Synthesis of Polyaniline Nanofiber and Copolymerization with Acrylate Through *In Situ* Emulsion Polymerization

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ABSTRACT: Polyaniline (PANI) was prepared, respectively, by direct mixed oxidation method in different acids. Scanning electron microscopy showed that high quality of PANI nanofibers can be obtained easily in hydrochloric acid, sulfuric acid, and acetic acid, especially in the sulfuric acid; infrared and ultraviolet spectra characterization showed all products were the doped PANI. Then, using complex emulsifiers, PANI was dispersed in acrylate emulsion by supersonic dispersion assisted with mechanical stirred to obtain mixed pre-emulsion, the result showed different PANI performed different dispersing stability in the pre-emulsion. More importantly, PANI–polyacrylate copolymer was prepared through multi-steps *in situ* emulsion polymerization using water-soluble azo (VA-044) as initiator. Experiment showed that good dispersing stability of PANI in the pre-emulsion was premise to obtain the final stable copolymer emulsion. Further, the micro-morphology and thermal property of the copolymer were studied by transmission electron microscopy, differential scanning calorimetry, and thermogravimetric analyzer. The result proved that acrylate occurred *in situ* polymerization on surface of PANI nanofibers, the presence of PANI increased glass transition temperature (T_g) and thermal decomposed temperature of the copolymer. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 627–635, 2012

Key words: nanofibers; stabilization; emulsion polymerization; copolymer

INTRODUCTION

Polyaniline (PANI) is one of the most intensively investigated conducting polymers due to its excellent environmental stability, low cost of raw material, ease of synthesis, relatively high level of electrical conductivity, and interesting redox property.[1–3] Now, PANI has been widely studied for potential applications in many domains such as electrochromic devices, rechargeable batteries, and electromagnetic interference shielding,[4,5] especially in anticorrosion application.[6–10] Nevertheless, the facility of PANI's application is restricted by its poor solubility, infusible, and almost nonprocessable properties.[11] To improve the processability of PANI, enormous efforts have been directly toward chemical modifications such as inserting substitutes either on phenyl ring or on nitrogen[12,13] and emulsion poly-

merization of aniline (ANI) in the presence of surfactants and water-soluble polymers[14,15]; In other way, through doping PANI with organic acids with long alkyl chain such as camphor sulfuric acid, dodecylbenzene sulfonic acid (DBSA), or copolymer acid.[16–18] In recent years, through *in situ* emulsion polymerization to prepare compound polymer explored new developed direction and new ideas for application of PANI.[14,19] For example, the introduction of PANI into polyacrylate though *in situ* emulsion polymerization was expected to improve the applied properties of polyacrylate such as radiation-reserve and high temperature-reserve.

Fortunately, development and application of nanotechnology in preparing PANI explored more broad application prospects for PANI. Nanostructure PANI was given many specific physical and chemical properties such as specific light absorption, catalytic, magnetic, and reactive due to the surface, quantum, and macroscopic quantum tunneling influences of nanomaterial.[20–23] In numerous nanostructures of the PANI, nanofiber which frequently showed one-dimensional nanoscale was concerned extensively especially in application due to it is simple synthesized method, furthermore, the morphology of PANI nanofiber was easy to be controlled or adjusted.[24–27]

In this paper, PANI nanofibers were synthesized by direct mixed oxidation method in various kinds

of acid. Morphology of PANI was investigated by the field-emission scanning electron microscopy (FE-SEM), and structure of products was characterized through the infrared (IR) and ultraviolet (UV) spectra. Then PANI nanofibers were dispersed in acrylate emulsion by supersonic dispersion assisted with mechanical stirring using complex emulsifiers of anion emulsifier (Na-DBSA) and nonionic emulsifier [octyl phenol ethoxylate-10 (OP-10)], the dispersing stability of PANI in the emulsion was studied in detail. More importantly, PANI–polyacrylate copolymer emulsion was prepared through multi-steps emulsion polymerization using water-soluble azo (VA-044) as initiator[28] to improve the stability of system. The micro-morphology and thermal property of the copolymer were studied by transmission electron microscopy (TEM), differential scanning calorimetry (DSC), and thermogravimetric analyzer (TGA).

EXPERIMENTAL

Materials

2,2′-Azobis(2-(2-imidazolin-2-yl) propane) dihydrochloride (VA-044) was purchased from Wako company, and ANI, ammonium peroxydisulfate, sodium formaldehyde sulfoxylate (SFS), and hydrochloric acid (HCl), phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4) acetic acid (HAC), oxalic acid, and acrylic acid were used directly without purification. Methyl methacrylate (MMA) and butylacrylate (BA), Sodium dodecyl benzene sulfonate (Na-DBSA), and octyl phenol ethoxylate-10 (OP-10) were analytical reagents.

Preparation of PANI

An aqueous solution of ANI (2 mmol) in $1M$ (to the oxalic acid, the acid concentration was $0.2M$ due to the limitation of solubility) acid (10 mL) and another solution of APS (1 mmol) in $1M$ (the solution of oxalic acid was $0.2M$) acid (10 mL) were prepared and poured the two solutions together with immediately magnetic stirring to ensure sufficient mixing before reaction begins. The reaction was carried out for 24 h at room temperature. The resulting PANI precipitates were purified by centrifugation using de-ionized water and ethanol, until the suspension reached a neutral pH value.

