

Facile Synthesis and Optimization of Conductive Copolymer Nanoparticles and Nanocomposite Films from Aniline with Sulfodiphenylamine

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Abstract: A new series of electrically conductive pure copolymer nanoparticles was facilely synthesized by using oxidative polymerization of aniline (AN) and sodium diphenylamine-4-sulfonate (SDP) in acidic media in the absence of stabilizer. The variation of the structure of the copolymer particles was comprehensively studied by carefully choosing several important parameters, such as the comonomer ratio, oxidant/monomer ratio, polymerization time and temperature, monomer concentration, acidic medium, and oxidant species. Analytical techniques used include IR and UV-visible spectroscopy, X-ray diffraction, laser particle analysis, atomic force microscopy, and trans-

mission electron microscopy. It was found that the particle size varied significantly with the above-mentioned polymerization parameters, only changes in the salt concentration in the aqueous testing solution had no noticeable effect. The polymerization conditions were optimized for the formation of copolymer nanoparticles with sought-after properties. The doped copolymer particles of AN/SDP (50:50) at an oxidant/monomer molar ratio of 0.5 exhibit a minimum length of 50 nm

and a minimum diameter of 44 nm. The bulk electrical conductivity of the copolymer particles increases greatly from 5.90×10^{-4} to $1.15 \times 10^{-2} \text{ S cm}^{-1}$ with increasing AN content. Compared with barely soluble polyaniline, the copolymers exhibit a remarkably enhanced solubility in most solvents, including NH_4OH and even water, due to the presence of the hydrophilic sulfonic groups. Nanocomposite films of the nanoparticles and cellulose diacetate exhibit a percolation threshold of down to 0.1 wt%, at which the film retains 98% of the transparency, 94% of the strength, and 5×10^7 times the conductivity of a pure cellulose diacetate film.

Keywords: aniline • conducting materials • copolymerization • nanostructures • nanotechnology

Introduction

Nanoscale conducting materials have recently attracted considerable interest from an interdisciplinary readership in a wide variety of fields.^[1–5] Polyaniline (PAN) is the most attractive advanced conducting polymer because of its ease of preparation, low cost, variable structure, performance stability, special doping mechanism, and its unique optical, magnetic, electrical, electrochemical, and electrochemomechanical properties.^[5–10] However, the main disadvantage of PAN

is its poor solubility in common solvents, except for *N*-methylpyrrolidone (NMP) and sulfuric acid, as well as its infusibility at traditional melt-processing temperatures. To improve its processability, many investigations into homopolymers of aniline (AN) derivatives or copolymers of AN with its ring-substituted or *N*-substituted derivatives have been performed. One successful approach to produce soluble PAN results from the introduction of sulfonic acid groups.^[11–16] The sulfonated PAN can be obtained either by a post-treatment (sulfonation) of the PAN with the appropriate reagents or by polymerizing sulfonic AN derivatives. Yue and Epstein reported the first sulfonic acid self-doped PAN by sulfonation of the PAN emeraldine base with fuming sulfuric acid.^[11] A water soluble 4-sulfonic diphenylamine homopolymer has also been synthesized.^[12] Unfortunately, the homopolymer had low molecular weight and polymerization yield. Chen and Hwang prepared a water-soluble copolymer, poly[AN-*co*-(*N*-propane sulfonic aniline)].^[13] Another copolymer of AN with sodium diphenylamine-4-sulfonate (SDP) was also prepared by means of oxidative polymerization.^[14] Therefore, sulfonic-group-contain-

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ing AN polymers have attracted interest owing to their largely improved solubility, self-doping nature, and potential for a number of applications.^[8,14]

Another important approach to remarkably improve the processability of PAN is based on the preparation of dispersed colloidal particles. PAN dispersions have been successfully prepared by polymerization of AN in micelles,^[9,16] emulsions,^[17] and reversed microemulsions^[18] as polymerization media. Kim et al. prepared colloidal PAN nanoparticles from sodium dodecyl sulfate micellar solution in aqueous media.^[16] Han et al. reported the preparation of conductive PAN nanoparticles with significantly enhanced processability and thermal stability in a micellar solution of dodecylbenzene sulfonic acid.^[9] PAN aqueous dispersions can also be prepared by using dispersion polymerization in the presence of suitable steric stabilizers, usually water-soluble polymers, such as poly(vinyl alcohol),^[19] poly(vinylpyrrolidone),^[20] poly(vinylmethyl ether),^[21] or cellulose ethers.^[22] Unfortunately, these emulsion and dispersion polymerization systems must include a large amount of external emulsifier, stabilizer, and dispersant, leading to multistep synthetic procedures and complicated compositions of the PAN nanoparticles, which seriously restrict their direct applications. A new technique in which the pure AN polymer nanoparticles are simply prepared by using oxidative polymerization in a relatively simple reaction medium without any external additives has been an important subject. The synthesis of these nanoparticles can be described as an emulsifier-free polymerization. However, a systematic investigation into a facile synthesis technique and the relationship between the polymerization conditions and the size of the AN copolymer nanoparticles has not been carried out so far.

The purpose of this article is to systematically investigate the effect of several important polymerization parameters, including the comonomer ratio and concentration, polymerization temperature and time, acidic medium, oxidant, and oxidant/monomer ratio on the polymerization yield, structure, and properties of the pure AN/SDP copolymer nanoparticles. Furthermore, a transparent composite film of the nanoparticles with cellulose diacetate (CDA) as a matrix was prepared and characterized. In particular, the optimization of the preparation conditions for the formation of the smallest nanoparticles and their nanofilms with the desired properties is also reported.

