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SHORT COMMUNICATION

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Synthesis of needle-like crystalline particles by chemical-oxidative dispersion polymerization of xylidine

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Abstract Chemical-oxidative dispersion polymerization of 3,5-xylidine was carried out in an aqueous medium with ammonium persulfate as an oxidant and polyvinylalcohol as a stabilizer. The polymerization proceeded smoothly at room temperature, resulting in a stable polyxylidine (PXy) dispersion. The produced PXy particles had two types of shapes: needle-like and spherical. Results obtained by electron diffraction and X-ray diffraction measurements indicated that the PXy needle-like particles had a crystalline structure.

Key words Xylidine – chemical-oxidative polymerization – dispersion polymerization – needle like particle – crystalline structure

Introduction

Armes and his coworkers reported that polypyrrole particles were produced by chemical-oxidative polymerization in an aqueous medium in the presence of iron (III) chloride as an oxidant and a pellet of the particles had electrical conductivities [1]. Abe and his coworkers showed that the chemical-oxidative polymerization of aniline in HCl aqueous solution was possible with ammonium persulfate (APS) as an oxidant [2]. Spherical and needle-shaped polyaniline particles were produced using various stabilizers by Vincent and coworker [3]. Toshima and coworker carried out the polymerizations of aniline and its derivatives such as 3,5-xylidine (Xy) using cerium(IV) sulfate or APS as an oxidant, and pointed out that no polymeric product was obtained from Xy with APS [4]. However, we obtained poly(3,5-xylidine)(PXy) by chemical-oxidative polymerization with APS in an aqueous medium. This difference seems to depend mainly on the difference in the ionization of Xy in both systems, which will be reported in a forthcoming article.

In this study, it is reported that needle-like crystalline particles are produced by chemical-oxidative dispersion polymerization of Xy, which starts from a homogeneous aqueous medium of Xy with APS and polyvinylalchohol (PVA) stabilizer.

Experimental

Xy, chlorobenzene, dimethylformamide (DMF), toluene, tetrahydrofuran (THF), and *N*-methyl-2-pyrrolidone (NMP) were used as received from Nacalai Tesque Co. APS of reagent grade was purified by recrystallization. Deionized water with a specific conductivity of 5×10^6 Ωcm was distilled once with a Pyrex distillator. PVA was supplied by Nippon Synthetic Chemical (Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%).

The chemical-oxidative dispersion polymerization of Xy was carried out at 25 °C under a nitrogen atmosphere in a glass cylindrical reactor with a magnetic stirrer.

The amount of unreacted Xy was measured by gas chromatography (Yanagimoto MFG Co., Ltd., G-2800F) with nitrogen as a carrier gas. Chromosorb WAW-DMCS (stationary phase, 25% polyethyleneglycol) was used as the column packing. DMF and chlorobenzene were used, as a solvent and as a standard reagent, respectively. The temperatures of the measurement were: injector, 250 °C; detector, 250 °C; column, 120 °C; column temperature was raised linearly to 180 °C on detection of a standard peak (a peak of chlorobenzene).

Thermogravimetric-differential thermal analysis (TG-DTA) was carried out with a Seiko Instruments TG/DTA 220U. For the measurements, the sample was analyzed from 25 °C to 500 °C with a heating rate of 10 °C/min under a nitrogen atmosphere.

PXy particles were observed with a Nikon MICROPHOT-FXA optical microscope, a JEOL JEM-200CX transmission electron microscope (TEM) and a Hitachi S-2500 scanning electron microscope (SEM).

The crystallinities of PXy particles were analyzed with electron diffraction and X-ray diffraction. The X-ray diffraction patterns were observed with a Rigaku RINT 2100 (40 kV, 20 mA).

Table 1 Recipes for the production of polyxylidine particles by chemical-oxidative dispersion polymerizations[a] in water and in HCl aqueous solution

Ingredient		No. 1	No.2
Xylidine	(g)	0.140	0.140
APS	(g)	0.527	0.527
PVA	(g)	0.014	0.014
Water	(g)	35.0	35.0
HCl[b]	(g)	—	0.121

[a] N_2; 25°C; 250 rpm; 24 h (No. 1), 48 h (No. 2)
[b] Hydrochloric acid, 35 wt% aqueous solution
Abbreviations: APS, ammonium persulfate; PVA, polyvinylalcohol

