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Polyaniline dispersions 8. The control of particle morphology

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Abstract

Polyaniline dispersions are obtained when aniline is oxidized in an acidic aqueous medium with ammonium peroxodisulfate in the presence of hydroxypropylcellulose. The progress of aniline polymerization has been monitored by the acidity changes and the formation of colloidal particles by dynamic light scattering. Submicrometre spherical polyaniline particles of good uniformity in size are produced at 0°C, while at 40°C the resulting objects have coral-like cylindrical morphology. A similar change of particle shape has been achieved at 0°C by the acceleration of polyaniline formation by addition of a mediator, *p*-phenylenediamine. The concept of the formation of spherical and non-spherical morphologies and the role of the autoacceleration effect in the dispersion polymerization of aniline are proposed. Polymerization in the frozen reaction mixture at -25°C yielded a macroporous composite. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polyaniline [1,2] (PANI) is one of the most frequently studied electrically conducting polymers. Since the paper by Armes and Aldissi [3] in 1989, there have been numerous reports on the preparation of PANI dispersions [4]. These are produced when PANI is prepared in the presence of a suitable steric stabilizer, usually a water-soluble polymer. Dispersions are composed of colloidally stable submicrometre PANI particles dispersed in the aqueous medium. Particles are protected from the aggregation by a surface layer of the attached stabilizer.

Polyaniline dispersions can be used for the processing of PANI, e.g., for the preparation of microstructured electrically conducting composite materials or films comprising PANI [5–8]. Some composites were reported to have extremely low percolation limits [9–12] due to the microphase separation caused by the incompatibility of the steric stabilizer and the matrix polymer. Dispersions have been used for the casting of the electrically conducting layer on polyethylene membranes [13,14]. Reports on the electrodeposition of PANI dispersions on metal surfaces [15–17] indicate the potential applications of PANI colloids in the field of anticorrosion protection of metals [18,19]. Polyaniline dispersions have been also investigated in relation to their ion-exchange performance [20–23] and electrophoretic behaviour [24]. The colour of particles allows for their easy detection; that is why they were used as model objects in isoperichoric focusing experiments [25,26].

Poly(*N*-vinylpyrrolidone) [15,16,27], poly(methyl vinyl ether) [9,10,28,29], poly(styrenesulfonic acid) [22,30], poly(ethylene oxide) [15,31,32] and in particular poly(vinyl alcohol) [5,15,16,20,22,23,27,30,33,34] have all been employed for the stabilization of PANI colloids produced in the dispersion polymerization [35,36] of aniline. The use of tailor-made copolymers has also been extensively studied [3,31,37–40]. The preparation of spherical PANI particles of a good uniformity has been described, when colloidal silica was used for the steric stabilization [41–43]. Cellulose ethers, namely methylcellulose [11,44] and ethyl(hydroxyethyl)cellulose [45], have only recently been applied for the preparation of PANI dispersions in aqueous alcohol. The feasibility of the use of another cellulosic derivative, hydroxypropylcellulose (HPC), this time in water, is reported in this paper.

Polyaniline particles of spherical, rice-grain, or needle-like morphology of varying polydispersity in size have been

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described. DeArmitt and Armes [38] observed that the particle morphology (spherical or rice-grain) had depended on the oxidant used for the polymerization. Vincent and Waterson [31] tested the effect of stabilizer architecture; stabilization by poly(ethylene oxide) yielded needle-like PANI particles, while graft-copolymer stabilizer based on poly(ethylene oxide) produced PANI spheres. Nagaoka et al. [22,23] reported that needle-like structure was produced when poly(vinyl alcohol) was used for the steric stabilization, while another stabilizer, sodium polystyrenesulfonate, produced spherical PANI particles. The deviations from the spherical shape after the increase of polymerization temperature have been reported for PANI dispersion stabilized with colloidal silica [41]. Chattopadhyay and Mandal [44] found that the morphology of PANI particles stabilized by methylcellulose could be controlled by the composition of the ethanol-water mixture (and, consequently, by the variation of adsorption efficiency of the stabilizer and the polymerization rate). This is why we have decided to investigate the influence of the rate of aniline polymerization on the morphology of PANI dispersion particles.

