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Monodisperse and isolated microspheres of poly(*N*-methylaniline) prepared by dispersion polymerization

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ABSTRACT

Monodisperse and isolated microspheres of poly(*N*-methylaniline) were successfully prepared through chemical polymerization of *N*-methylaniline by $S_2O_8^{2-}$ in adipic acid containing poly(vinylpyrrolidone) (PVP). Mean diameters of the microspheres with smooth surfaces changed from 320 to 100 nm by increasing the reaction temperature from 25 to 75 °C. The concentration of PVP did not affect much the size of microspheres, but the increased PVP concentration led to longer induction times for the onset of dispersion polymerization.

1. Introduction

Since the early work of Armes et al. in 1987, a number of studies have been devoted to preparation of colloidal particles comprising conducting polymers such as polypyrrole, polyaniline (PANI), poly(3,4-ethylenedioxythiophene), and poly(*o*-toluidine) [1–7]. The conducting polymers have advantages of light weight, low environmental load, and possible low cost over metals as electrically conductive materials. Because of their unique properties as well as the conductive nature, they have been investigated as materials for primary and secondary batteries, a variety of sensors, electrochromic devices, conductive paints, and antistatic coatings [8]. When they are attempted to use as functionality materials, however, we readily encounter a problem of processability in most applications [9]. This problem is due mainly to a low solubility of these polymers in common solvents. One way for improving this processability problem is to prepare conducting polymers in colloidal forms as suggested by Armes et al. [1]. Up to now, colloidal particles composed of conducting polymers have been obtained by using polymeric stabilizers or by microemulsion processes [10–15]. Ultrafine silica particles have also been used to form PANI dispersions [16].

Recently, we have found that without any templates or steric stabilizers, electrochemical or chemical oxidation of *N*-methylaniline (NMA) under appropriate conditions leads exceptionally to the formation of micro- to submicrometer-sized spheres with smooth surfaces [17–20]. This was the first report on the self-assembling nature of NMA for the microsphere formation. Clarification of its detailed mechanisms may allow us to get a hint to design monomer structures for creating soft, conductive, and intentional-shaped materials. From this point of view, the finding of the self-assembling formation of microspheres from NMA is of great interest and also the smooth-surfaced conductive microspheres are of practical importance because of a negligible scattering of light on their smooth surfaces. The resulting poly(*N*-methylaniline) (PNMA) has the advantage of stability over its parent polymer, PANI, because imide groups of PANI are blocked by methyl groups and thus the oxidative degradation is reduced in PNMA. Although this accompanies a lowering of conductivities,

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PNMA films still have reasonable conductivities of 10^{-4}–10^{-2} S cm^{-1} [2,21,22]. Unfortunately, however, the PNMA microspheres obtained earlier were not uniform in diameter and fused in part to the electrode surface or with each other when prepared electrochemically or chemically [18,20].

In the present study, a successful formation of monodisperse and isolated PNMA microspheres with smooth surfaces is described. We also report that by changing the reaction temperature and reaction time, the mean diameters of the PNMA microspheres can be controlled.