Preparation of PANI-acrylate pre-emulsion

A 30 g acrylate monomers (MMA: BA = 1: 1), 1.5 g emulsifiers (Na-DBSA: OP-10 = 2: 1), 0.05 g SFS, 60 g distilled water, and various kinds of PANI (at different amounts) were added in flask equipped with a mechanic stirrer and then supersonic vibration

(using the KQ-50 supersonic oscillator) assisted with mechanical stirring at about 3000 rpm for 0.5 h to prepare pre-emulsion.

Preparation of PANI–polyacrylate copolymer emulsion

A 30 g pre-emulsion were poured in flask equipped with a mechanic stirrer and stirred at about 300 rpm, then was purged with nitrogen at 50°C. The remaining pre-emulsion and 10 mL 0.5% $K_2S_2O_8$ solution were added dropwise to solution, the addition was completed over 2 h, then 0.04 g VA-044 was added, and the reaction continued for an additional 3 h. The copolymer emulsion was obtained when cooled to room temperature naturally.

Characteristic

Morphology of PANI were characterized by the FE-SEM (JSM 6700F). Printing SEM micrographs and selecting 10 typical fibers or positions at least in the micrographs, the average diameter and length of the fibers were measured by ruler with 1 mm accuracy and were calculated according to scales of the micrographs. Molecular structure of PANI was characterized by the VERTEX70 IR spectrometer using pellets with KBr and the UV–vis spectrum was measured on a Cary 500 UV–vis–NIR spectrophotometer (the products were dispersed in de-ionized water).

Pre-emulsion was poured into test tubes to stand to observe emulsion status at different times and was took a photograph by digital cameral. Particle morphology of copolymer was determined by TEM (JEM-1200EX). An aqueous solution of osmic acid was used to increase the contrast in the TEM pictures. Glass transition temperature (T_g) and thermal decomposed temperature of the copolymer were characterized by DSC (DSC204F1) and TGA (TGA204F1), respectively.

RESULTS AND DISCUSSION

The effects of different acids on PANI morphology

As can be seen from Figure 1, PANI nanofibers can be obtained in three kinds of inorganic acids, moreover the diameter of all fibers was less than 100 nm. In detail, PANI obtained in HCl system possessed uniform diameter which was about 65 nm in average and surface of single nanofiber was relatively smooth; however, there was a little of PANI nanoparticles attached on surface of fibers, furthermore length of the fibers in range of 200–400 nm was shorter [Fig. 1(a)]; PANI obtained in H_3PO_4 system also showed a certain of fiber morphology with diameter of 40–60 nm, but there were a large number
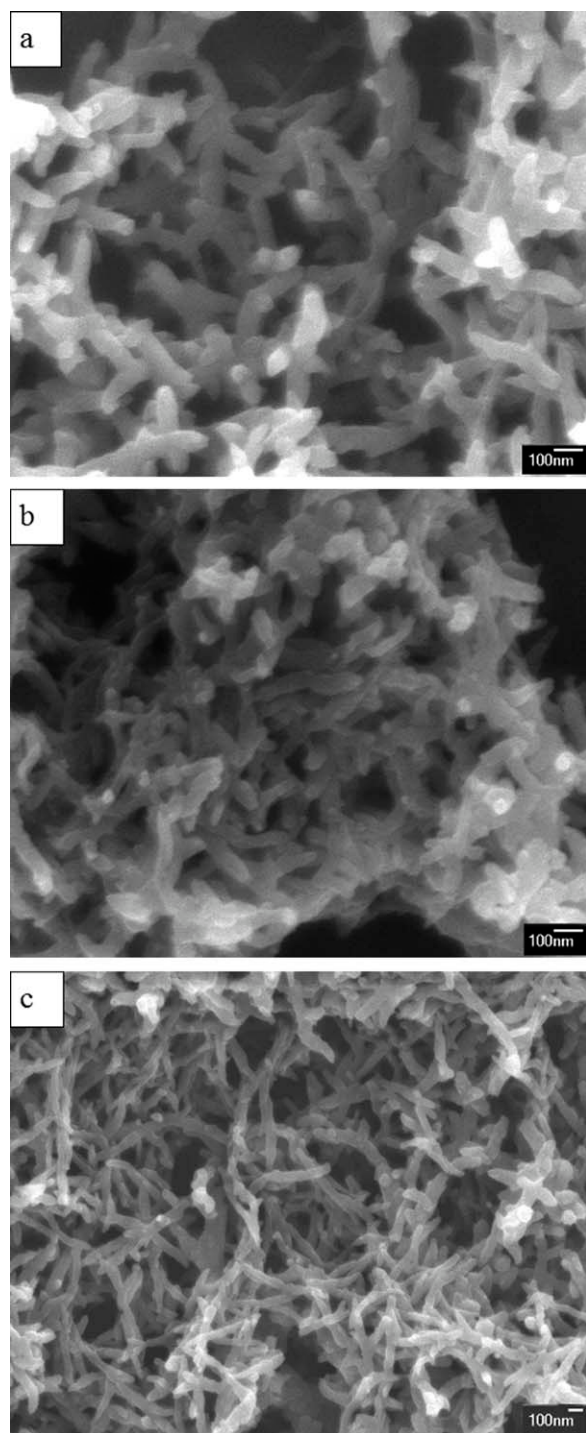
Figure 1 SEM images of polyaniline synthesized by the direct mixed oxidation method in different inorganic acids: (a) hydrochloric acid; (b) phosphoric acid; (c) sulfuric acid.

of nanoparticles aggregates existing [Fig. 1(b)]; PANI obtained in H_2SO_4 system possessed the best morphology with uniform diameter which was about 70 nm, furthermore, the fibers reached to several microns in length and formed dense network structure [Fig. 1(c)].

