

Microspheres of Conducting Poly(*N*-methylaniline)

Rahul PATIL, Kei SANADA, Xiaoqing JIANG, Yutaka HARIMA,[†]
Kenji MASAOKA,* Sumio YAMASAKI,* and Jun YANO**

Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

**Faculty of Engineering, Kyushu Sangyo University, Matsukadai 2-3-1, Higashi-ku, Fukuoka 813-8503, Japan*

***Department of Engineering, University of East Asia, Ichinomiya-Gakuencho 2-1, Shimonoseki 751-8503, Japan*

(Received March 1, 2004; Accepted April 22, 2004; Published July 15, 2004)

ABSTRACT: Microspheres of conducting poly(*N*-methylaniline) were obtained by a potential-sweep polymerization of *N*-methylaniline in 1 M HClO₄ solution. The average diameter of the microspheres grown from 0.8 M monomer concentration by sweeping potential at 50 mV s⁻¹ for 12 cycles was 1.9 μm. The size of microspheres could be controlled by changing several experimental parameters including scan rate, monomer concentration and cycle number. Among different acids used for polymerization process, only HClO₄ and HBF₄ showed ability of microspheres formation. The increase in size of alkyl group at *N*-position of aniline ring tended to inhibit the growth of microspheres. The formation of microspheres probably occurs through oligomer-coupled polymerization process.

[DOI 10.1295/polymj.36.549]

KEY WORDS Microspheres / Poly(*N*-methylaniline) / Electrochemical Polymerization / Oligomer-coupled Polymer /

Among various conducting polymers, polyaniline (PANI) has been the best studied for the past two decades.^{1–3} The derivatives of PANI have also attracted considerable attention especially due to their higher solubility in common solvents than PANI.^{4–6} Although several reports are available on ring alkyl substituted^{7,8} and ring alkoxy substituted PANI,^{6,9,10} *N*-alkyl substituted aniline still remains less attentive in spite of the fact that they are useful in certain applications. Barbero *et al.* have used chemically produced poly(*N*-methylaniline) (PNMA) as a substrate for diazonium ion coupling in order to ensure preferential attack on the ring and to protect the amine nitrogen from possible exposure.¹¹ The chemical properties of PNMA essentially differ from those of PANI since in PNMA the proton exchange sites are irreversibly blocked by methyl substituents. As a consequence, the deprotonation of the imino groups and proton expulsion during the second oxidation step of PANI is not observed in PNMA. The absence of the second oxidation process in PNMA reduces a risk of the oxidative deterioration by hydrolysis during the electrochemical oxidation, and this fact is an advantage of PNMA over PANI.

Very few reports are available on the physicochemical properties of PNMA^{12–14} and further works are needed for understanding its properties in more depth. Since detailed physical properties and the rates of the electrochemical processes are likely to depend on film morphology, it is of interest to gain insight into mor-

phological features of electrochemically grown conducting polymer films. In this regard, several reports on morphological features of PANI and its ring substituted derivatives are available in the literature.^{15–18} All of them have reported either fibrillar or granular morphology, depending upon various deposition parameters. Here, we report that PNMA possesses interesting property to form microspheres. Microspheres of functional materials are very useful for encapsulation, drug delivery, development of artificial cells and protection of biologically active agents (*e.g.*, proteins, enzymes or DNA).^{19–21} If we can isolate these microspheres from surface of the electrode, they will be useful in such kind of applications. Earlier, some reports are available in the literature mentioning electrochemical synthesis of spherical PANI particles using suitable polymeric stabilizers.^{22,23} However, in the present work, microspheres are obtained without any addition of steric stabilizer and this clearly suggests that growth mechanism in case of PNMA proceeds *via* a path different from that for PANI and its ring substituted derivatives.