Results and Discussion

Copolymerization of AN and SDP monomers: A typical example of the variation of the open-circuit potential (OCP) and temperature of the AN/SDP (50:50) copolymerization solution with polymerization time is shown in Figure 1; this provides insight into the polymerization process. The solution changes from colorless to light green, then green, and finally to dark green with dropwise addition of the oxidant. At point **A** the solution becomes light green with an accom-

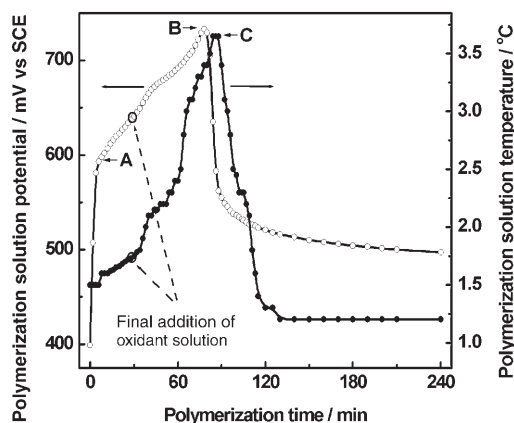


Figure 1. Typical open-circuit potential (OCP, \circ) and temperature (\bullet) of a polymerization solution during the AN/SDP (50:50) polymerization.

panying drastic potential increase, indicating the beginning of the chain propagation. With a continuous addition of the oxidant, the mixture darkens gradually along with a continuous rise in potential that reaches a maximum at point **B** about one hour after the last addition of oxidant. This is followed by a sharp potential decrease. The temperature of the polymerization system rises steadily up to point **C**, after which the temperature first decreases rapidly and then reaches a nearly constant value. It appears that the AN/SDP copolymerization process is exothermic. The variation of solution OCP displays three stages: drastic rise, gradual rise, and fast decline. The drastic OCP rise can be ascribed to the addition of the oxidant. The gradual OCP rise is caused by the dissociation of persulfate ions to radical anions ($\text{SO}_4^{\cdot-}$) and anions (SO_4^{2-}) in the presence of monomers. The formed oligomers can act as reducing agents in this stage. The oxidized oligomers could propagate subsequent polymerization with residual monomers by means of an electrophilic aromatic substitution mechanism. The fast OCP decline is attributed to the completion of the polymerization.

The variation of the OCP and the time taken to reach the maximum OCP with differing AN/SDP ratios of the polymerization solution are listed in Table 1. With increasing SDP content, both the ΔOCP and the time required to

Table 1. The polymerization characteristics of the AN/SDP copolymer salts with an $(\text{NH}_4)_2\text{S}_2\text{O}_8$ /monomer molar ratio of 0.5 in 1.0 M HCl at 1 °C for 24 h.

AN/SDP ^[a]	OCP _{initial} [mV] vs SCE	OCP _{max} [mV] vs SCE	ΔOCP ^[b] [mV] vs SCE	t at OCP _{max} [min]	Yield [%]
100:0	391	790	399	23	83.0
90:10	420	793	373	74	51.0
80:20	366	742	375	76	42.0
70:30	383	744	361	76	38.7
50:50	398	734	336	78	27.8
30:70	370	780	410	90	19.5
0:100	382	732	350	73	15.3

[a] Molar ratio. [b] $\Delta\text{OCP} = \text{OCP}_{\text{max}} - \text{OCP}_{\text{initial}}$.

reach the maximum OCP exhibit a maximum at the AN/SDP molar ratio of 30:70, regardless of the lower oxidation potential of the SDP monomer relative to the AN monomer. On the contrary, AN homopolymerization also exhibits a maximal Δ OCP, but the shortest time required to reach the maximum OCP. This implies that the polymerization between AN and SDP monomers is not a simple addition of their homopolymerizations, but a real copolymerization as a result of a strong chemical interaction between AN and SDP monomers.

The copolymerization yield for the formation of the fine AN/SDP copolymer particles decreases steadily from 83.0 to 15.3 wt% with increasing SDP content from zero to 100%, as also listed in Table 1. The yield decrease is attributed to the losses that occur in the washing step^[13,14] and also to the lower polymerizability of the SDP monomer, which contains a sulfophenylene side group exhibiting greater steric hindrance than that of the AN monomer.

IR spectra of the AN/SDP copolymers: IR spectra for the copolymers with varying SDP content from 0 to 100% are shown in Figure 2. A broad absorption band at 3452–

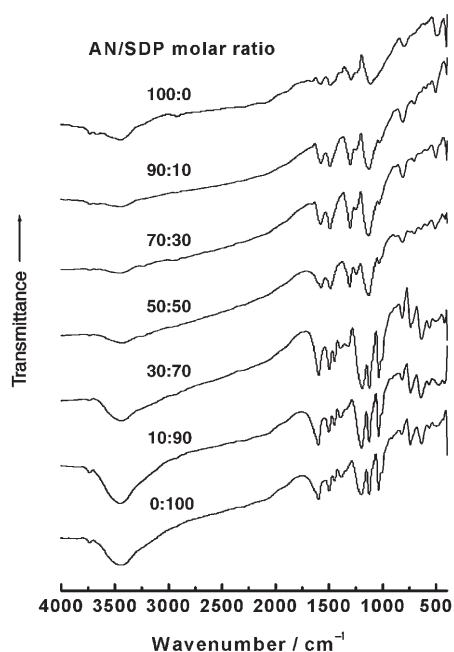


Figure 2. FTIR absorption spectra of the copolymer salts prepared with whole AN/SDP molar ratios with an $(\text{NH}_4)_2\text{S}_2\text{O}_8$ /monomer molar ratio of 0.25 in 1.0 M HCl at a polymerization temperature of 25 °C and reaction time of 24 h.