2. Experimental

2.1. Polyaniline dispersions

Aniline hydrochloride (0.2 M) was oxidized with ammonium peroxodisulfate (0.2 M) in the presence of 2 wt% of hydroxypropylcellulose (Klucel GF, Aqualon GmbH, Germany; moisture content 8.0 wt%) to obtain PANI dispersion particles. Aniline hydrochloride (259 mg) was dissolved in 5 ml of 4 wt% aqueous solution of HPC and water was added to 8 ml. The solution was brought to the desired temperature in a Haake F3-C thermostat and 2 ml of 1 M aqueous ammonium peroxodisulfate (= 456 mg of peroxodisulfate) maintained at the same temperature was added to start the polymerization. *p*-Phenylenediamine dihydrochloride dissolved in water was introduced to the reaction mixture to accelerate the formation of PANI when desired.

2.2. Acidity measurements

The changes in the acidity of the reaction mixture were recorded with a PHM64 Research pH Meter (Radiometer, Denmark) using a glass pH electrode with a calomel reference.

2.3. Dynamic light scattering

A DLS-SLS-5000 Laser Light-Scattering Spectrometer/Goniometer (ALV, Germany) equipped with Nd:YAG laser DPY 315 II (Adlas, Germany) operating at $\lambda_0 = 532$ nm and Multiple Tau Correlator ALV-5000 was used for dynamic light scattering (DLS) measurements. 10 μl of reaction mixture was diluted in 60 s intervals with 10 ml of 1 M hydrochloric acid at room temperature. At low concentration of the reactants after dilution, the polymerization was stopped. The dilute mixture was then immediately characterized by DLS to determine the hydrodynamic radius, R_h.

2.4. Scanning electron microscopy

The dispersions were dialysed in semipermeable membrane tubings (Spectra/Por1, Spectrum Medical Industries, USA) against an excess of water to remove low-molecular-weight components. A droplet of dispersion diluted by isopropanol was evaporated on a mica support. Samples for the scanning electron microscopy were sputter-coated with a 4 nm platinum layer and a JSM 6400 JEOL electron microscope was used to take micrographs.

2.5. Electrical conductivity

Digital multimeter Solartron-Schlumberger 7841, Keithley 220 current source, Keithley 705 scanner with Keithley 7052 matrix scanner card were used in the four-probe measurement based on the van der Pauw theorem [46].

3. Results and discussion

3.1. The concept of particle formation

To account for various morphologies of PANI dispersion particles reported in the literature [22,31,38,41,44], the following model of particle formation is proposed.

At the beginning of the aniline polymerization, all components of the reaction mixture, monomer (aniline hydrochloride), oxidant (ammonium peroxodisulfate) and steric stabilizer (HPC), are soluble in the aqueous medium and the reaction proceeds under homogeneous conditions. Polyaniline is insoluble under the same conditions and small primary PANI particles (several nm to tens of nm in size [9]) precipitate in the aqueous phase as the polymerization proceeds. A fraction of primary particles has the attached (grafted, adsorbed or entangled) stabilizer on them. Both the primary particles with and without steric stabilizer aggregate into larger objects of submicrometre size, the dispersion particles (Fig. 1). Three factors affect the formation of dispersion particles: (1) the rate at which PANI is produced; (2) the efficiency of the stabilizer attachment; and (3) the diffusion and transport processes involved in the formation of the dispersion particle from primary particles.

When the primary PANI particles are produced slowly during polymerization, they can efficiently become attached to the steric stabilizer. The locally reduced concentration of the free stabilizer is compensated by the diffusion of the stabilizer from the other regions. A sufficient quantity of the incorporated stabilizer and the diffusion-controlled aggregation of primary particles lead to the formation of

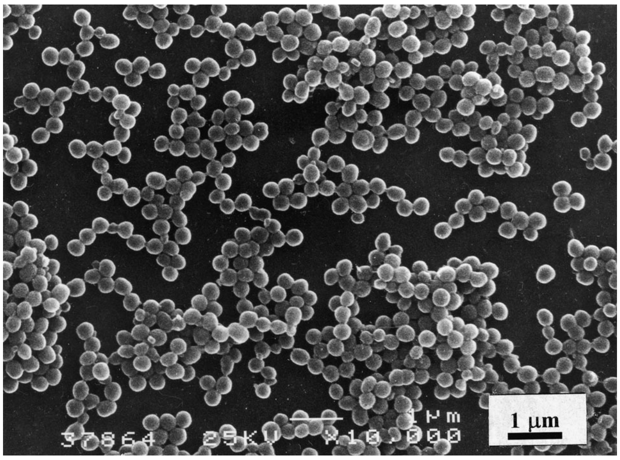


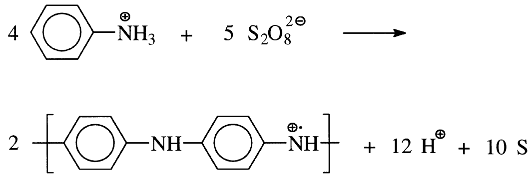
Fig. 1. Polyaniline dispersion particles stabilized by hydroxypropylcellulose prepared at 0°C.