EXPERIMENTAL

N-Methylaniline (Sigma Aldrich Japan K.K.) was used after distillation under reduced pressure. Gold-coated electrodes were prepared by vacuum evaporation of gold (40 nm) on to a glass slide coated with 2 nm Cr underlayer. Three-electrode system was em-

[†]To whom correspondence should be addressed (Fax: +81-824-24-5494, E-mail: harima@mls.ias.hiroshima-u.ac.jp).

ployed for polymerization process in which each compartment was separated by porous glass filter. The gold-coated glass and Pt electrode served as working and counter electrode, respectively. Electrolyte solution was prepared by dissolving appropriate amount of *N*-methylaniline monomer in 1 M HClO₄. The gold coated glass (1 cm × 1 cm) was dipped in electrolyte solution and PNMA film was deposited by cycling the potential between -0.1 V and 0.85 V vs. Ag|AgCl|NaCl (satd.) as a reference electrode. Films were obtained by varying various deposition parameters including monomer concentration, cycle number and scan rate. Each time the cycling was stopped at 0 V, and films were removed and washed with water. The vacuum dried films were coated with 2 nm Pt layer by sputtering prior to scanning electron microscope (SEM) analysis. The electrochemical measurements were performed using a potentiostat equipped with a function generator (Hokuto-Denko Co., Ltd., HAB-151). The morphological features were examined using a JEOL JSM-6320FS scanning electron microscope. *In-situ* absorption spectra were recorded on a Shimadzu UV-3101 PC spectrophotometer. All the measurements were made at room temperature.

RESULTS AND DISCUSSION

Figure 1 represents a cyclic voltammogram of a PNMA film grown from 0.8 M *N*-methylaniline solution. Two redox couples are evident in the cyclic vol-

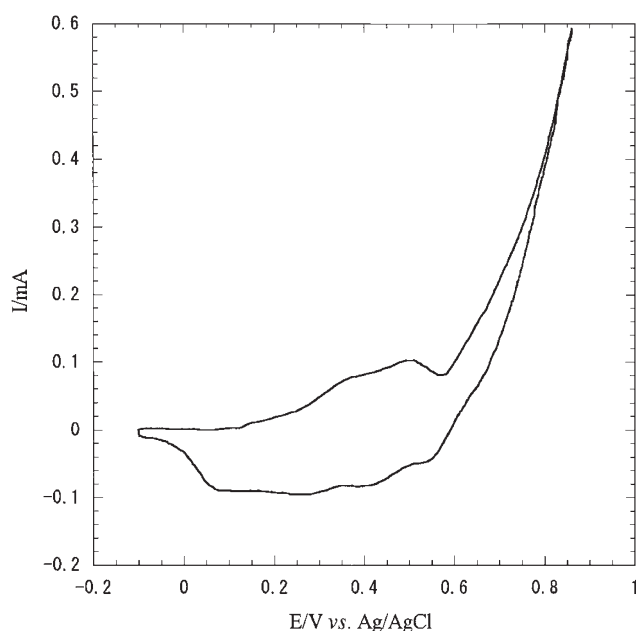


Figure 1. Cyclic voltammogram of PNMA film recorded during electropolymerization of NMA (4th cycle). The parameters used for recording cyclic voltammogram are the same as that of sample 5 in Table I.

tammogram mainly at $E_{pa_1}/E_{pc_1} = 0.34/0.28$ V and $E_{pa_2}/E_{pc_2} = 0.48/0.40$ V, respectively. The third redox couple ($E_{pa_3}/E_{pc_3} = 0.60/0.54$ V) is also clearly seen in the first few cycles (in Figure 1 only reduction peak at 0.54 V is noticed). Apart from this, additional cathodic peak is also visible at 0.06 V and this peak later merges with the cathodic peak at 0.28 V (E_{pc_1}). The three redox couples in the cyclic voltammogram are mainly attributed to the formation of radical cations (E_{pa_1}/E_{pc_1}), hydrolysis product such as benzoquinone (E_{pa_2}/E_{pc_2}) and diradical dication (E_{pa_3}/E_{pc_3}). The PNMA films obtained in the present case are adhering completely to the gold-coated glass substrates.

Figure 2 represents SEM images of a PNMA film at different magnifications, prepared by cycling the po-