3443 cm^{-1} is ascribed to the N–H stretching vibration,^[23] which suggests the presence of secondary amino groups (–NH–) in the polymers. The absorption at 1596–1574 cm^{-1} is associated with the quinoid-ring stretching vibration. A strong absorption at 1496–1491 cm^{-1} is attributed to the benzenoid rings of the copolymers. As the SDP content rises from 0 to 70 mol%, an increase in the relative intensity

ratio of quinoid to benzenoid structures occurs. A medium peak at 1287–1300 cm^{-1} is due to the C–N stretching vibration in alternate quinoid–benzenoid–quinoid units. A shoulder peak at 1238–1243 cm^{-1} is ascribed to the C–N stretching vibration in the benzenoid–benzenoid–benzenoid triad sequence. The IR absorption of the copolymers exhibits a reduced intensity at 791–817 cm^{-1} with an increase in the SDP content; this indicates that the peak is indeed attributable to the C–H out-of-plane bending vibration of the *p*-substituted benzene rings on the AN unit.^[14] The peaks at 1121–1126 and 1025–1035 cm^{-1} can be ascribed to the S=O asymmetric stretching vibration and the symmetric stretching vibration of the SO_3^- group on the SDP unit,^[13,14] respectively, because the intensity of these peaks increased significantly as the SDP content increased. A strong S–O stretching band is observed at 695–704 cm^{-1} . In particular, the peak at 1025–1035 cm^{-1} is present in seven of the SDP-unit-containing polymers, but is absent in the PAN spectrum. These results show that the obtained AN/SDP polymers are real copolymers rather than a mixture of AN and SDP homopolymers. In addition, it is seen from Figure 2 that the IR spectra of the copolymers illustrate a vigorous change with increasing SDP content from 50 to 70 mol%. This change signifies that the molecular structure is directed by the presence of AN units with a SDP content of 0–50 mol%, but by the SDP unit with a SDP content of 70–100 mol%.

UV-visible spectra of the AN/SDP copolymers: The UV-visible absorption spectra of all AN/SDP copolymers in Figure 3 exhibit two absorption bands; the first band at 313–

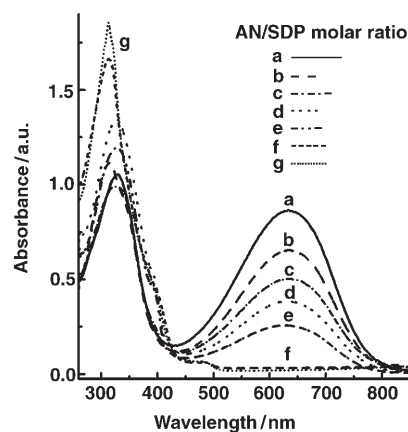


Figure 3. UV-visible absorption spectra of the copolymer salts with AN/SDP molar ratios of a) 100:0, b) 90:10, c) 70:30, d) 50:50, e) 30:70, f) 10:90, and g) 0:100 in NMP at $1 \times 10^{-2} \text{ g L}^{-1}$ at an oxidant/comonomer molar ratio of 0.25.

326 nm owing to a π – π^* transition,^[14] and the second band around 628–635 nm from a n – π^* excitation band associated with the excitation of the benzenoid to the quinoid ring in the polymer chain. The band intensity at 313–326 nm increases gradually while the absorbance at 628–635 nm be-

comes steadily weaker with increasing SDP content, which indicates a remarkably lower concentration of the quinone imine units at higher SDP concentration; this is in agreement with the FTIR spectroscopy results. Simultaneously, the exciton band near 628–635 nm undergoes a hypsochromic shift with increasing SDP content,^[15] suggesting a decrease in the extent of conjugation but an increased band gap. The blueshift with increasing SDP is presumably due to the steric effects of sulfophenylene side groups that produce torsional twists and therefore shorten the conjugation lengths.^[8] This is substantially consistent with the following conductivity results.

Size and morphology of the AN/SDP copolymer particles:

The preparation of PAN nanoparticles by conventional microemulsion and dispersion polymerizations involves a large amount of external stabilizer, which leads to impure nanoparticles. In this study, unexpected fine nanoparticles of AN/SDP copolymers were easily and directly obtained by chemically oxidative precipitation polymerization in acidic aqueous media without any external stabilizer. The comonomer ratio, oxidant/monomer ratio, polymerization time and temperature, monomer concentration, acidic medium, and oxidant type have been carefully optimized for the formation and stable existence of the copolymer nanoparticles, as discussed below.