spherical dispersion particles [31,44] (Fig. 1). The oxidation of aniline is autoaccelerated [47–49], i.e. the presence of PANI promotes the polymerization of aniline. Because of autoacceleration, polymerization takes place preferentially at the close proximity of existing PANI, i.e. at the surface of dispersion particles. That is why these grow and no new dispersion particles are nucleated during polymerization [43]. The final dispersion particles thus have a low polydispersity.

When the rate of PANI formation is much faster than the diffusion of the stabilizer, a local depletion of the free stabilizer by primary particles may occur at PANI surfaces where the polymerization takes place. In these volume elements the polymerization then proceeds in the absence of the stabilizer, i.e. in the precipitation mode. More and more primary particles without steric stabilizer are then produced by an autoacceleration mechanism. Also in this case they need not diffuse over long distances before they aggregate. The shape of the dispersion particles is likely to be affected by the topology of polymerization. The polymerization-controlled particle growth is expected to give rise to non-spherical morphologies. To test this hypothesis, dispersions were prepared at various rates of PANI formation and their morphology has been observed.

3.2. Polymerization of aniline at various temperatures

One of the ways to increase the rate of PANI formation is to increase the reaction temperature. The green emeraldine form of PANI [50,51] results when aniline hydrochloride dissolved in water is oxidized with ammonium peroxodisulfate:



(1)

Both chloride and sulfate counterions compensate for the positive charges on PANI chain. Protons produced during the polymerization increase the acidity of the medium. The acidity measurements thus have been used to monitor the progress of polymerization (Fig. 2). The minimum observed on the time dependences of pH can be associated with the end of the polymerization [48,49]. The glass electrode becomes covered by PANI film as polymerization proceeds. Because of the autoacceleration mechanism [47–49], the oxidation of aniline takes place preferentially close to this film. The locally increased concentration of protons at the electrode surface is responsible for the overshooting to low pH values and for the observation of the minimum. After the polymerization has been completed, the concentration of protons equilibriates and pH levels off at a higher value. At 0°C the minimum of pH is reached after 23 min, at 20°C the reaction is completed at 9 min and the polymerization is still faster at 40°C (Fig. 2).

Dynamic light-scattering experiments show that the PANI particles grow as the polymerization of aniline proceeds (Fig. 3). The formation of particles becomes faster as the reaction temperature increases. The particle growth is finished soon after the production of PANI is over (cf. the position of minima on time dependences of pH in Fig. 2).

When the polymerization proceeds at 0°C, the spherical dispersion particles are completed after 26–28 min and their

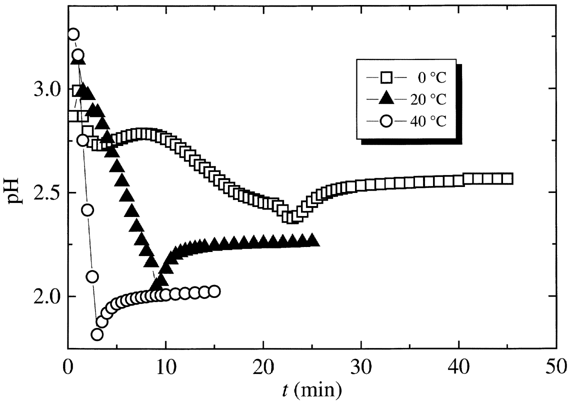


Fig. 2. Changes of acidity during the dispersion polymerization of aniline hydrochloride at various temperature.