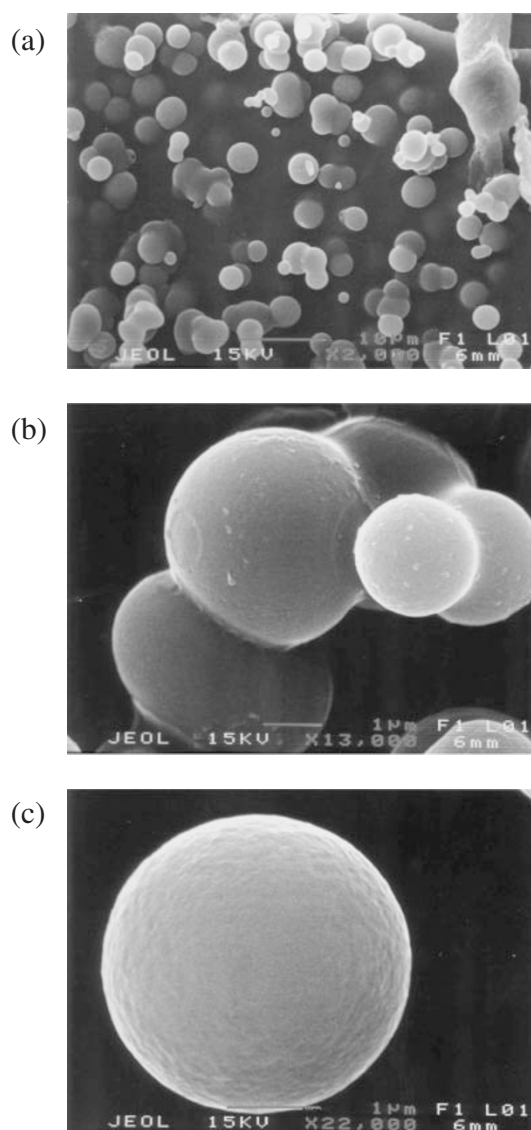


Figure 2. SEM pictures of PNMA film taken at different magnifications of (a) 2000×, (b) 13,000× and (c) 22,000×. The PNMA film was prepared from 0.8 M monomer concentration in 1 M HClO₄ at 50 mV s⁻¹ by cycling potential for 12 times.

tential 12 times between -0.1 and 0.85 V vs. Ag|AgCl|NaCl (satd.) at a sweep rate of 50 mV s $^{-1}$ in 1.0 M HClO $_4$ solution containing 0.8 M *N*-methylaniline. Many spherical shape microstructures are seen in the SEM picture of Figure 2a at a magnification of $2000\times$. The average diameter of microspheres is around 1.9 μm with a rather wide distribution in size. At a higher magnification of $13,000\times$, one can notice that some of the microspheres of different sizes are fused with each other (Figure 2b). However, isolated microspheres of various sizes are also seen in the micrographs. For example, Figure 2c shows a micrograph of one such isolated microsphere having a diameter of 3.5 μm . Noteworthy here is that such isolated microspheres are an integral part of the polymer film and are visible over entire surface of PNMA films.

The size of these microspheres depended on several factors including monomer concentration, scan rate and cycle number. These results are summarized in Table I. When the PNMA film was grown from a lower monomer concentration of 0.2 M with all other parameters being kept unchanged, the average diameter of microspheres was 0.95 μm , smaller than 1.9 μm obtained for the 0.8 M monomer concentration (sample 1 and 3 in Table I). Interestingly, lowering of the monomer concentration down to 0.05 M did not yield microspheres at all. The scan rate also affected the size of microspheres. At 10 mV s $^{-1}$, the average size of microspheres is around 4.3 μm , whereas the size of microspheres reduced to 1.2 μm when the scan rate was 100 mV s $^{-1}$ (sample 7 and 8, Table I). Furthermore, the number of microspheres and the size were affected by the cycle number. The average microsphere sizes corresponding to 2, 4, 8 and 12 cycles were found to be 0.70 , 1.3 , 1.7 and 1.9 μm , respective-

Table I. Average diameters of PNMA microspheres as a function of monomer concentration, scan rate and cycle number

Sample number	Monomer concentration /M	Scan rate /mV s $^{-1}$	Cycle number	Average diameter of microspheres / μm
1	0.2	50	12	0.95
2	0.4	50	12	1.7
3	0.8	50	12	1.9
4	0.8	50	8	1.7
5	0.8	50	4	1.3
6	0.8	50	2	0.7
7	0.8	10	12	4.3
8	0.8	100	12	1.2

For all samples the potential used for cycling was in the range of -0.1 V to $+0.85$ V. Electrolyte solution was prepared in 1 M HClO $_4$ solution.