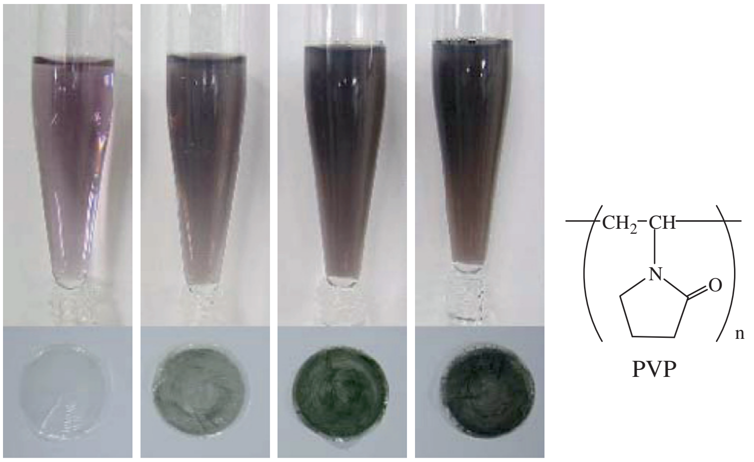
2. Experimental

NMA (Sigma–Aldrich, Japan) used as monomer was of reagent grade and distilled under reduced pressure. Adipic acid (Wako Chemicals) and $(NH_4)_2S_2O_8$ (APS) (Sigma–Aldrich, Japan) were also of reagent grade and used as received without purification. Poly(vinylpyrrolidone) (PVP) (K-30, Junsei Chemicals) was used without further purification. The chemical structure of PVP is shown in Fig. 1. The morphology and diameter of PNMA microspheres were observed with a JEOL JSM-6320F field-emission scanning electron microscope (SEM). A thin Pt layer was sputtered on the sample prior to the SEM measurements. Chemical polymerization was carried out by adding a 25 ml aqueous solution of APS (25 mM) into a 25 ml water containing NMA (25 mM), adipic acid (25 mM), and a given weight of PVP, unless otherwise stated. Absorption spectra were taken on a Shimadzu UV-3101 PC spectrophotometer, where measurements were made in a quartz cell of a 10 mm optical pathlength.

3. Results and discussion

It has been already found that the sorts of acid and oxidant, and the concentration ratio of acid to monomer are critical for the self-assembling formation of microspheres with smooth surfaces by oxidative polymerization of NMA [20]. The morphologies of PNMA were granular or fibrous when prepared in HNO_3, HCl, and H_2SO_4, while in acid solutions such as $HClO_4$, HBF_4, and adipic acid, PNMA microspheres with smooth surfaces were obtained. The result implies that the lyophilicity of anions in acids is closely related to the difference in morphology of the resulting polymers and that dopant anions with higher lyophilicity yield microspheres with smooth surfaces. Among oxidizing agents tested, only APS gave microspheres with smooth surfaces. Microspheres were also formed when $K_2Cr_2O_7$ was used, but their surfaces were very rough like aggregation of smaller particles. It was found also that the increased concentration ratio of adipic acid to NMA at a constant APS concentration resulted in the formation of microspheres with coarse surfaces. On these bases, throughout this study adipic acid and APS were used and the concentration ratio of NMA to adipic acid was kept constant at unity. Although polymer particles with smooth surfaces were obtained under appropriate conditions in our previous studies, most of them were deposited after centrifugation because of their aggregation in solution. In the present study, chemical polymerization was carried out in the presence of PVP which has been frequently used as a steric stabilizer in dispersion polymerization.

Upper photographs of Fig. 1 show supernatant solutions of PNMA in centrifuging tubes obtained after centrifugation at 3000 rpm for 5 min, where polymerization was carried out for 24 h at 25 °C by adding a 25 ml aqueous solution of APS (25 mM) into a 25 ml water containing NMA (25 mM), adipic acid (25 mM), and a given weight of PVP. Lower photographs represent precipitates obtained by filtrating the respective supernatant solutions by the membrane filter of 15 nm in pore size. In the absence of PVP, the supernatant solution is amaranth purple and a negligible amount of precipitates is observed as shown in the lower photograph of Fig. 1a. When the amount of



(a) no PVP (b) 0.1 g PVP (c) 0.5 g PVP (d) 1 g PVP

Fig. 1. Photographs of (upper) supernatant solutions of PNMA prepared in the presence of (a) 0, (b) 0.1, (c) 0.5, and (d) 1 g PVP after being centrifuged at 3000 rpm for 5 min and of (lower) precipitates obtained by filtrating the supernatant solutions by membrane filters of 15 nm in pore size. Chemical structure of PVP is also shown. Polymerization conditions: [NMA] = [adipic acid] = [APS] = 25 mM, reaction time = 24 h, and reaction temperature = 25 °C.

PVP is increased, both the supernatant solution and the membrane filter become darker (Fig. 1b–d). This indicates first that polymer particles greater than 15 nm in diameter are dispersed in the supernatant solutions even after aggregated particles being eliminated by centrifugation and second that their amounts increase with the amount of PVP added.