It can be seen from Figure 2 that PANI nanofibers were synthesized in HAC and oxalic acid, but no

nanofibers were obtained in acrylic acid. In detail, PANI nanofibers obtained in the HAC were around 50 nm in diameter and excess 500 nm in length; however, there is a little of nanoparticles or short fibers attached on part of fibers to effect uniform of diameter [Fig. 2(a)]; PANI obtained in the oxalic acid system showed a certain of fiber morphology
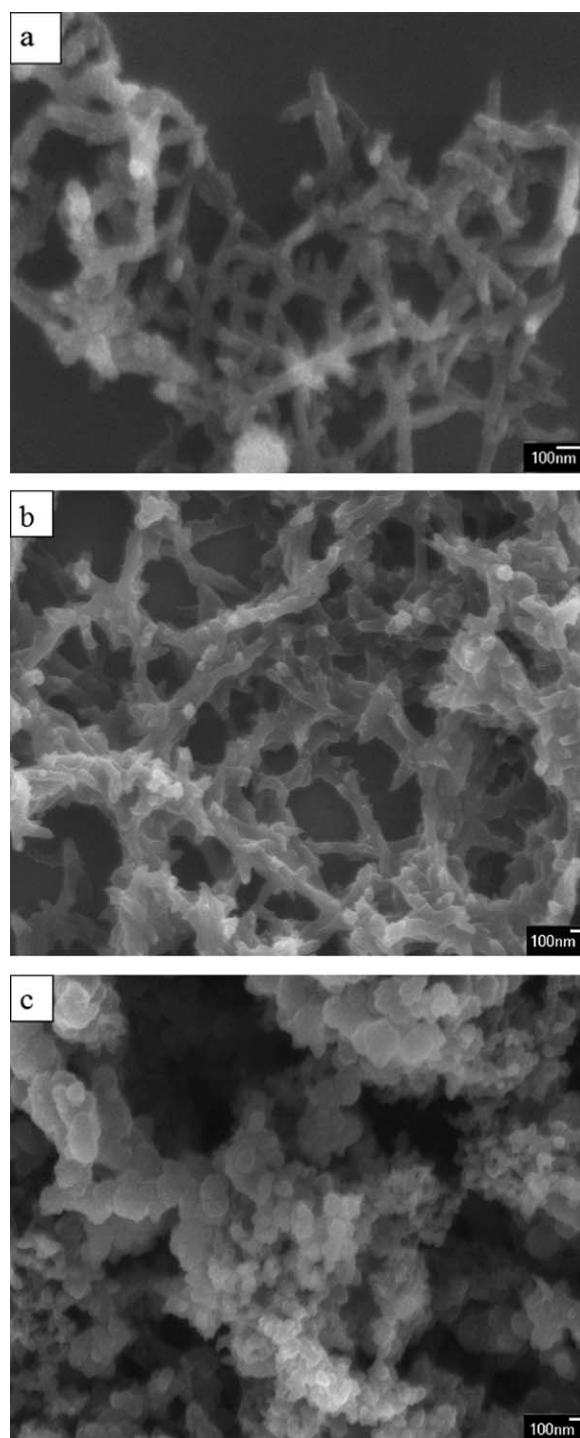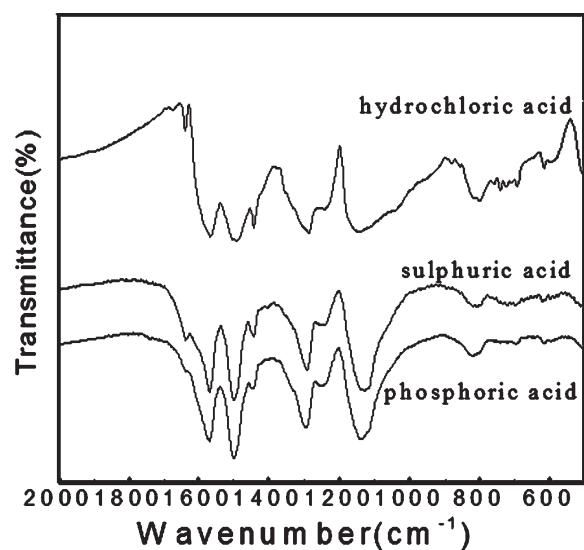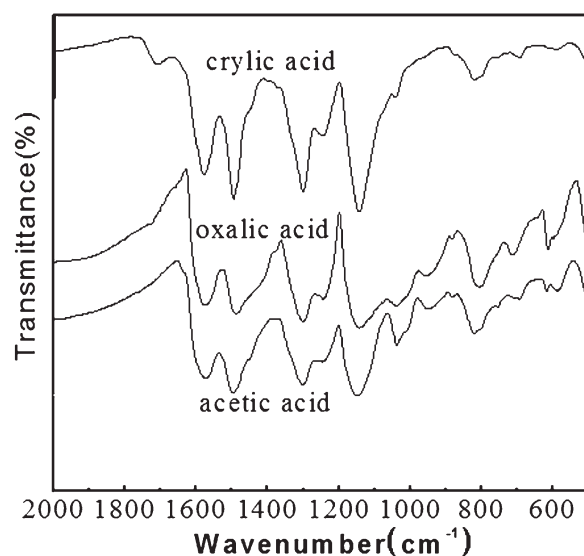