Optimization of the comonomer ratio: It was found that, for the AN/SDP copolymer particles with increasing SDP content from 0 to 60 mol %, the mean diameter and its standard deviation initially decreased significantly from 10.16 μm to 95.1 nm and from 4.777 μm to 81.0 nm, respectively, followed by a slight increase to 171 nm and 119 nm, respectively (Figure 4a). The copolymer particles with an SDP content of 50 mol % exhibit a minimal diameter of 95.1 nm, which is much smaller than the smallest polysulfoanisidine particles with a mean diameter of 218 nm, as obtained by a laser particle analyzer (LPA).^[8] That is to say, the AN/SDP copolymer containing one sulfonic group on every two units exhibits a much stronger ability to stabilize the formation and existence of the nanoparticles than the polysulfoanisidine containing one sulfonic group on every unit. The reason for this is that the sulfonic groups connected to the AN/SDP polymer chains by a phenylene bridge, just like poly(styrene-*co*-styrenesulfonate),^[24] are much freer than those connected directly to the polysulfoanisidine chains.^[8] Therefore, the AN/SDP copolymer should be more appropriate for the facile synthesis of the nanoparticles than polysulfoanisidine. In fact, the polysulfoanisidine and sulfoanisidine/ethylaniline copolymer can form stable sub-micrometer particles, but not nanoparticles.^[8] The decrease of the particle diameters with increasing SDP content is attributed to the existence of the negatively charged sulfonic groups on the SDP units, acting as an internal stabilizer for the nanoparticles with high surface energy. Similar results were observed when the emulsifier-free copolymerization of styrene and sodium styrene sulfonate was studied.^[24] The sulfonic groups in the polymer

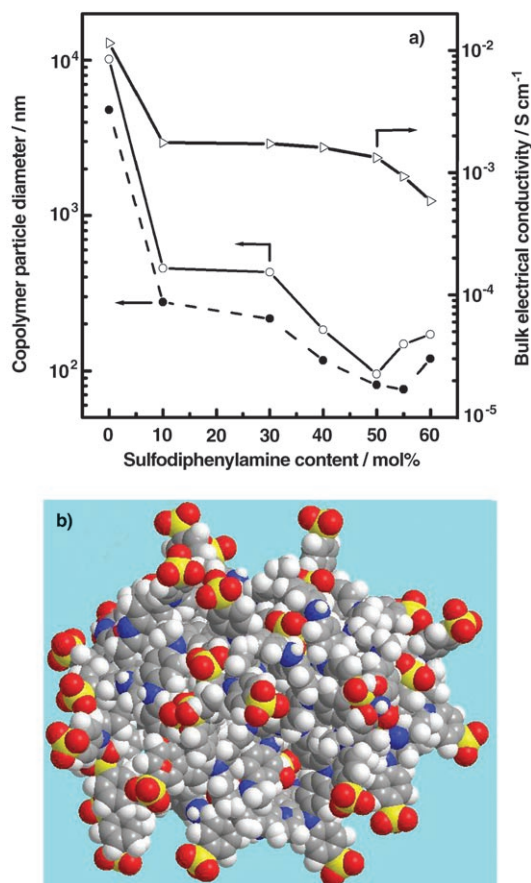


Figure 4. a) The variation of the mean diameter (\circ) and its standard deviation (\bullet , determined by LPA), and the electroconductivity (Δ) of the ultrasonically dispersed AN/SDP copolymer salt particles with SDP content. For the copolymerization, an $(\text{NH}_4)_2\text{S}_2\text{O}_8$ /monomer molar ratio of 0.25 in 1.0 M HCl, a reaction temperature of 25 °C, and a reaction time of 24 h were used; b) The simulated steric macromolecular model of a random AN/SDP (50:50) copolymer ($\text{DP}_n=32$) at minimal energy. Yellow, red, blue, gray, and white spheres represent S, O, N, C, and H atoms, respectively.

chains tend to move onto the surface of the particles, as shown in Figure 4b. Therefore, the sulfonic groups engender a strong static repulsion among the particles and further efficiently stabilize the nanoparticles. The copolymers tend to exhibit a more folded chain configuration as SDP content increases, leading to the formation of smaller particles. Moreover, the nanoparticles with the mean diameter of 95.1 nm were stable in aqueous solution for one year. However, the AN/SDP (45:55 and 40:60) copolymer particles are larger than the AN/SDP (50:50) copolymer particles because the former exhibits slightly more swelling in water and a looser assembly structure. Slightly larger standard deviations of the diameters could be ascribed to the flocculating action of the water-soluble SDP-rich oligomers generated during the nucleation and propagation steps of the copolymerization process.^[24] Note that the mean diameter and its standard deviation of the copolymer particles are dependent on the AN/SDP ratio because of a strong copolymerization effect between both of the monomers. It is concluded

that the AN/SDP molar ratio of 50:50 is optimal for the facile synthesis of copolymer nanoparticles.

The morphology of the AN/SDP (50:50) copolymer nanoparticles was further observed by atomic force microscopy (AFM), as shown in Figure 5a. It seems that the virgin doped copolymer particles are largely ellipsoidal. A typical

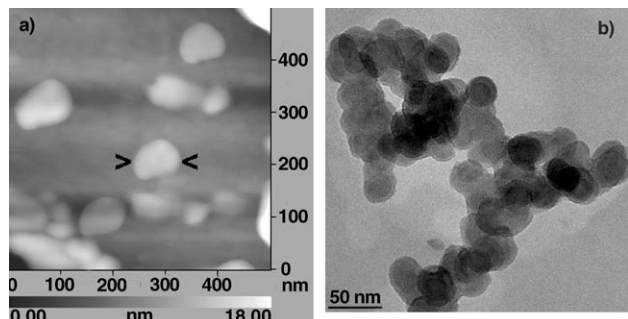


Figure 5. AFM (a) and TEM (b) images of the particles of HCl-doped AN/SDP (50:50) copolymer salt with an $(\text{NH}_4)_2\text{S}_2\text{O}_8$ /monomer molar ratio of 0.25 in 1.0 M HCl at 25 °C.