The particles collected on the membrane filters were subjected to SEM observations after being washed with water and alcohol repeatedly, and dried in vacuum for 24 h at room temperature. Fig. 2 depicts SEM images of the polymer particles obtained from the solutions with 0, 0.1, 0.5, and 1 g PVP. When no PVP was added to the solution, it was difficult to observe particles. As shown in Fig. 2a, a small number of particles found had varying sizes below 0.3 μm in diameter and most of smaller particles were aggregated as in our previous experiments [20]. When the PVP amount is 0.1 g (Fig. 2b), the number of microspheres is increased, although the size of the particles is still not uniform and they are fused in part. In the presence of PVP equal to or above 0.5 g, a number of microspheres with a uniform size of ca. 0.3 μm in diameter are observed (Fig. 2c and d). Importantly, microspheres obtained in the presence of a sufficient amount of PVP are not fused, but isolated. This can be more clearly seen from the inset of Fig. 2d which was observed with a diluted supernatant solution. In addition, the sizes of microspheres were almost independent of the amount of PVP beyond 0.5 g so far as the reaction temperature is the same. In the literature, a number of papers describe the formation of micro- to submicrometer-sized particles based on conducting polymers. However, this may be the first to report the formation of monodisperse and isolated microspheres with smooth surfaces.

Growth processes of microspheres in solutions with and without PVP were examined at 25 °C by measuring absorption spectra of the solutions at different reaction times. The spectroscopic measurements were made by taking out 0.1 ml of the solutions and after diluting them 40 times by ethanol to quench the reaction. In this experiment, the solutions were not filtrated. Figs. 3 and 4 depict typical spectral changes of the solutions resulting from polymerization with no PVP and 0.6 g PVP, respectively, as a function of time after the start of polymerization. In both experiments, the main absorption band at 720 nm which is ascribable to a quinoid form of PNMA in the oxidation state evolves with time, although the evolution features are quite different from each other. In the absence of PVP, the 720-nm band along with the absorption background due to a light scattering from polymer particles increase from the beginning of polymerization, whereas in the PVP solution neither of them appear up to 20 min except a small absorption band at 510 nm. The 510-nm band observed commonly in Figs. 3 and 4 is ascribable to oligomeric species [23]. In the electrochemical polymerization of NMA, *in situ* absorption measurements showed a clear absorption band at 440 nm at an initial stage of polymerization and was ascribed to intermediate species whose lifetime was as long as 100 s [18]. This absorption band is not seen during the present experiments in both solutions with and without PVP, because the intermediate species, most likely radical cations, are quenched by ethanol.

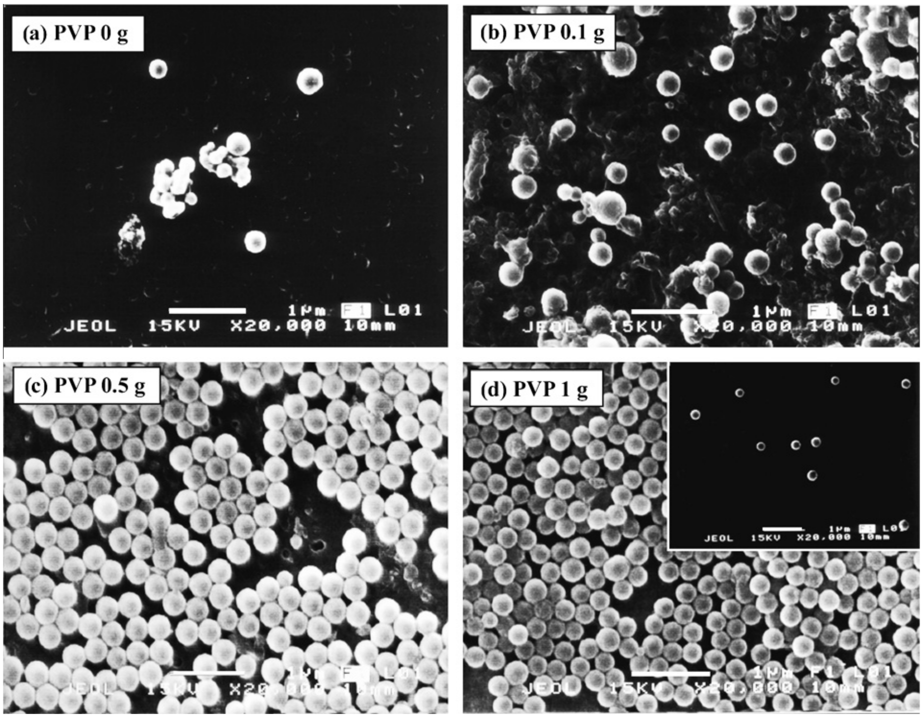


Fig. 2. SEM pictures of polymer particles obtained from the solutions with (a) 0, (b) 0.1, (c) 0.5, and (d) 1 g PVP. Polymerization conditions are the same as in Fig. 1. The inset of (d) is obtained by diluting the solution.