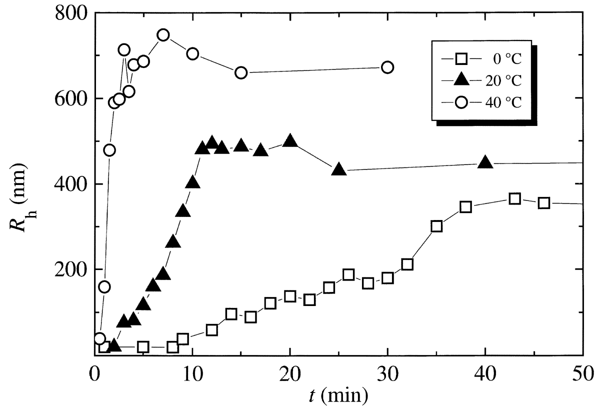


Fig. 3. Dependence of the hydrodynamic radius, R_h, of objects produced in dispersion polymerization of aniline hydrochloride at various temperature.

hydrodynamic radius, $R_h = 200$ nm, is in accordance with the size observed by microscopy (Fig. 1 and Fig. 4a). An additional increase of the hydrodynamic radius up to $R_h = 360$ nm is detected afterwards (Fig. 3) and then the particle size does not change any more. This is explained by the limited post-polymerization aggregation of dispersion particles [52]. When dispersions are characterized by DLS in monthly intervals, the aggregates are still present even after 1 year. They can be decomposed by 30 min treatment of dilute dispersions in an ultrasonic bath. Once destroyed, aggregates do not recover.

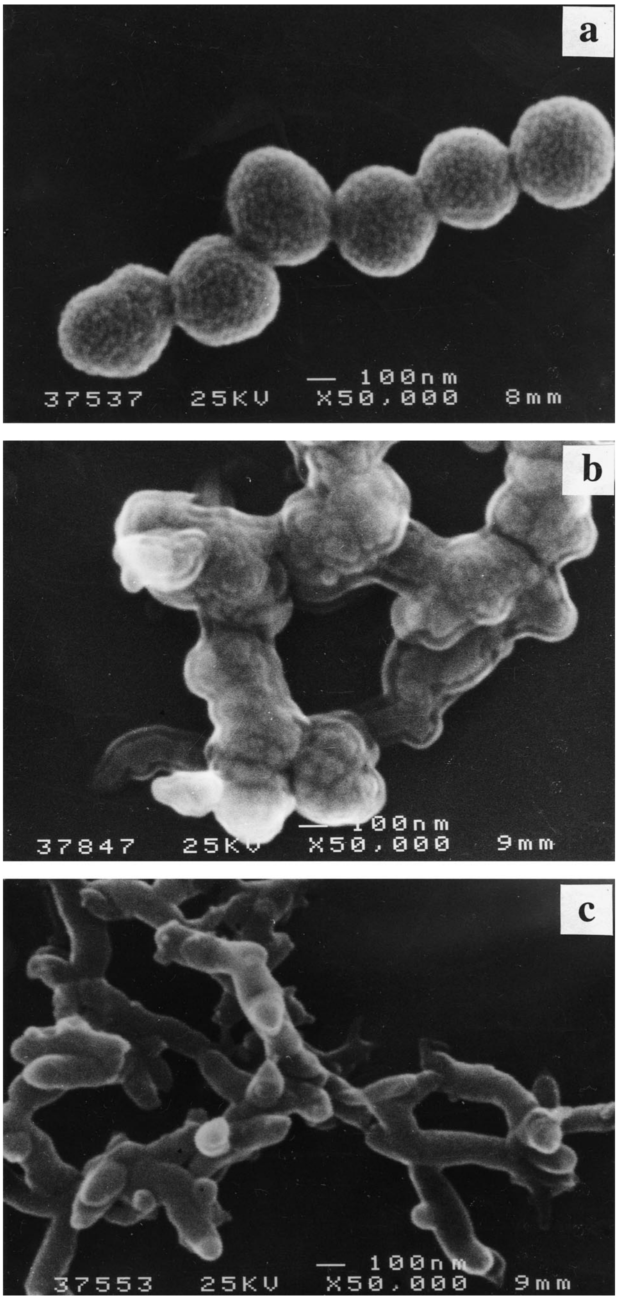


Fig. 4. Particles formed in dispersion polymerization of aniline hydrochloride at (a) 0°C; (b) 20°C; and (c) 40°C.

The transition from the spherical shape (Fig. 4a) through distorted intermediate structure (Fig. 4b) to coral-like morphology (Fig. 4c) can be seen when the rate of PANI formation increases at higher temperature.