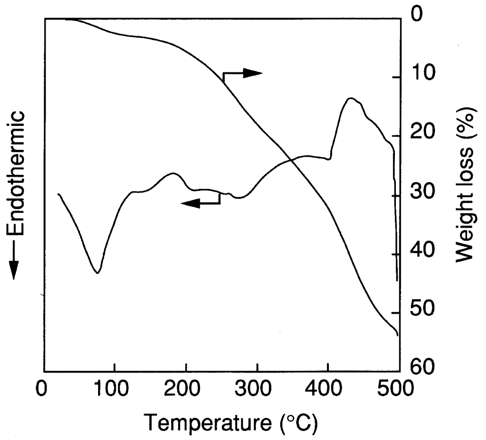

Fig. 1 TG-DTA curves of polyxylidine particles produced by chemical-oxidative dispersion polymerization in water under the conditions of No. 1 listed in Table 1

Results and discussion

Dispersion polymerization of Xy was carried out in water under conditions No. 1 listed in Table 1. In this system, when APS aqueous solution was added, the color of the solution began to turn orange at once, became brown after 1 h, and then gradually deepened to black in 24 h. The polymerization was not stopped by adding radical inhibitors such as hydroquinone and by cooling.

The conversion was calculated from the amount of unreacted Xy measured by gas chromatography. As the detection time was about 45 min even by rising column temperature linearly, sampling had to be done every 1 h. Even at 25 °C, the polymerization was very rapid and the conversion reached about 90% by 1 h. Since the polymerization proceeds not by chain reaction but by consecutive reaction, the conversion does not necessarily correspond to the polymer yield. The color changed even at the conversion of nearly 100%. The produced PXy dispersion had a good colloidal dispersibility.

After enough centrifugal washing with distilled water and drying under reduced pressure, the solubilities of the obtained PXy particles to several organic solvents were examined. Toluene, THF, and DMF partially dissolved the PXy powder and the solutions turned yellowish, but almost all of the particles were not soluble at all. For NMP, the solution became brown, and the swollen particles were observed in the solution. This coloring is probably due to the dissolution of low molecular weight products.

Figure 1 shows TG-DTA curves of the PXy particles. Three weight losses were observed mainly at around 100 °C, 250 °C, and 400 °C in the thermogravimetric curve. The weight loss at around 100 °C is mainly due to the evaporation of water. From 100 °C to 400 °C the weight gradually decreased, which is probably assigned to the removal of low molecular weight products. From the exothermal at 400 °C in the differential thermal curve, it seems that the weight loss of about 400 °C is due to decomposition of the PXy.

Figure 2 shows optical, TEM and SEM photographs of the PXy particles. The PXy particles had a needle-like shape. The long axial size of the needle-like particles was of the order of 10 μm and the average aspect ratio was about 13. In the TEM and SEM photographs, it was observed that a lot of about 100 nm sized spherical particles were also produced. The PXy produced in HCl aqueous solution under conditions No. 2 listed in Table 1 had only

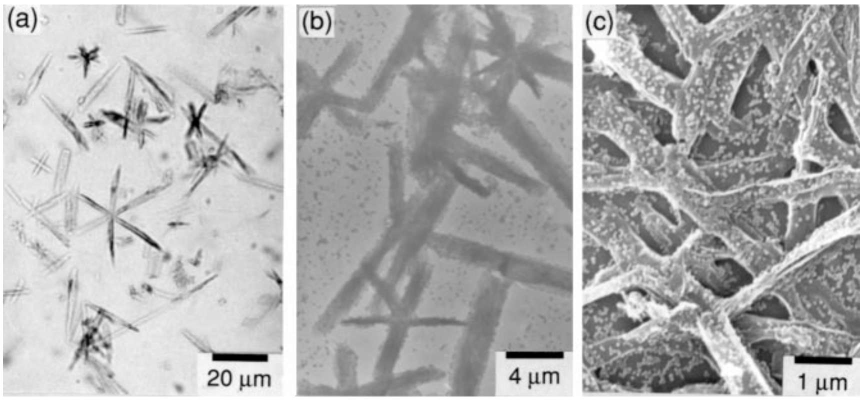

Fig. 2 Optical (a), TEM (b) and SEM (c) photographs of polyxylidine particles produced by chemical-oxidative dispersion polymerization in water under the conditions of No. 1 listed in Table 1

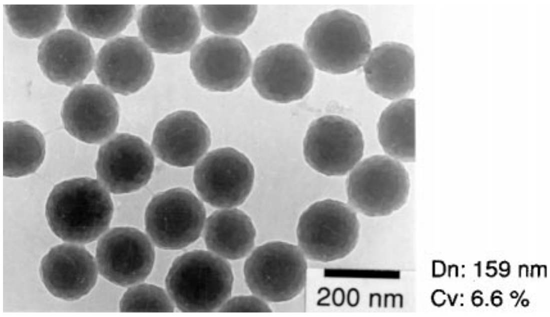

Fig. 3 TEM photograph of polyxylidine particles produced by chemical-oxidative dispersion polymerization in HCl aqueous solution under the conditions of No. 2 listed in Table 1

a spherical shape as shown in Fig. 3. This point will be discussed later.