Figure 2 SEM images of polyaniline synthesized by the direct mixed oxidation method in different organic acids: (a) acetic acid; (b) oxalic acid; (c) acrylic acid.
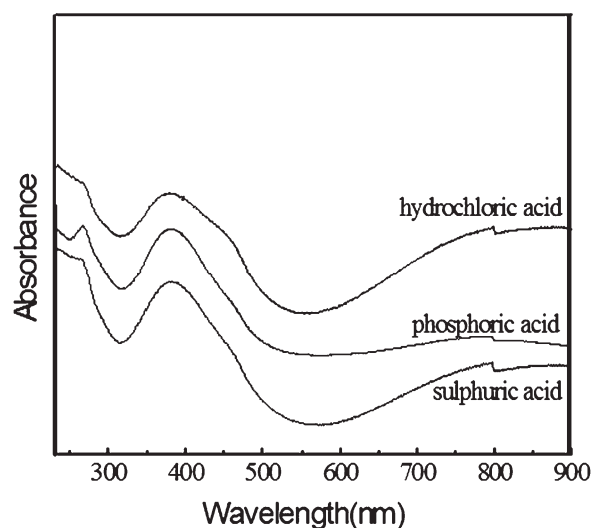
(a)

(b)

Figure 3 FTIR spectrum of polyaniline synthesized in different acids: (a) inorganic acids; (b) organic acids.

with diameter of 80–120 nm, but there were a large number of PANI granular aggregates existed and single nanofiber was shorter in length [Fig. 2(b)]; products obtained in the acrylic acid appeared morphology of flake aggregates and some nanoparticles attached on part of the aggregates [Fig. 2(c)].

Structure characterization of PANI

As important and basic information, molecular structure message of product was revealed by the IR spectrometer. It can be seen from Figure 3 that the IR peak distribution of PANI products prepared in both inorganic acid and organic acids are similar in

general. In IR spectrometer, the presence of characteristic absorption peaks at around 1570 cm^{-1} and 1480 cm^{-1} corresponding to stretching vibration absorption peak of C=C bonds which belong to quinone-ring and benzene-ring, respectively; the absorption peak emerged at around 1300 cm^{-1} corresponding to stretching vibration of C—N bond in benzene-ring; the absorption peaks at around 1140 cm^{-1} and 810cm^{-1} corresponding to plane bending vibration of C—H bonds which belong to quinone-ring and benzene-ring, respectively. In addition, there were some minor differences between the IR peak distributions of PANI prepared in inorganic acid and organic acids. In the IR spectrometer of PANI prepared in inorganic acid [Fig. 3(a)], the weak characteristic absorption peak

(a)
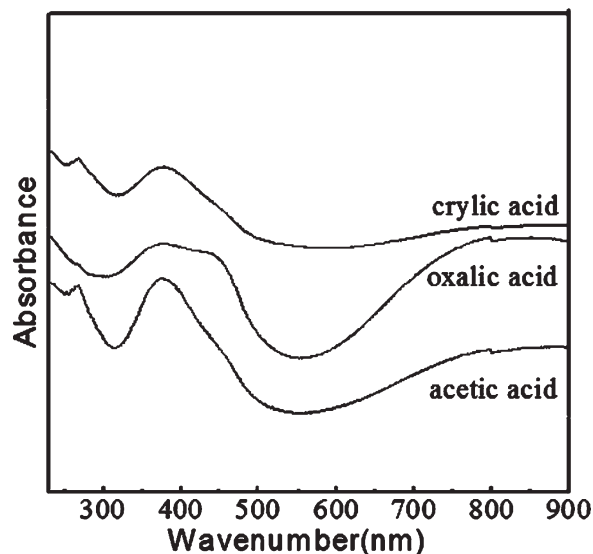
(b)

