS] = 0.050 M; 24 h; 25 °C.

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