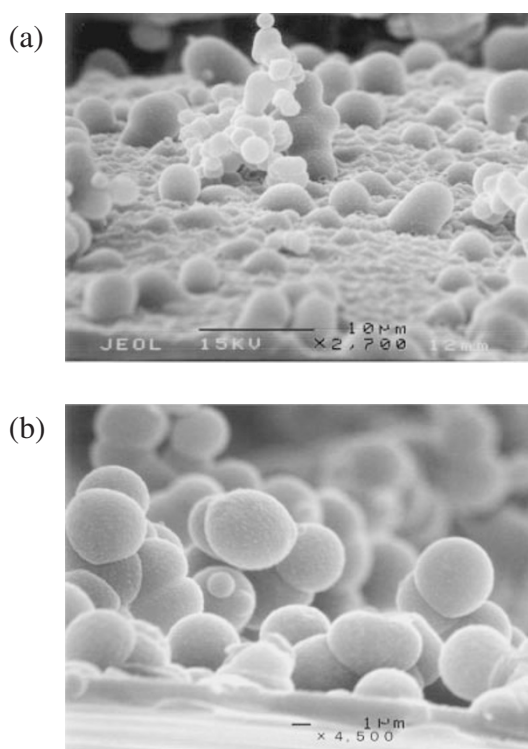


Figure 3. Bird's eye views of PNMA film taken at different magnifications of (a) $2,700\times$ and (b) $4,500\times$. The PNMA film was the same as that of Figure 2.

ly (Table I). Important to mention here is that the generation of microspheres starts at very early stages of polymerization process and completely spherical polymer structures are visible even when the potential was swept just for two times. Up to four cycles, the surface of the polymer on which microspheres were scattered was comparatively smooth. After 8 cycles, however, the polymer surface was almost completely covered with microspheres.

Bird's eye views of a PNMA film at 12 cycles are presented in Figure 3. Figure 3a shows a wave-like platform comprising various sphere-like structures at different stages of growth. At a higher magnification of $4,500\times$, the growth of microspheres on the surface of polymer is seen more clearly and several microspheres interconnect with each other leading to large clusters as depicted in Figure 3b. The clusters in Figure 3b look like cultivated button-shaped mushroom. These clusters are dominantly present on the polymer surface. The thickness of the dense part of PNMA layer was found to be 1.6 μm from a cross sectional view of the film.

The successful formation of microspheres strongly depended on the sort of dopant anions and the substituents attached to *N*-position. Among a series of substituted PANIs, only PNMA showed the formation of microspheres significantly (Figure 4). Although microspheres were observed on the film surface in case

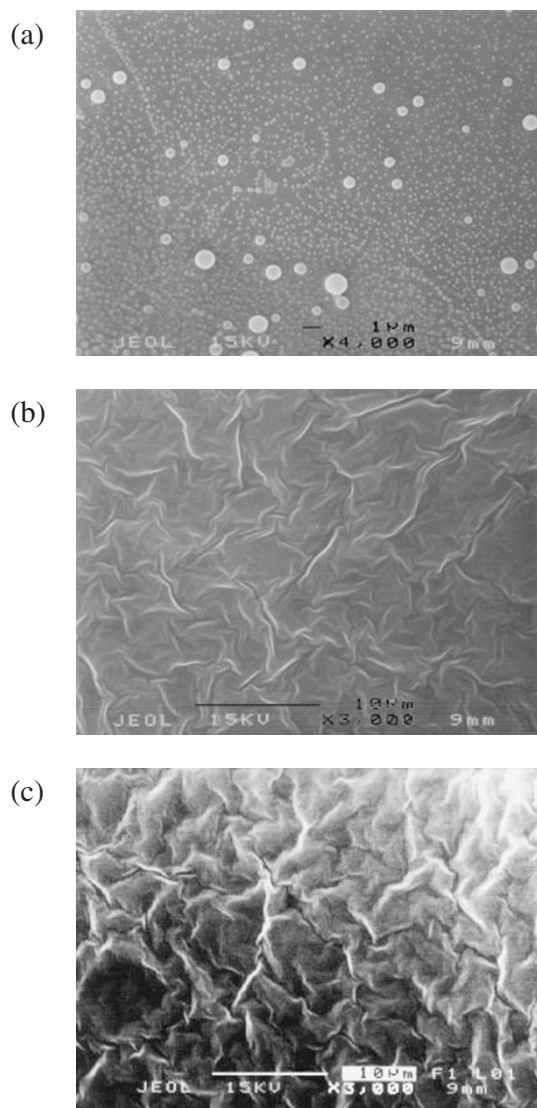


Figure 4. SEM pictures of different derivatives of PANI: (a) poly(*N*-ethylaniline) (PNEA), (b) poly(*N*-propylaniline) (PNPA) and (c) poly(*N*-butylaniline) (PNBA). Monomer concentrations were 0.8 M for PNEA and PNPA and 0.4 M for PNBA. The films were prepared at scan rate of (50 mV s^{-1}) by cycling potential for 12 times.