Figure 4 UV–vis spectrum of polyaniline synthesized in different acids: (a) inorganic acids; (b) organic acids.
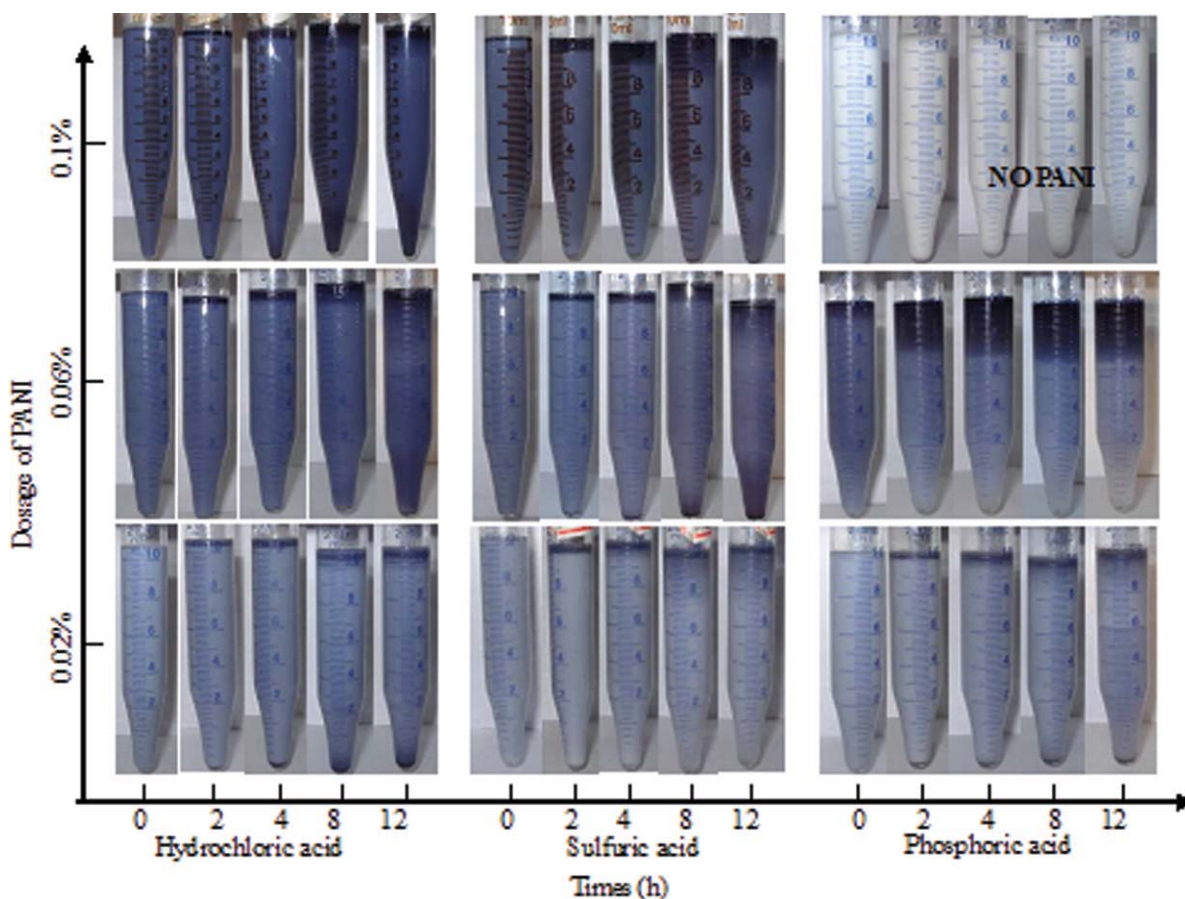
Figure 5 Dispersing photographs of pre-emulsion with different amount of inorganic acids-doped polyaniline at different times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

emerged at around 1440 cm^{-1} corresponding to plane bending vibration of saturated C—H which indicated existence of conjugate structure of PANI. However, in the IR spectrometer of PANI prepared in organic acid [Fig. 3(b)], the multi absorption peak appeared at 950–1050 cm^{-1} corresponding to bending vibration of O—H of carboxylic acid which indicated existence of carboxylic acid in PANI molecular.

As another basic molecular structure characterization, the UV–visible absorption spectra of PANI were showed in Figure 4. It can be seen from Figure 4 that for PANI samples prepared in HCl, H_2SO_4, H_3PO_4, HAC, and acrylic acid, UV absorption peaks emerged at 280 nm, 390 nm, and 800 nm; but for the PANI prepared in oxalic acid, absorption peaks emerged at 360 nm, 450 nm, and 800 nm. In these peaks, the absorption peak at 280 nm (360 nm for oxalic acid doped PANI) attributed to π–π^* transition of benzene-ring; the peaks at 390 nm (450 nm for oxalic acid doped PANI) attribute to the transition absorption of polaron to π^*, and the tail peak at 800 nm belong to the absorption of polaron after doped by proton. All this information further indicated that all products obtained in different acids were doped-PANI. In addition, compared with other samples,

absorption peaks of the sample prepared in oxalic acid were red-shift at 360 nm and 450 nm. The red-shift indicated low energy needed for π–π^* transition which illustrated the existence of stronger conjugation in PANI molecular. The possible reason was that strong reducing ability of oxalic acid prevented high degree oxidation of PANI and maintained products at the state of moderate oxidation which possessed strong conjugation.