3.3. Acceleration of polyaniline formation by a mediator

The rate of aniline polymerization be efficiently increased at fixed temperature by the introduction of small amounts of

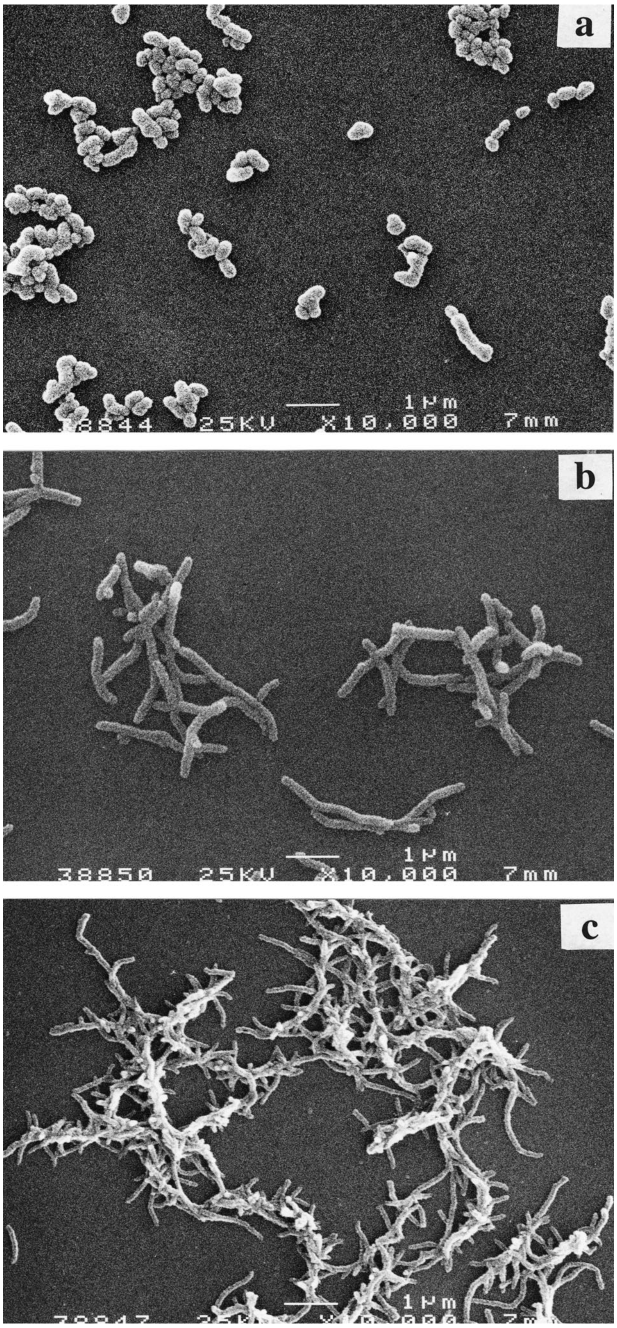


Fig. 5. Products of the dispersion polymerization of aniline hydrochloride (0.2 M) accelerated by addition of (a) 2×10^{-5} M; (b) 2×10^{-4} M; and (c) 2×10^{-3} M *p*-phenylenediamine dihydrochloride at 0°C.

so-called mediators. *p*-Phenylenediamine (*p*-PDA) and its derivatives have earlier been reported [49] to promote the formation of PANI (for the quantitative assessment of *p*-PDA efficiency see Fig. 2b in Ref. [49]). The spherical shape of particles prepared at 0°C in the absence of the mediator (Fig. 1 and Fig. 4a) changes to the rice-grain morphology when the rate of PANI formation has been moderately increased by the addition of 2×10^{-5} M *p*-PDA (Fig. 5a) (aniline/*p*-PDA molar ratio = 10^4). The coral-like cylindrical morphology (Fig. 5b) was produced under similar conditions at higher reaction rate in the presence of 2×10^{-4} M *p*-PDA. A more detailed inspection reveals that the cylinders have about 200 nm diameter (Fig. 6). The granular surface of cylinders is composed of small primary particles (with attached HPC), similarly to the surface of spherical objects (Fig. 4a). The branched dendritic structure based on cylindrical elements developed when the polymerization rate was still faster at 2×10^{-3} M *p*-PDA (Fig. 5c). A macroscopic precipitate of fractal appearance was obtained at 2×10^{-2} M *p*-PDA (aniline/*p*-PDA molar ratio = 10). Also these experiments indicate that the particle morphology is controlled by the rate of PANI formation.