ellipsoid has a length and diameter of 90 and 67 nm, respectively. These values are even smaller than the smallest ethylaniline/sulfoanisidine (70:30) copolymer particles with a diameter of 120–160 nm, as determined by AFM.^[8] When inspecting the AFM image in Figure 5a, it is more likely that the ellipsoids are aggregates of two or three particles with sizes of approximately 34 nm. It appears that both LPA and AFM methods reveal that the AN/SDP polymer particles are smaller than the ethylaniline/sulfoanisidine polymer particles;^[8] this suggests that the AN/SDP polymer nanoparticles are unusual rather than the ethylaniline/sulfoanisidine polymer sub-micrometer particles. Note that the particle size revealed by AFM is considerably smaller than that observed by LPA because of the contraction caused by an exclusion of water inside the particles during drying; AFM samples are in dry state whereas LPA samples are swollen with water because the copolymers contain a large amount of hydrophilic sulfonic groups. The doped AN/SDP (50:50) copolymer ellipsoids were also observed by using transmission electron microscopy (TEM), as shown in Figure 5b. TEM analysis revealed that the particles have a more uniform length and diameter of 50 and 44 nm, respectively. These values are even smaller than those found by using AFM because of the much greater shrinkage of particles due to larger losses of absorbed water in the high vacuum environment during TEM measurements.^[24] The

size distribution of the AN/SDP (50:50) copolymer nanoparticles was also observed by using AFM analysis, as shown in Figure 6. The AFM image reveals that the doped copolymer particles exhibit a mean diameter of 60.2 nm in a diameter range from 11 to 130 nm. Similarly, the TEM image shows that the copolymer particles have a diameter range from 6 to 60 nm with a mean diameter of 33 nm. Obviously, the particle size revealed by TEM analysis is again confirmed to be substantially smaller than that found by AFM analysis.

In summary, the existence of sulfonic groups on the copolymer chains permits the particle size to be readily controlled by varying the SDP content. Here, the sulfonic groups act as internal stabilizers and provide strong static repulsion and steric hindrance amongst the particles and further efficiently stabilize nanoparticles. The optimal AN/SDP molar ratio to easily prepare the nanoparticles is 50:50. Therefore, the AN/SDP molar ratio was fixed at 50:50 for the following study on the optimization of other polymerization conditions for the synthesis of the copolymer nanoparticles.

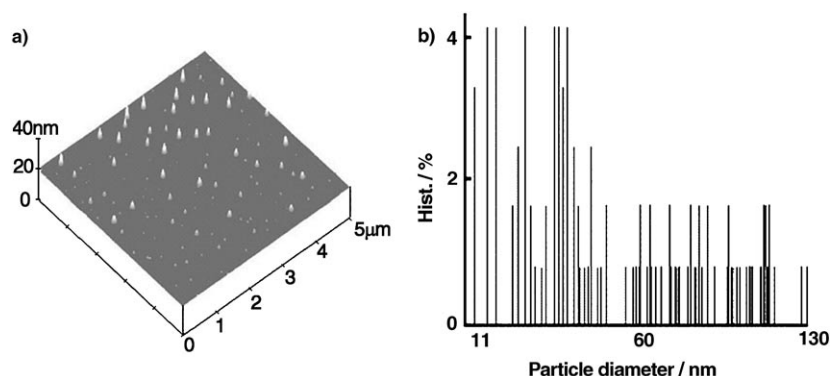


Figure 6. Typical three-dimensional AFM image (a) and distribution diagram (b) of ultrasonically dispersed particles of the AN/SDP (50:50) copolymer salts formed at an $(\text{NH}_4)_2\text{S}_2\text{O}_8$ /monomer molar ratio of 0.25 for a polymerization time of 24 h in 1.0 M HCl at 25 °C.

Optimization of the oxidant/monomer ratio: The influence of the oxidant/monomer ratio on the mean diameter and its standard deviation of AN/SDP (50:50) copolymer particles is shown in Figure 7. It is seen that the mean diameter and standard deviation decrease significantly when the oxidant/monomer molar ratio is changed from 1.25 to 1.0, but only decrease slightly when the oxidant/monomer ratio is changed from 1.0 to 0.25, and exhibit the smallest values of 95.1 and 81.0 nm at an oxidant/monomer ratio of 0.25. At a lower oxidant concentration, more SDP cation radicals form relative to AN cation radicals because the SDP monomer, containing electron-withdrawing sulfophenylene groups, is more easily oxidized than the AN monomer. Generally, *N*-aryl-substituted AN monomers are more reactive than AN monomers, whereas their radicals are less reactive because substitution on the nitrogen atom can considerably enhance the stability of the radical intermediate.^[25] Therefore, lower

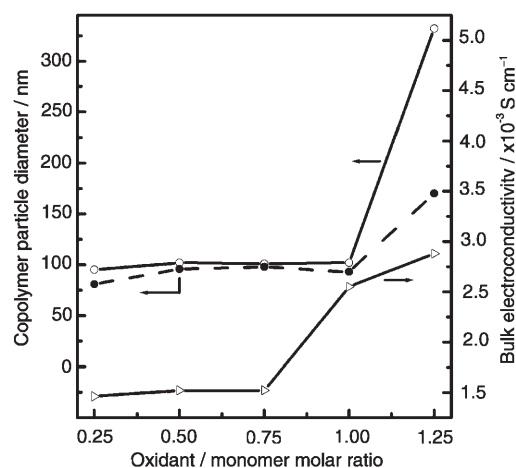


Figure 7. The variation of the mean diameter (○) and its standard deviation (●, determined by LPA), and the conductivity (△) of the AN/SDP (50:50) copolymer salt particles dispersed ultrasonically with the oxidant/monomer molar ratio during the copolymerization with ammonium peroxydisulfate as oxidant in 1.0 M HCl at a reaction temperature of 25 °C for 24 h.