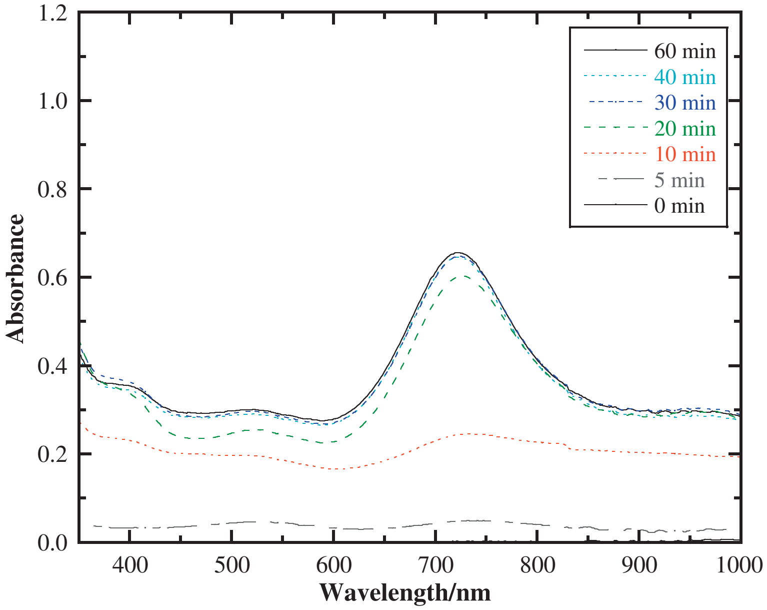


Fig. 3. Absorption spectra during chemical polymerization of NMA in the absence of PVP. The measurements were made by diluting the solutions 40 times by ethanol. Polymerization conditions: [NMA] = [adipic acid] = [APS] = 25 mM and reaction temperature = 25 °C.

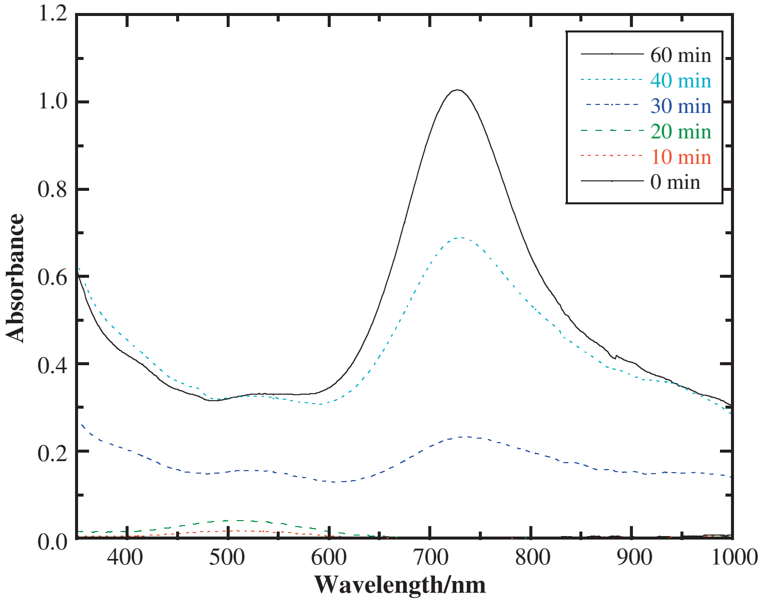


Fig. 4. Absorption spectra during chemical polymerization of NMA in the presence of 0.6 g PVP. The measurements were made by diluting the solutions 40 times by ethanol. Polymerization conditions: [NMA] = [adipic acid] = [APS] = 25 mM and reaction temperature = 25 °C.