The needle-like shape gives an interesting feature in the crystalline structure. As described in the introduction, Vincent et al. produced needle-like polyaniline particles, but they did not refer to the crystallinity. So we examined the crystallinity of the PXy needle-like particles by electron diffraction and X-ray diffraction measurements, after removing the spherical particles by centrifugal washing. For a comparison, the same measurements were carried out for the PXy spherical particles produced in HCl aqueous solution, because of the small amount of PXy spherical particles produced in water.

Figure 4 shows electron diffraction patterns and TEM photographs of the needle-like and spherical particles. The

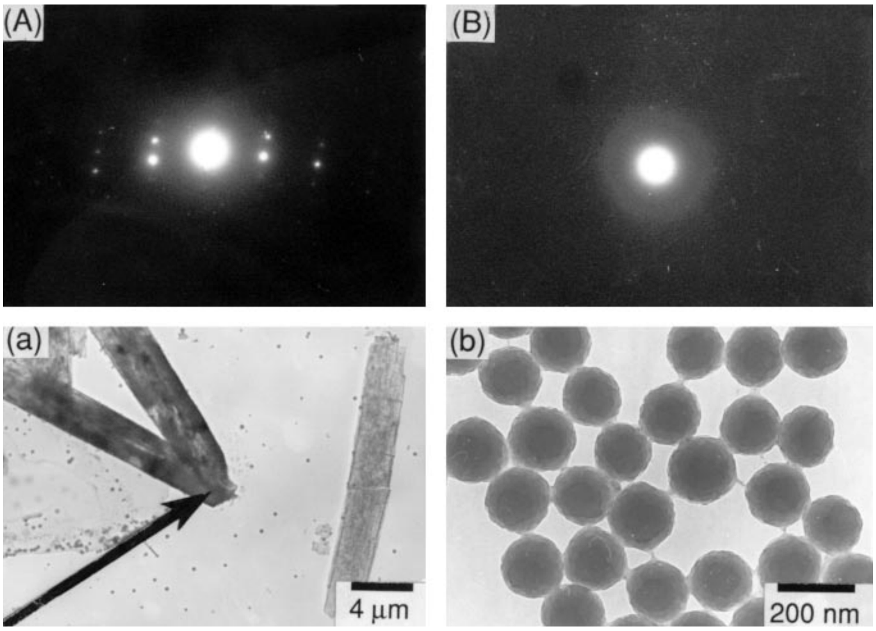

Fig. 4 Electron diffraction patterns (A, B) and TEM photographs (a, b) of the needle-like (A, a) and spherical (B, b) polyxylidine particles which were, respectively, produced by chemical-oxidative dispersion polymerizations in water and in HCl aqueous solution

electron diffraction pattern at the part of the needle-like particles, which is pointed with an arrow in the TEM photograph, had spots due to crystallinity, whereas that at the spherical particles did not.

Figure 5 shows X-ray diffraction patterns of both particles. The pattern of the needle-like particles had clear peaks due to crystallinity, whereas that of the spherical particles had only amorphous broad peak.

From these results, it is clear that the needle-like crystalline particles were produced by chemical-oxidative dispersion polymerization of xylidine in an aqueous medium.

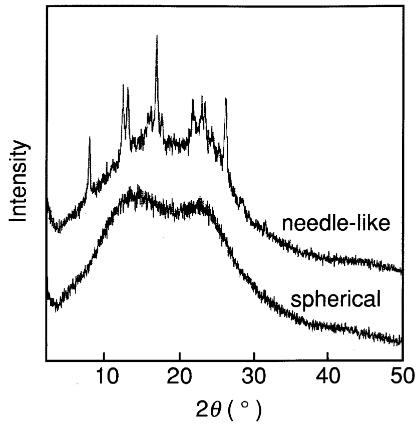

Fig. 5 X-ray diffraction patterns of the needle-like and spherical polyxylidine particles which were, respectively, produced by chemical-oxidative dispersion polymerizations in water and in HCl aqueous solution

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