of poly(*N*-ethylaniline), the number density and size of microspheres were smaller than that of PNMA. For poly(*N*-propylaniline) and poly(*N*-butylaniline), on the other hand, the surface of the film was found to be relatively free of microspheres. It was also found that the nature of dopant anion affects the microsphere formation ability. Among five different acids employed for polymerization of *N*-methylaniline, only HBF_4 and HClO_4 yielded microspheres embedded in a compact PNMA layer. On the other hand, SEM images of Cl^- , NO_3^- and SO_4^{2-} doped PNMA revealed granular or coral structures.

In order to get a detail insight into the growth process of microsphere, the in-situ absorption spectra were recorded during electropolymerization of *N*-methyl-

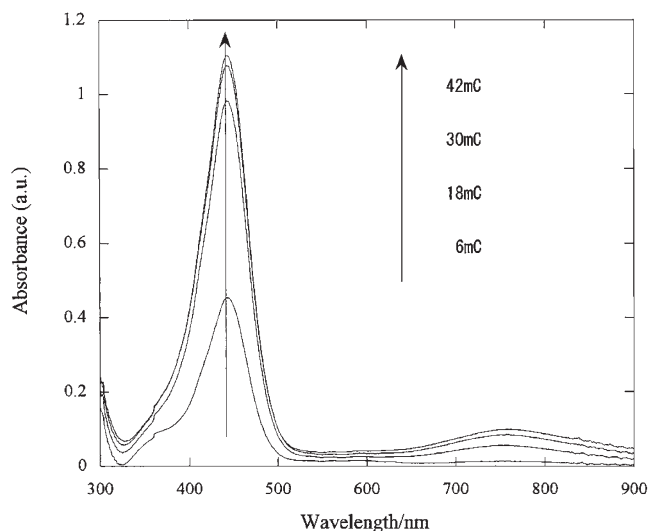


Figure 5. (a) *In-situ* absorption spectra recorded during electropolymerization of NMA. Monomer concentration was 5 mM.

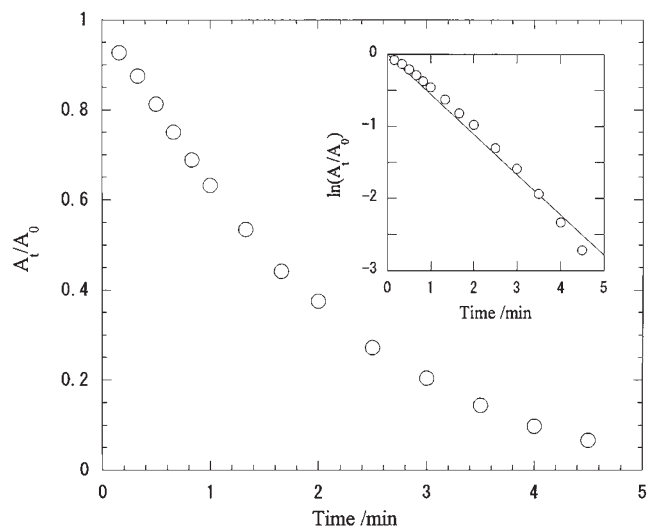


Figure 6. Decay of absorbance at 440 nm after interrupting electrolysis. Inset shows plot of $\ln(A_t/A_0)$ vs. time. The slope value represents lifetime of intermediate species.

aniline. From Figure 5 one can notice that the peak at around 440 nm enhances as a function of the amount of charges passed through the electrode. This absorption peak is ascribable to intermediate species generated in early stages of polymerization process and plays vital role in formation of polymer as elaborated in details in the later part of discussion. Interestingly, when we interrupted the polymerization process, this species showing a peak at 440 nm undergoes decay (Figure 6). The lifetime of intermediate species has been deduced from the plot of $\ln(A_t/A_0)$ vs. time (inset, Figure 6). Furthermore, when we took SEM micrographs of PNMA film kept in the electrolyte solution after electrolysis, several larger size microspheres were observed on the polymer surface