Fig. 5 illustrates growth features of microspheres in solutions with different PVP amounts evaluated from the absorption spectra such as shown in Figs. 3 and 4, where the absorbance at 720 nm subtracted by the absorption background is used as a measure of the quantity of microspheres. When the solution contains no PVP, the growth curve exhibits a sigmoidal character and the absorbance reaches a plateau at ca. 20 min. With 0.1 g PVP, no significant change of the curve is seen except for the increase of absorbance in the plateau region. By increasing the PVP amount further, however, the onset of the absorbance increase starts to delay, showing the presence of an induction period for the start of polymerization. The increase of the PVP amount also leads to a slight increase in maximum absorbance. In view of the fact that the measured absorbance includes contribution from both fused and isolated microspheres, and a greater PVP amount tends to prevent aggregation of microspheres, this suggests an

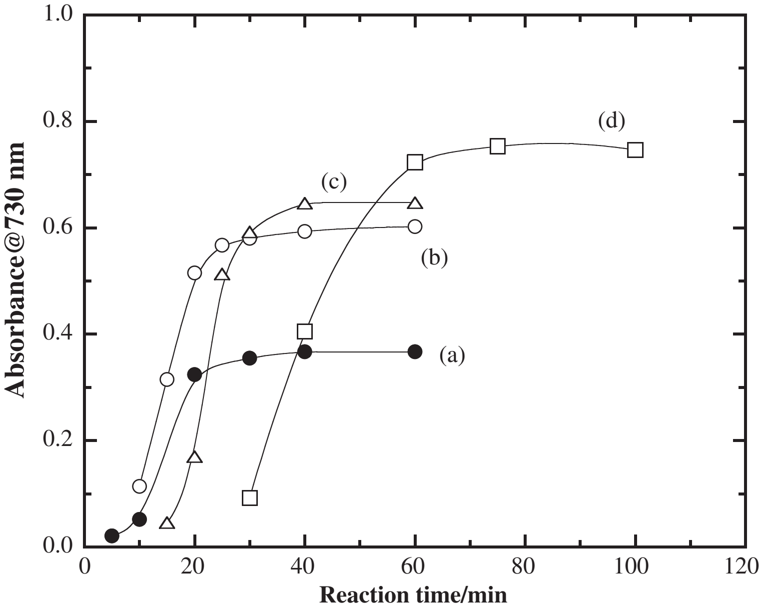


Fig. 5. Changes in absorbance at 720 nm with time observed in solutions with (a) 0, (b) 0.1, (c) 0.3, and (d) 0.6 g PVP. Other polymerization conditions: [NMA] = [adipic acid] = [APS] = 25 mM and reaction temperature = 25 °C.

enhanced conversion yield of NMA to isolated PNMA microspheres by adding PVP. The presence of induction periods is characteristic of chemical and electrochemical polymerization processes for the PANI family, and has been explained reasonably in terms of the two-step polymerization consisting of a homogeneous oxidation of monomers and a heterogeneous oxidation of monomers on the surface of oxidized polymers [23–25]. The first oxidation process is a rate-determining step and the rate constant of the second step, k_2, is known to be orders of magnitude higher than the first one, k_1. A higher ratio of k_1/k_2 results in a longer induction period. In the present case, it is likely that PVP reduces the rate of the second step by making the polymer particles stabilized, which may also lead to effective isolation of individual microspheres.

Growth of microspheres during the induction period was studied with SEM, where polymerization was made in solutions with 0.6 g PVP at different reaction temperatures of 25, 50, and 75 °C. We observed polymer particles deposited on the membrane filters without centrifugation of the resulting solutions. SEM images of precipitates obtained at 25 °C and at different polymerization times are shown in Fig. 6. At 360 s after polymerization, we see small and isolated particles. They grow rapidly with time until their diameter reaches 320 nm which is close to the mean diameter of microspheres obtained after 24 h in the solutions with 0.5 and 1 g PVP at 25 °C (Fig. 2). Afterwards, no appreciable change in the number and diameter of microspheres was observed until 30 min when the 720-nm absorption band due to PNMA microspheres starts to increase abruptly (see Fig. 5). It is interesting to note here that even in the induction period for polymerization microspheres are generated in solutions, although their number is extremely small compared with that observed at 24 h after polymerization. Most likely, there are a limited number of nuclei to mediate polymerization of NMA in solutions. When the temperature is raised to 50 °C (Fig. 7), both the size and number of microspheres increase with time, although the microsphere size stays constant at 120 nm after 180 s. At the reaction temperature of 75 °C (Fig. 8), microspheres generated at 10 s are as small as 40 nm. The size increases with time: 60 nm at 20 s and 100 nm at 180 s, but no significant increase in the number of microspheres is observable in this time range. The results of the SEM observations are summarized in Fig. 9 as a plot of mean diameter vs. reaction time, together with a similar plot for polymerization without PVP at 25 °C. It is readily seen that the saturation values of microsphere sizes are determined by the reaction temperature and they are 320, 130, and 100 nm at 25, 50, and 75 °C, respectively. We find also from Fig. 9 that microspheres start and stop growing in a relatively short period of 2 min or less, depending on the polymerization temperature. The feature is in clear contrast to the gradual increase of microsphere sizes observed for polymerization in solutions without PVP, although mean diameters of microspheres obtained at the same temperature of 25 °C do not differ much in solutions with and without PVP.