oxidant content can result in the formation of copolymers containing more SDP units, which leads to smaller particle sizes. On the other hand, a higher oxidant content is beneficial for the formation of the AN cation radicals, and therefore the concentration of the AN intermediates is greater than that of the SDP intermediates. This is favorable for the formation of larger copolymer particles and suggests that the optimal oxidant/monomer molar ratio is 0.25–1.0 for the synthesis of the copolymer nanoparticles.

Optimization of the polymerization time: It can be seen from Figure 8 that the particle size and its standard deviation of AN/SDP (50:50) copolymer salt particles are significantly dependent on polymerization time.^[8] The copolymers

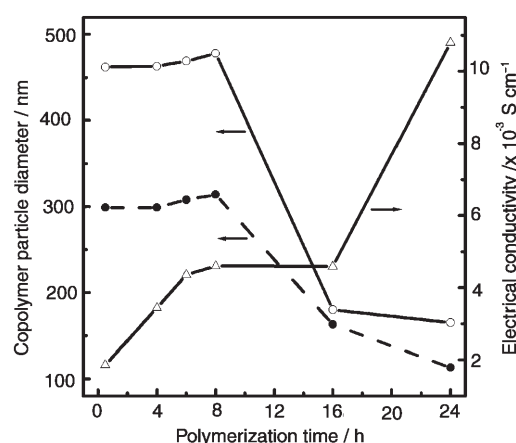


Figure 8. The variation of the mean diameter (○) and its standard deviation (●, determined by LPA), and the conductivity (△) of the AN/SDP (50:50) copolymer salt particles with polymerization time during the copolymerization with an $(\text{NH}_4)_2\text{S}_2\text{O}_8$ /monomer molar ratio of 0.5 in 1.0 M HCl at 25 °C.

form relatively small particles of around 460 nm in a polymerization time period of 0.5–8 h. The mean size and standard deviation then dramatically decrease to much smaller values of 165 and 113 nm, respectively, at 24 h. The variation of particle size with polymerization time indicates that a relatively long polymerization time is beneficial to obtain uniform small particles. This is because an agglomeration of the initial small particles might occur at the earlier polymerization stage thus producing large particles that are consequently smashed up at a later polymerization stage. The agglomeration of the initially formed small particles should be a relatively spontaneous process, whereas the smashing up and uniformization of the large particles formed later could be attributed to continual and vigorous stirring during the polymerization process. It is concluded that a long polymerization time of about 24 h is beneficial to the formation and stabilization of uniform small particles.

Optimization of the polymerization temperature: It is found that polymerization temperature significantly influences the size of AN/SDP (50:50) copolymer particles with a fixed $(\text{NH}_4)_2\text{S}_2\text{O}_8$ /monomer molar ratio (0.25) in 1.0 M HCl. With elevation of the polymerization temperature from 1 to 30 °C, the mean diameter and its standard deviation of the particles first exhibit a decrease and then an increase. The nanoparticles with mean diameters of 91, 93, and 95 nm were obtained at 15, 20, and 25 °C, respectively. The particles formed at 1 °C are the biggest (157 nm), partly due to the lower polymerizability of the SDP monomer (containing a sulfophenylene side group with greater steric hindrance than the AN monomer), which leads to fewer sulfonic groups on the polymer chain. However, at a high temperature, the particles could agglomerate easily because of the higher growth rate of the copolymer particles.^[26] Thus, it can be concluded that a temperature that is too low or too high does not favor the formation of the copolymer nanoparticles and that 15–25 °C is suitable for the preparation of AN/SDP (50:50) copolymer nanoparticles.

Optimization of the monomer concentration: It can be seen from Figure 9 that the monomer concentration is also an important factor that could be used to regulate the formation of the copolymer nanoparticles. Both the size and standard deviation increase with an increase in monomer concentration from 0.025 to 0.4 M in 1.0 M HCl at about 25 °C. When more monomer was added, the oxidant was consumed faster; this led to the formation larger particles. It appears that the lower the monomer concentration, the smaller the formed particles are. However, a monomer concentration that is too low could result in the efficiency and conductivity of the particles being too low. Consequently, the optimal monomer concentration should be around 0.025 M for the formation of the nanoparticles.

Optimization of the acid as polymerization medium: It was found that the diameter of the AN/SDP (50:50) copolymer particles (at an oxidant/monomer molar ratio of 0.5 in 1.0 M

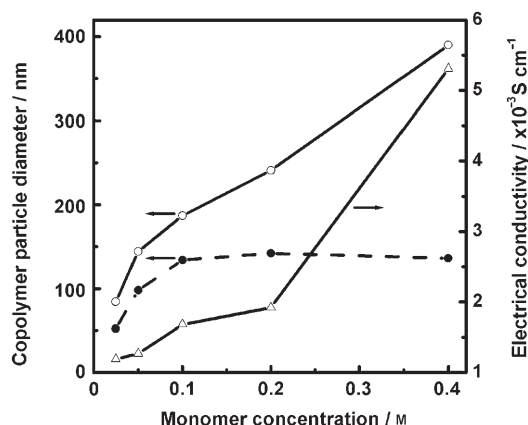


Figure 9. The variation of the mean diameter (○) and its standard deviation (●, determined by LPA), and conductivity (Δ) of the ultrasonically dispersed AN/SDP (50:50) copolymer salt particles with monomer concentration during the copolymerization. A fixed $(\text{NH}_4)_2\text{S}_2\text{O}_8$ /monomer molar ratio of 0.5 in 1.0 M HCl at 25 °C were the conditions used.