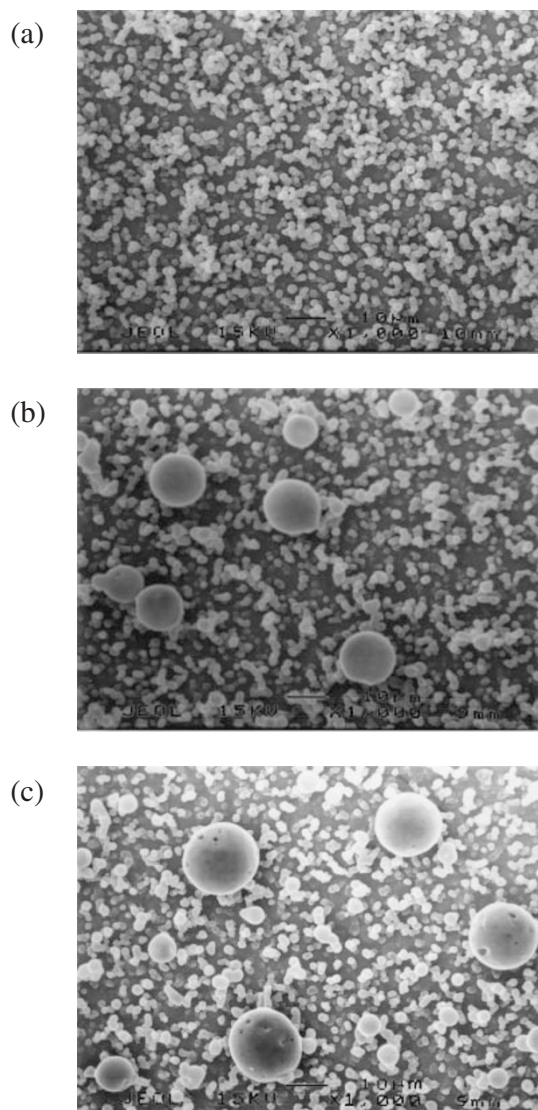


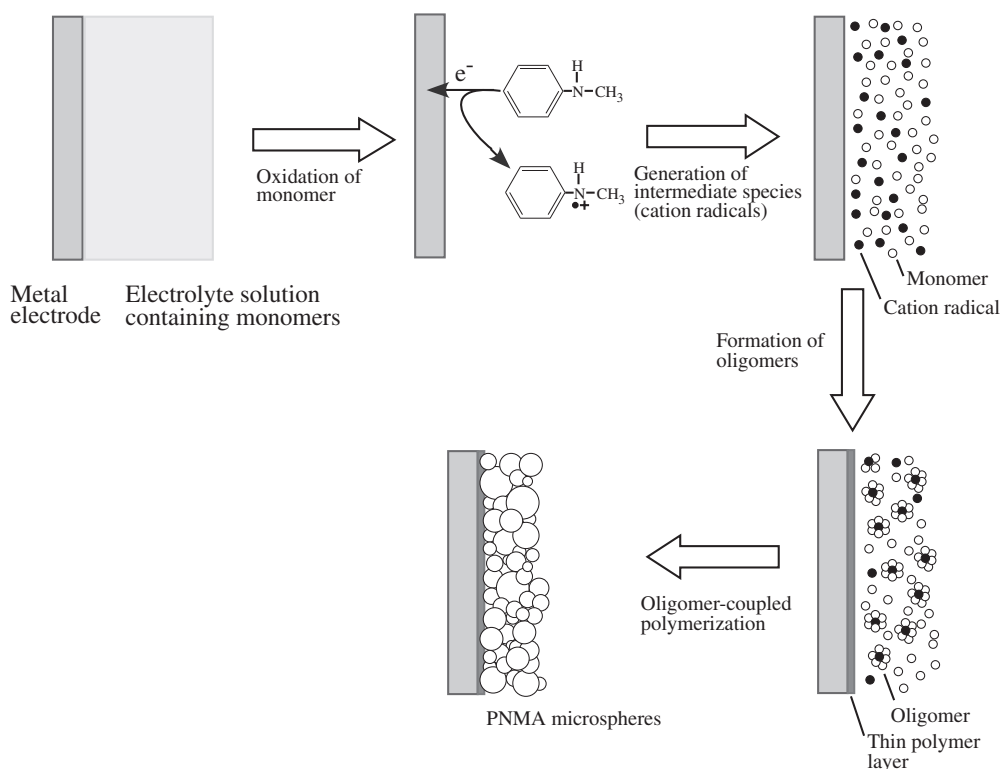
Figure 7. SEM pictures of (a) PNMA film removed immediately after electrolysis, (b) 10 min after electrolysis and (c) 15 min after electrolysis. The films were grown from 1 M HClO₄ solution containing 0.8 M *N*-methylaniline.