FT-IR spectra of PNMA microspheres prepared under different conditions are compared in Fig. 10. These spectra have common absorption bands at 821, 1496, and 1575 cm^{-1} due to para-disubstituted aromatic ring, C=C stretching of benzenoid ring and C—N stretching of quinoid ring, respectively, demonstrating that the microspheres have structures characteristic of polyaniline and its derivatives reported earlier [2,26–28]. A broad band due to $\mathrm{ClO_4^-}$ appears at 1101 cm^{-1} for PNMA microspheres prepared in $\mathrm{HClO_4}$ solution (Fig. 10a), while a sharp band at 1040 cm^{-1}

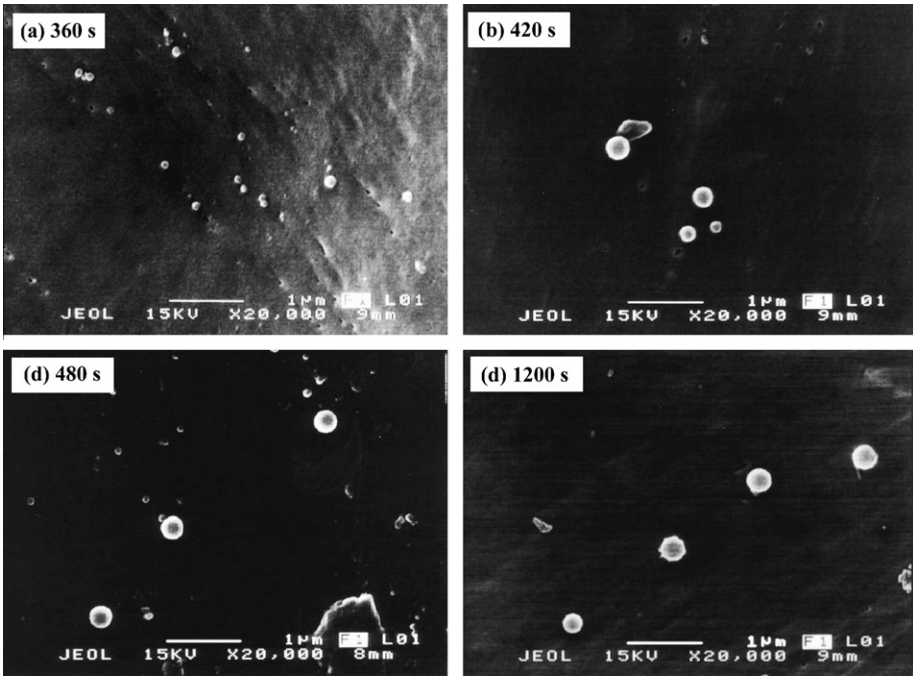


Fig. 6. SEM images of polymer particles formed at 25 °C (a) 360, (b) 420, (c) 480, and (d) 1200 s after polymerization in solutions with 0.6 g PVP. Other polymerization condition: [NMA] = [adipic acid] = [APS] = 25 mM.