Supersonic dispersing stability of PANI in acrylate emulsion

It can be seen from Figures 5 and 6 that the stability of all pre-emulsion declined when adding PANI compared to the pre-emulsion without PANI. Figure 5 showed stability of pre-emulsion mixed with PANI prepared in inorganic acids. It is obviously that pre-emulsion mixed with HCl-doped PANI showed the best dispersing stability, the following was the pre-emulsion mixed with H_2SO_4-doped PANI, the pre-emulsion mixed with H_3PO_4-doped PANI showed the worst dispersing stability. Furthermore, with increasing amount of PANI, the dispersing stability of all samples declined gradually.
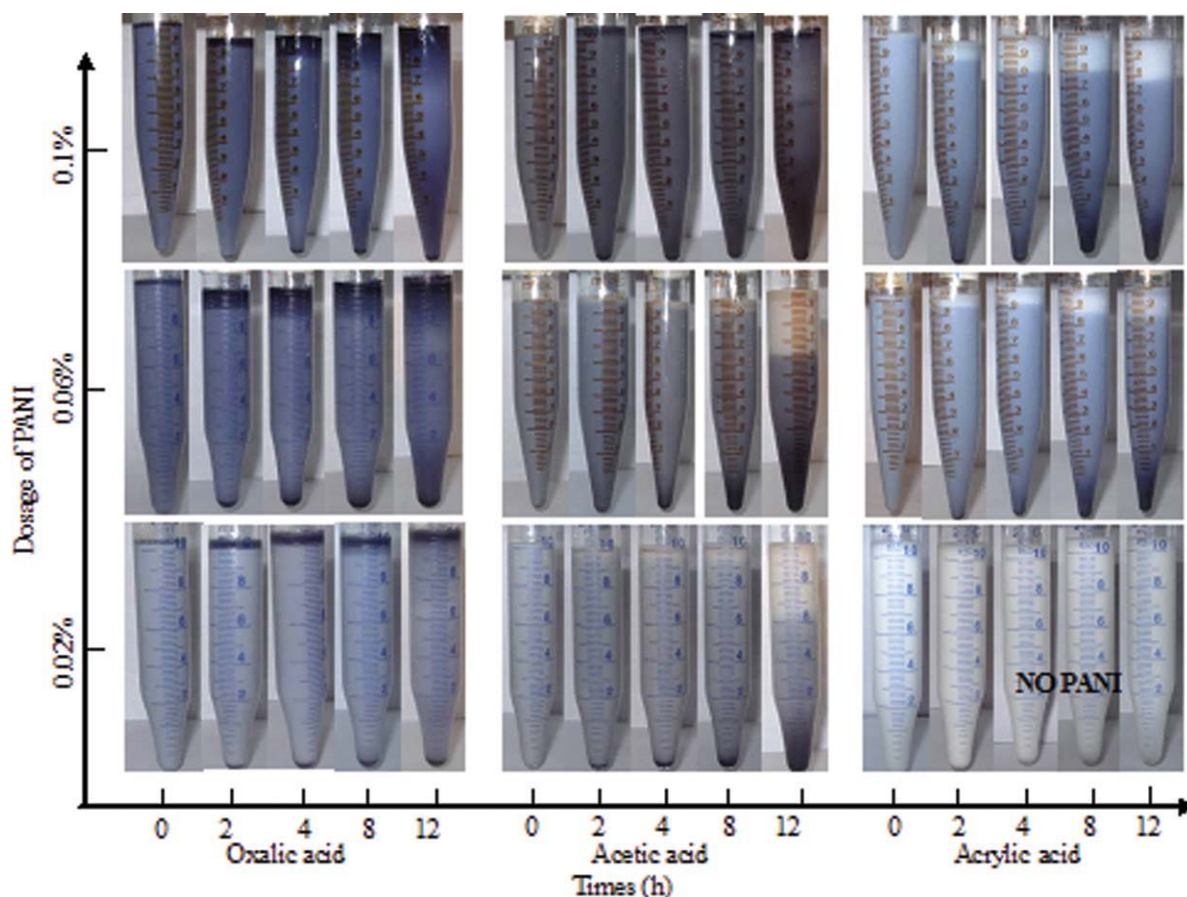
Figure 6 Dispersing photographs of pre-emulsion with different amount of organic acids-doped polyaniline at different times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In detail, the pre-emulsion mixed with PANI prepared in HCl and H_2SO_4 can be basically maintained uniform emulsion when stood at initial 4 h, only small amount of PANI suspension on the top of emulsion. However, the pre-emulsion mixed with H_3PO_4-doped PANI occurred apparent stratification just stood for initial 2 h when amount of PANI reached to 0.06%, a large number of PANI enriched on the top of emulsion; Figure 6 showed stability of pre-emulsion with PANI prepared in organic acids. It can be seen from Figure 6 that dispersing stability of all samples also declined gradually with increasing amount of PANI. In detail, the pre-emulsion mixed with acrylic acid-doped PANI showed the best dispersing stability, the following was the pre-emulsion mixed with HAC-doped PANI. In addition, as a strong acid, compared the oxalic acid with other three inorganic strong acids was more suitable, comparison fact was that the pre-emulsion with oxalic acid-doped PANI showed the close stability with the pre-emulsion mixed with H_3PO_4-doped PANI and also occurred apparent stratification at initial 2 h when amount of PANI reached to 0.06%.

Considering PANI morphology and property of doped acids, the possible reasons were deduced

that: PANI nanofibers obtained in HCl is shorter in length and no crosslinking phenomenon existed, so it was easy to disperse; PANI nanofibers obtained in H_2SO_4 was perfect but is longer in length and mingled into together to form dense network structure which bring some difficulty for dispersing; PANI products obtained in H_3PO_4 and oxalic acid showed only a certain of fiber morphology and a large number of granular aggregates existed to bring more difficulty for dispersing; PANI products obtained in HAC also showed perfect fiber morphology and is relatively short in length but notable network structure existed to bring some trouble for dispersing; PANI products obtained in acrylic acid showed no fiber structure but most of flake aggregates, however, good compatibility between acrylic acid and acrylic ester (similar substance possess good compatibility) lead to good dispersing stability.