3.4. Polymerization in the frozen state

The reaction mixtures used in this study freeze below −10°C. When the polymerization is carried out at −25°C in the frozen state [53], the transport of primary particles leading to the formation of dispersion particles is not feasible. The macroporous composites are produced instead (Fig. 7). The size of pores is reduced when the concentration of the steric stabilizer is increased. The final morphology of composites is likely to be affected by the size and shape of ice crystals.

3.5. Composite film prepared from dispersion

Dispersions contain a substantial amount of low-molecular-weight compounds (residual aniline hydrochloride, ammonium sulfate, etc.). These can be removed by dialysis if they are detrimental to the further use of dispersions, e.g., in the preparation of films. The free HPC stabilizer remains in the dispersion even after dialysis. The film cast on polystyrene dish from the acidified dialysed dispersion prepared at 0°C could be easily separated from the support. It contained 5.3 wt% of nitrogen (by elemental analysis) compared with 11.3 wt% of nitrogen in PANI hydrochloride prepared in the absence of the steric stabilizer. There was therefore 46.9 wt% of PANI hydrochloride in the composite film. If the conversion of aniline to PANI reached the limit of 80%, as expected from stoichiometry given by Eq. (1) for an equimolar aniline/peroxodisulfate ratio, the composite would contain 48.2 wt% of PANI. The film was brittle because of the high PANI content. Its electrical conductivity was 0.046 S cm^{-1}. Polyaniline prepared under the same conditions in the absence of HPC had a conductivity of 2.5 S cm^{-1}.

4. Conclusions

Hydroxypropylcellulose can be used as a steric stabilizer in the dispersion polymerization of aniline in aqueous medium. The morphology of dispersion particles can be varied from well-defined spheres to coral-like objects by increasing the polymerization temperature from 0 to 40°C. The polymerization rate has been alternatively increased at fixed temperature by addition of a mediator, *p*-phenylenediamine, to reaction mixture. Similar changes in the particle morphology (ranging from spherical, rice-grain, cylindrical to fractal) have been observed. The non-spherical objects are obtained at a higher rate of aniline polymerization. The balance between the diffusion-controlled formation of spherical dispersion particles and polymerization-controlled local precipitation of PANI determines the final morphology of dispersion particles. The macroporous composites are produced instead of dispersions when the polymerization of aniline proceed in the frozen reaction mixture at − 25°C.

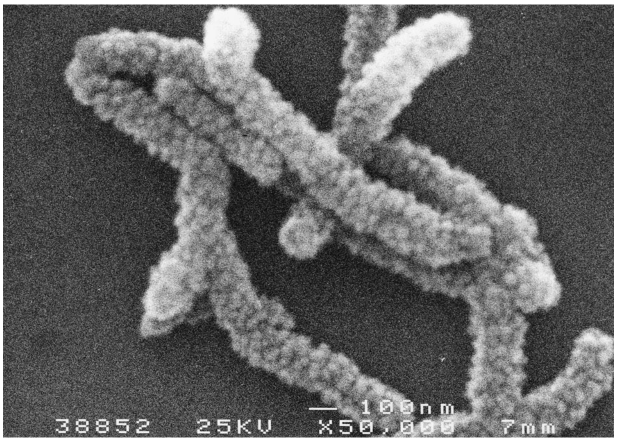


Fig. 6. A detail of the coral-like cylindrical morphology shown in Fig. 5b.

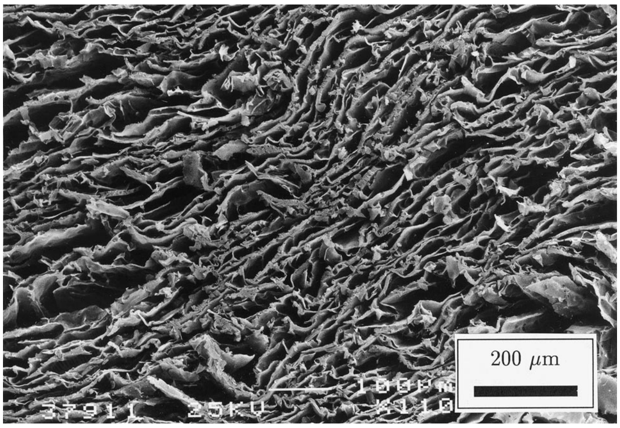


Fig. 7. Macroporous PANI–HPC composite obtained by the polymerization in the frozen reaction mixture at − 25°C.

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