acidic aqueous solution at 25 °C) increases steadily by changing the acid polymerization medium from HCl to H_2SO_4 , HNO_3 , or H_3PO_4 (Table 2). That is to say, the parti-

Table 2. The effect of acidic medium and oxidant type on the diameter and bulk conductivity of AN/SDP (50:50) copolymer salt particles with an oxidant/monomer molar ratio of 0.25 at a comonomer concentration of 0.2 M in a 1.0 M acidic aqueous solution at 25 °C.

	Particle size			Bulk conductivity [S cm^{-1}]
	Number-average diameter [nm]	Standard deviation [nm]	Polydispersity index	
Acid medium with a fixed oxidant of $(\text{NH}_4)_2\text{S}_2\text{O}_8$				
HCl	95	81	1.06	1.92×10^{-3}
H_2SO_4	147	71	1.10	1.72×10^{-3}
HNO_3	156	84	1.13	1.12×10^{-3}
H_3PO_4	158	78	1.12	1.44×10^{-3}
Oxidant in a fixed acid medium of HCl				
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	95	81	1.06	1.92×10^{-3}
$\text{Na}_2\text{S}_2\text{O}_8$	145	67	1.09	1.14×10^{-3}
$\text{K}_2\text{S}_2\text{O}_8$	160	91	1.14	1.47×10^{-3}
$\text{H}_2\text{O}_2/\text{FeCl}_2$ ^[a]	164	93	1.16	2.09×10^{-3}

[a] 500:1 molar ratio.

cle size and distribution are significantly dependent on the nature of the acid because proton transfer always accompanies the oxidative copolymerization. In particular, the polydispersity index, defined as (weight-average diameter)/(number-average diameter), seems to increase slightly in a narrow range from 1.06 to 1.13. This signifies that the particles synthesized in this way all exhibit narrow dispersity. When HCl was employed, the smallest size and narrowest size distribution were observed, possibly due to the tightest assembly of the HCl-doped polymer chains as a result of it possessing the smallest anion relative to the other investigated acids. Consequently, the HCl aqueous solution is believed to be the optimal medium for the synthesis of AN/SDP copolymer nanoparticles.

The acid concentration, moreover, dramatically affects the formation of the copolymer particles, as shown in Figure 10. The particles formed in 1.0 M HCl are the smallest, implying that the 1.0 M HCl concentration is of great benefit to produce and stabilize the smallest particles.

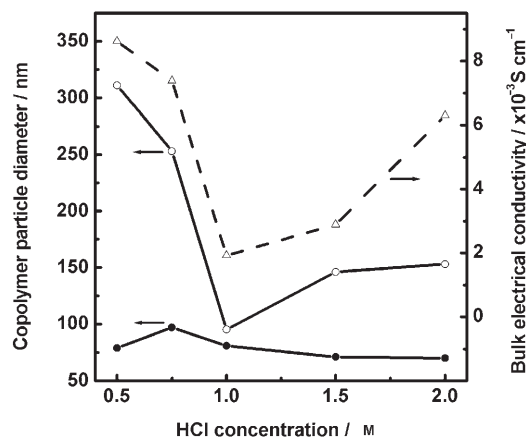


Figure 10. The variation of the mean diameter (○) and its standard deviation (●, determined by LPA), and the conductivity (Δ) of the AN/SDP (50:50) copolymer salt particles dispersed ultrasonically with HCl concentration for the copolymerization with an $(\text{NH}_4)_2\text{S}_2\text{O}_8$ /monomer molar ratio of 0.25 at 25 °C for 24 h.

Optimization of the oxidant type: Four important oxidants— $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\text{Na}_2\text{S}_2\text{O}_8$, $\text{K}_2\text{S}_2\text{O}_8$, and $\text{H}_2\text{O}_2/\text{FeCl}_2$ —were used in the copolymerization system. The influence of oxidant species on the particle size distribution of the AN/SDP (50:50) copolymers is displayed in Table 2. The particles formed with only $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as oxidant are the smallest and have the narrowest size distribution. However, $\text{H}_2\text{O}_2/\text{FeCl}_2$ as oxidant results in the biggest particle size and the broadest size distribution. This suggests that the oxidant cation species in the reaction medium with the same anion would influence the formation and stabilization of the nanoparticles. It appears that $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is the optimal oxidant to prepare the nanoparticles.