Compared Figure 5 with Figure 6, an interesting phenomenon was found that all PANI prepared in strong acid system floated in standing process and most of them enriched in acrylate phase on the top of emulsion after stratified; whereas all PANI prepared in weak acid system sink in standing process and most of them concentrated in water phase on the bottom of
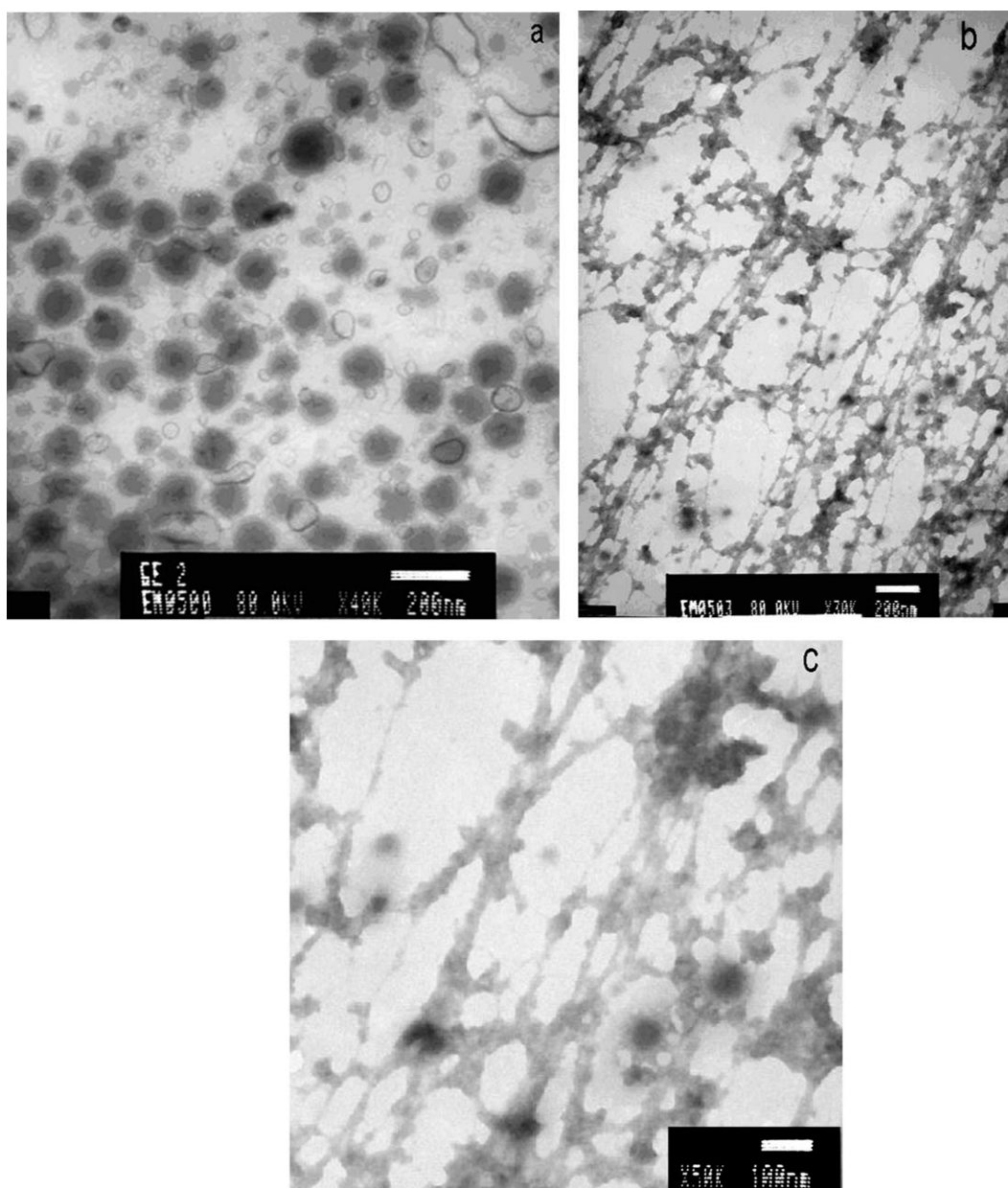
Figure 7 TEM photographs of (a) polyacrylate; (b) PANI–polyacrylate copolymer; (c) section-enlarged.

emulsion after stratified. It is generally believed that lipophilic of PANI with long chains was greater than hydrophilic, under floating effect of emulsifiers, PANI with lipophilic was easy to be brought in light acrylate phase. However, PANI prepared in weak acids was relatively short in chain length moreover a lot of oligomers existed, all these endowed PANI with a certain degree of hydrophilic which promoted PANI to sediment in water phase under effect of gravity.

Micro-morphology and thermal properties of the compounds polymer

The impact of dispersing stability on polymerization was great. In polymerization, relatively short initi-

ated period (20–30 min) and higher conversion was discovered in pre-emulsion with good dispersing stability, the final polymer emulsion with no obvious acrylate odor was provided with better stability and no stratification occurred after holding for a week; On the contrary, relatively long initiated period (about 1 h) and lower conversion was detected in the pre-emulsion with poor dispersing stability, the final emulsion with sharp acrylate odor possessed very poor stability and appeared apparent stratification after holding for 4–6 h (the top layer is dark emulsion phase, the below is transparent water phase).

In this part, the stable copolymer emulsion containing HCl-doped PANI was selected as an example to
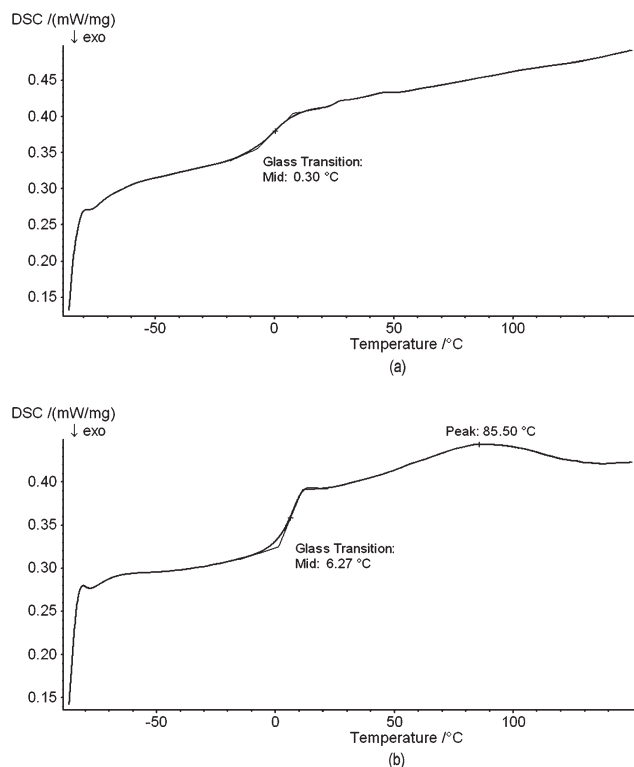
Figure 8 DSC curves of (a) polyacrylate and (b) PANI–polyacrylate copolymer.