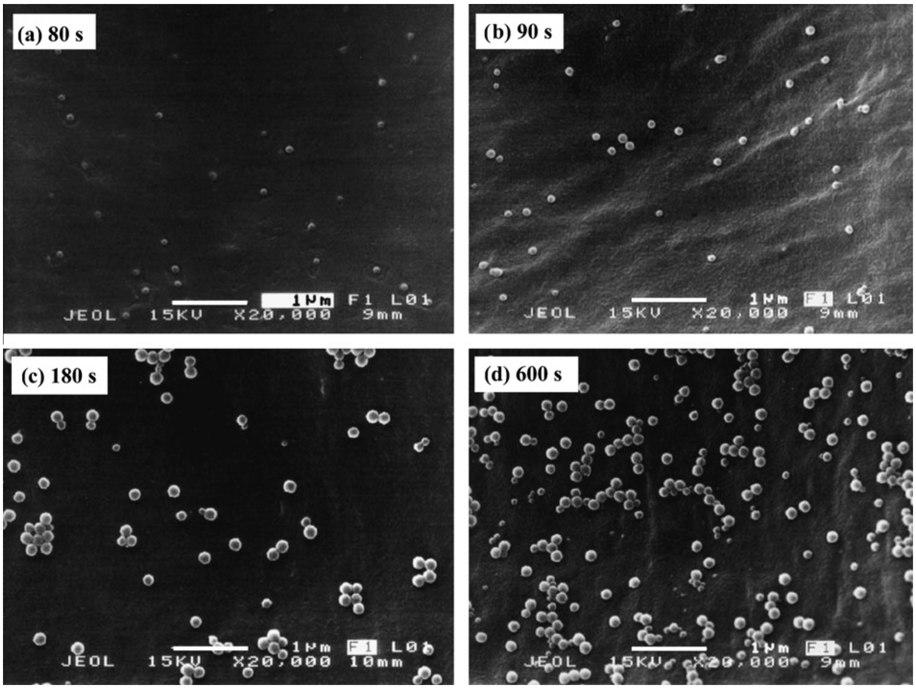


Fig. 7. SEM images of polymer particles formed at 50 °C (a) 80, (b) 90, (c) 180, and (d) 600 s after polymerization in solutions with 0.6 g PVP. Other polymerization condition: [NMA] = [adipic acid] = [APS] = 25 mM.

observed for PNMA microspheres prepared in adipic acid with and without PVD is ascribable to carboxyl group of adipic acid (Fig. 10a and b). The results indicate that corresponding anions are incorporated into PNMA microspheres. In addition, a small absorption band is seen at 1680 cm^{-1} for all the polymers prepared. The wavenumber

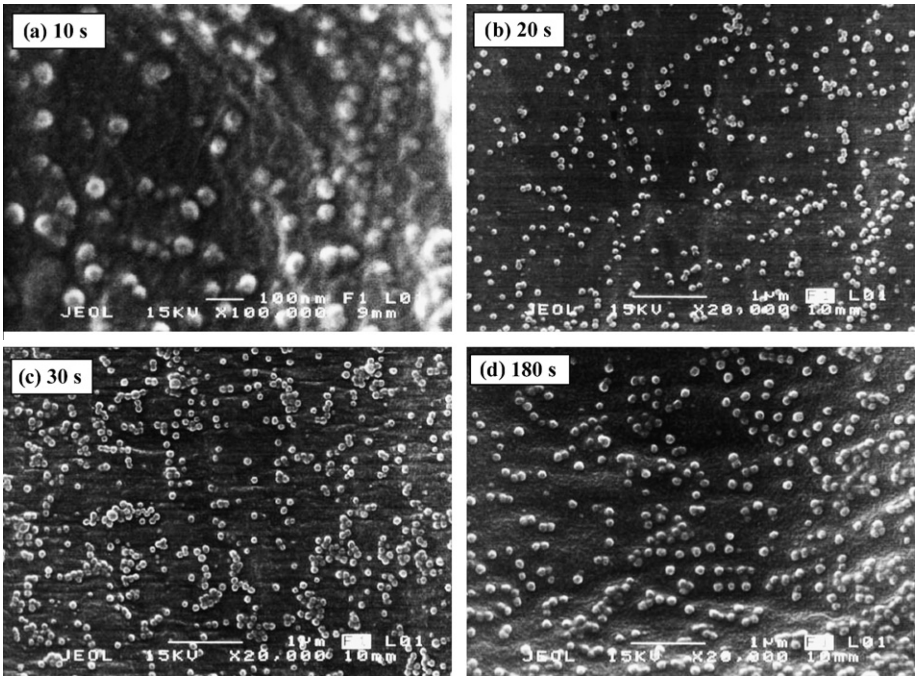


Fig. 8. SEM images of polymer particles formed at 75 °C (a) 10, (b) 20, (c) 30, and (d) 180 s after polymerization in solutions with 0.6 g PVP. Other polymerization conditions: [NMA] = [adipic acid] = [APS] = 25 mM.