(Figure 7). This observation clearly indicates that the intermediate species produced during initial stages of polymerization process interacts with the oligomers present in the solution after electrolysis.

Although it is difficult to elucidate exact growth mechanism of microspheres, we presume that the polymerization process that occurs in solution plays a crucial role in the formation of PNMA microspheres. It is well documented in the literature that electropolymerization of *N*-methylaniline proceeds via an EC mechanism, *i.e.*, electrochemical oxidation of a monomer followed by a coupling of the resulting intermediate species with the monomer.²⁴ Successive couplings of the oligomeric species occur in solution and a polymer chain will reach a critical length required for precipitation. A similar mechanism is

postulated for the nucleation and growth of PANI and *N*-(3-sulfopropyl)aniline, although the intermediate species for PNMA are much long-lived compared with the one for PANI and its ring alkylsubstituted derivatives.^{25–27} The lifetime of intermediate for PNMA in the present case is determined to be 100 s much longer than a few seconds reported for PANI. This implies that for PNMA the coupling reaction can take place in solution slowly and isotropically. Thus, polymerization initiated around some nucleation center in solution might be responsible for the formation of isotropic small particles of PNMA, *i.e.*, conducting microspheres. The increase in the size of microspheres on keeping the film in the solution after electrolysis clearly indicates that interaction of intermediate with monomer is a predominant step in yielding conducting microspheres. The overall mechanism has been summarized in Scheme 1. The intermediate species showing a characteristic band at 440 nm might be ascribed to radical cations, which were postulated to be formed in early stages during the electrooxidation of aniline and related compounds in previous works.^{25–27}

The film formation process and the resulting film structure of PANI are known to be affected by anions and the different types of mechanisms have been discussed in terms of potential-step chronoamperograms.²⁸ We have observed the difference in chronoamperogram during electropolymerization of PNMA between the two anion groups, *i.e.*, BF₄[−] and ClO₄[−], and Cl[−], NO₃[−] and SO₄^{2−}.²⁹ After the initial current maximum, PNMA films prepared in solutions containing either of anions of the latter group showed an increase in current with time, indicating a marked enhancement of an effective surface area due to a polymer growth accompanying a nucleation on the substrate. For ClO₄[−] and BF₄[−], the use of which gave microspheres, on the contrary, the current decayed with time, suggesting precipitation of solution grown microspheres on the dense layer of PNMA film. At present, we are not in a position to comment further on the effect of anions on the microsphere formation. However, it is interesting to recall the Hofmeister series of anions representing their lyophilicity, ClO₄[−] > BF₄[−] > I[−] > NO₃[−] > Br[−] > Cl[−] ≫ HCO₃[−] ~ OAc[−] ~ SO₄^{2−} ~ HPO₄^{2−}. Only the two of the most lyophilic anions give microspheres, hinting the possible dependence of PNMA microsphere formation on the nature of anions. To give more validity to the above statement, PNMA polymerization was carried out using mixed acids (*i.e.*, HClO₄ and H₂SO₄). When concentration of HClO₄ was reduced to 20%, the formation of microsphere was totally inhibited suggesting that lyophilic nature of anion is an important criteria in governing microsphere formation. The four probe conductivity of PNMA film com-



Scheme 1.

prising of microsphere was found to be 0.74 S cm^{-1} , indicating a conducting nature of the microspheres. The molecular formula deduced from the elemental analysis ($\text{C}_7\text{H}_{6.69}\text{N}_{1.03}(\text{ClO}_4)_{0.38}$) was consistent with a single repeat unit and the maximum doping level of PNMA thus found was around 38%.