study the effect of PANI on micro-morphology and thermal properties of the copolymer. The TEM micrographs of pure polyacrylate and PANI–polyacrylate copolymer was given in Figure 7 which showed apparent difference between pure polyacrylate and PANI–polyacrylate copolymer. The morphology of pure polyacrylate was normal sphere [Fig. 7(a)], but the morphology of copolymer was fiber with crosslinking network. It was reasonable to consider that *in situ* emulsion polymerization of acrylate occurred on the surface of PANI nanofibers which was the reactive position and finally covered the surface of fibers [Fig. 7(b)]. In addition, due to the random of polymerization, a little of spherical polyacrylate latex was investigated in section-enlarged graph [Fig. 7(c)] but did not effect the whole structure. All this information indicated that surface of nanofibers possessed higher reactivity due to the nanoscale surface influence.

As a basic thermal property parameter, T_g of the copolymer increased due to the crosslinked network structure of PANI nanofibers. Figure 8 showed that the T_g of PANI–polyacrylate copolymer was 5.97°C higher than pure polyacrylate. In addition, there was only one T_g at the range of −50 to 150°C [Fig. 8(b)] what indicated that the production was dominant copolymer of PANI and polyacrylate. This truth is consistent with the result of the TEM.

The other important thermal property of polymer–TGA curves of pure polyacrylate and copolymer of

PANI and polyacrylate were given in Figure 9 which clearly showed thermal decomposed temperature of about 21.86% copolymers [Fig. 9(b)] was 58.2°C higher than pure polyacrylate [Fig. 9(a)]. However, there was about 66.32% of copolymer decomposed completely at 393.2°C which was approached to the complete decomposed temperature of pure polyacrylate (392.1°C). So it was rational to conclude that there was certain ratio of copolymer which was provided with firm combination between PANI and polyacrylate. This truth revealed the presence of strong adhesion between PANI and polyacrylate although the combination between PANI and polyacrylate was not firm for most of the copolymer at high temperature.

CONCLUSIONS

PANI products were prepared, respectively, by the direct mixed oxidation method in different acids. SEM showed that high quality PANI nanofibers can be obtained easily in HCl, H_2SO_4, and HAC, especially in the H_2SO_4, nanofibers with uniform diameter and several microns in length were obtained; IR and UV spectra characterization showed all products were the doped PANI.

By supersonic dispersion assisted with mechanical stirring, PANI was dispersed in acrylate emulsion to
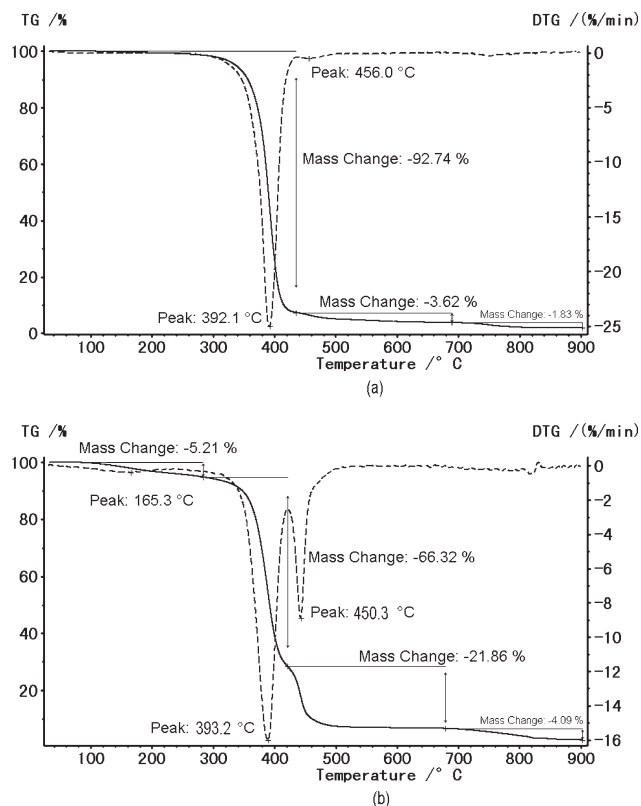

Figure 9 TGA curves of (a) polyacrylate and (b) PANI–polyacrylate copolymer.

make pre-emulsion. HCl, acrylic acid, and H_2SO_4-doped PAN showed well dispersing stability in the pre-emulsion. Through multi-steps *in situ* emulsion polymerization, PANI–polyacrylate copolymer was prepared using the water-soluble azo as initiator. TEM characterization of the products indicated occurrence of *in situ* polymerization on the surface of PANI nanofibers. DSC and TGA analysis of the copolymer illustrated introducing of PANI increased the T_g of polyacrylate by 5.97°C and even improved the thermal decomposed temperature of about 21.86% copolymer by 58.2°C.

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