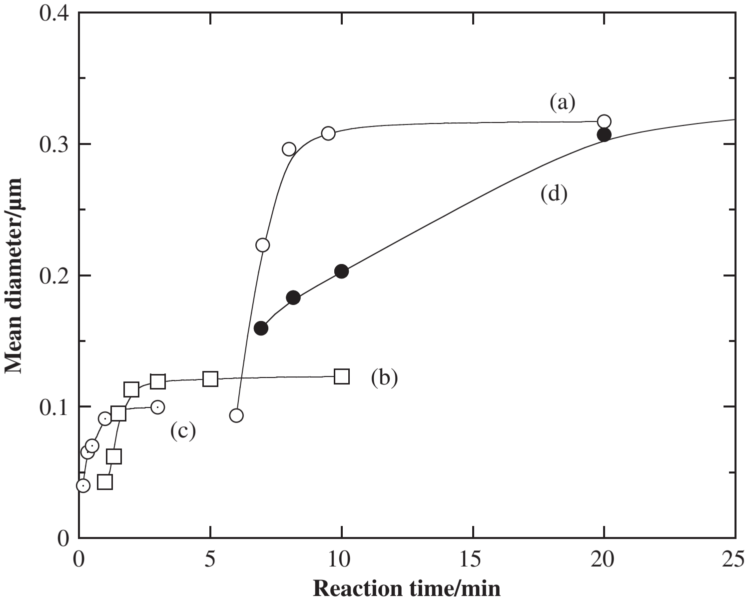


Fig. 9. Plots of mean diameter of microspheres vs. reaction time for polymerization in solutions with 0.6 g PVP at (a) 25, (b) 50, and (c) 75 °C, and (d) in solution without PVP at 25 °C. Other polymerization condition: [NMA] = [adipic acid] = [APS] = 25 mM.

is very close to 1650 cm^{-1} that has been ascribed to carbonyl group of PVP. Because this absorption band appears even for microspheres prepared in solutions without PVD, PNMA microspheres formed in the presence of PVP may include only a negligible amount of PVP, if any.

4. Conclusions

In the presence of PVP, chemical polymerization of *N*-methylaniline by $(NH_4)_2S_2O_8$ in adipic acid yielded monodisperse and well-isolated PNMA microspheres with

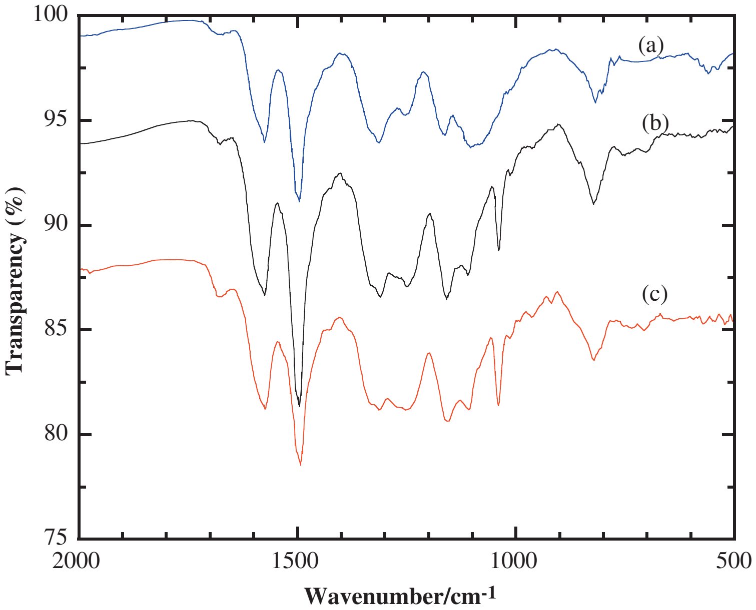


Fig. 10. FT-IR spectra of PNMA microspheres obtained from solutions containing (a) $HClO_4$, (b) adipic acid, and (c) adipic acid + 0.6 g PVP. Other polymerization conditions: [NMA] = [acid] = [APS] = 25 mM, reaction time = 24 h, and reaction temperature = 25 °C.

smooth surfaces. Mean diameters of the microspheres were primarily controlled by the reaction temperature: 320–100 nm for the change in temperature from 25 to 75 °C. Induction periods were present for the polymerization and enhanced by increasing the amount of PVP. It was found further that the limited number of microspheres grew even in the induction period and the growth time was as short as a few minutes at 25 °C and much shorter at elevated temperatures.

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