Acknowledgment. One of the authors (R. Patil) acknowledges a Grant-in-Aid for Scientific Research No. 15750156 from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES

1. A. G. MacDiarmid and A. J. Epstein, *Faraday Discuss. Chem. Soc.*, **88**, 317 (1989).
2. H. S. Nalwa, Ed., "Handbook of Organic Conductive Materials and Polymers," Vol. 2, John Wiley & Sons, New York, N.Y., 1997.
3. T. A. Skotheim, R. L. Elsenbaumer, and J. F. Reynolds, Ed., "Handbook of Conducting Polymers," 2nd ed., Marcel Dekker, New York, N.Y., 1998.
4. J. W. Chevalier, J. Y. Bergeron, and L. H. Dao, *Macromolecules*, **25**, 3325 (1992).
5. G. Zotti, N. Comisso, G. D'Aprano, and M. Leclerc, *Adv. Mater.*, **4**, 749 (1992).
6. W. A. Gazotti Jr. and M. A. DePaoli, *Synth. Met.*, **80**, 263 (1996).
7. Z. H. Wang, A. Ray, A. G. MacDiarmid, and A. J. Epstein, *Phys. Rev. B*, **43**, 4373 (1991).
8. P. Ocon, P. Herrasti, J. M. Vara, L. Vazquez, R. C. Salvarezza, and A. J. Arvia, *J. Phys. Chem.*, **98**, 2418 (1994).
9. A. G. Bedekar, S. F. Patil, R. C. Patil, and K. Vijayamohanan, *J. Mater. Chem.*, **5**, 963 (1995).
10. A. Raghunathan, P. K. Kahol, and B. J. McCormick, *Synth. Met.*, **100**, 205 (1999).
11. G. Planes, G. M. Morales, M. C. Miras, and C. Barbero, *Synth. Met.*, **97**, 223 (1998).
12. T. Lindfors and A. Ivaska, *J. Electroanal. Chem.*, **531**, 43 (2002).
13. R. Sivakumar and R. Saraswathi, *Synth. Met.*, **138**, 381 (2003).
14. Q. Hao, M. Rahm, D. Weiss, and V. Mirsky, *Microchim. Acta*, **143**, 147 (2003).
15. W. S. Huang, B. D. Humphrey, and A. G. MacDiarmid, *J. Chem. Soc., Faraday Trans. 1*, **82**, 2385 (1986).
16. M. Fujii, K. Arai, and K. Yoshino, *J. Phys.: Condens. Matter*, **3**, 7207 (1991).
17. A. G. Bedekar, S. F. Patil, R. C. Patil, and C. Agashe, *Polym. J.*, **27**, 319 (1995).
18. A. G. Bedekar, S. F. Patil, R. C. Patil, and C. Agashe, *J. Phys. D: Appl. Phys.*, **27**, 1727 (1994).
19. E. Mathlowitz, J. S. Jacob, Y. S. Jong, G. P. Carina, D. E. Chickering, P. Chaturvedi, C. A. Santos, K. Vijayaraghavan, S. Montgomery, M. Basett, and C. Morrell, *Nature*, **386**, 410 (1997).
20. H. Huang and E. E. Resen, *J. Am. Chem. Soc.*, **121**, 3805 (1999).
21. G. Shuhorukov, L. Dahne, J. Hartmann, E. Donnath, and H. Mohwald, *Adv. Mater.*, **12**, 112 (2000).
22. H. Eisazadeh, K. J. Gilmore, A. J. Hodgson, G. Spinks, and G. G. Wallace, *Colloids Surf. A*, **103**, 281 (1995).

23. H. Eisazadeh, G. Spinks, and G. G. Wallace, *Polym. Int.*, **37**, 87 (1995).
24. A. Malinauskas and R. Holze, *Ber. Bunsenges. Phys. Chem.*, **101**, 1859 (1997).
25. A. Malinauskas and R. Holze, *Electrochim. Acta*, **43**, 2413 (1998).
26. A. Malinauskas and R. Holze, *Electrochim. Acta*, **44**, 2613 (1999).
27. E. M. Genies and M. Lapkowski, *J. Electroanal. Chem.*, **236**, 189 (1987).
28. R. Cordova, M. A. del Valle, A. Arratia, H. Gomez, and R. Schrebler, *J. Electroanal. Chem.*, **377**, 75 (1994).
29. J. Yano, F. Takamura, K. Masaoka, S. Yamasaki, Y. Ota, and A. Kitani, *Synth. Met.*, **135–136**, 417 (2003).