The effect of salt concentration on the particle size: The relationship between the particle size and NaCl concentration in an aqueous test solution is shown in Figure 11. It was found that the mean diameter and polydispersity index of the particles remain almost constant with changing NaCl concentration from 0 to 1.0 M. That is to say, the electrostatic coupling of particles through the surface charges was not found with decreasing ionic strength. This implies that the presence of salt in the testing medium does not influence the stabilization of the nanoparticles. It appears that pure water serves as a suitable standard aqueous test solution for nanoparticles with a large amount of sulfonic groups. The diameter of poly(styrene-co-styrenesulfonate) latexes obtained by dynamic light scattering measurement in pure water is confirmed to be just slightly larger than that observed by TEM.^[27]

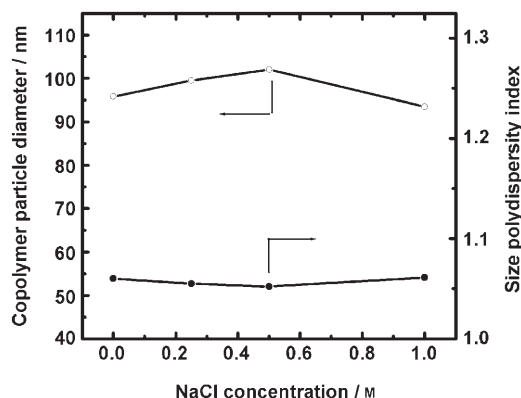


Figure 11. The variation of the size and size distribution (determined by LPA) of the ultrasonically dispersed AN/SDP (50:50) copolymer salt particles with NaCl concentration in an aqueous medium. The particles were synthesized in the copolymerization medium of 1.0 M HCl with an $(\text{NH}_4)_2\text{S}_2\text{O}_8$ /monomer molar ratio of 0.25 at 25 °C for 24 h.

It can be concluded that the formation of AN/SDP copolymer nanoparticles is especially attributed to the existence of negatively charged sulfonic groups on the SDP units. The sulfonic group, acting as an internal stabilizer, can produce electrostatic repulsion among the particles and further efficiently stabilize the particles. In particular, the nanoparticles formed in this way, just like aminoquinoline/ethyl-aniline copolymer nanoparticles,^[28] are relatively pure because the contamination from the external stabilizer is completely excluded. The pure particles could further be applied easily and directly to the preparation of transparent electro-conducting nanocomposite films with high performance, as discussed below.

Properties of the AN/SDP copolymer particles

Bulk electrical conductivity: As shown in Figure 4a, the pressed pellets of the virgin HCl salts of the AN/SDP copolymer particles exhibit a decreased bulk conductivity from 1.15×10^{-2} to $5.9 \times 10^{-4} \text{ Scm}^{-1}$ with increasing SDP content from zero to 60 mol%. The reason for this decrease could be that the steric influence of the sulfophenylene side group can cause a twist in the polymer backbone. This twist will decrease the chain's coplanarity and introduce a barrier to the intrachain transfer and interchain jumping of the electrons, thereby shortening the conjugation length.^[14,15] A similar decrease in the conductivity was observed for AN/(3-amino-benzene sulfonic acid) copolymers.^[29]

As illustrated in Figures 7–9, the conductivity of the AN/SDP (50:50) copolymers steadily increases with an increase in

the oxidant/monomer ratio, monomer concentration, or by extending the polymerization time, because of an increase in the oxidized-state content or molecular weight and therefore conjugation length. However, the conductivity of the copolymers varies unusually with HCl concentration (Figure 10) and polymerization temperature (data not shown). The conductivity of the particles first decreases from $2.09 \times 10^{-3} \text{ Scm}^{-1}$ to the lowest value of $1.33 \times 10^{-3} \text{ Scm}^{-1}$ at 15 °C and then increases up to the highest value of $2.65 \times 10^{-3} \text{ Scm}^{-1}$ as a result of elevating the polymerization temperature from 1 to 30 °C. That is to say, the conductivity is lowest for the smallest particles prepared in 1.0 M HCl or at 15 °C. It appears that the conductivity also varies remarkably with particle size. Larger particles have a higher conductivity whereas the nanoparticles have a lower conductivity, because the former consists of longer conjugated chains and a lower interface resistance in the pressed pellets. However, particle sizes that are too small will produce stronger nanoeffects, that is, stronger interface resistance between the nanoparticles, and more localized electrons due to some lattice defects.^[30] It can also be seen from Table 2 that the conductivity of the copolymers significantly changes with acidic medium and oxidant species. The copolymer nanoparticles formed in HCl exhibit the highest conductivity, indicating that the acid medium species have a stronger effect on the conductivity than particle size. The largest copolymer particles formed with $\text{H}_2\text{O}_2/\text{FeCl}_2$ exhibit the highest conductivity, but the smallest copolymer nanoparticles formed with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as oxidant exhibit the second highest conductivity, implying that both particle size and oxidant species have a significant effect on the conductivity.

Solubility: The solubility and solution color of the AN/SDP copolymer salts in various solvents are listed in Table 3. It can be seen that all polymers are mainly soluble in polar solvents such as NMP and formic acid, both with a high polarity index, but only slightly soluble in THF with a low polarity index. The solubility of the polymers becomes low in DMSO and DMF but high in formic acid, NH_4OH , and water with increasing SDP content. This result suggests that the solubility is primarily controlled by molecular structure.

Table 3. The effect of AN/SDP ratio on the solubility and solvatochromism of AN/SDP copolymer salt particles with an $(\text{NH}_4)_2\text{S}_2\text{O}_8$ /monomer molar ratio of 0.25 in 1.0 M HCl at a polymerization temperature of 25 °C for 24 h.

AN/SDP molar ratio	Solubility ^[a] (solution color, ^[b] UV/Vis maximum absorption wavelength [nm])						
	THF	DMF	DMSO	NMP	HCOOH	NH_4OH	Water
Polarity index	4.2	6.4	6.5	6.7	20 ^[c]	–	10
100:0	SS	PS (bg)	PS (bg,630)	MS (b,633)	MS (g,755)	IS	IS
90:10	SS	PS (bg)	PS (bg)	MS (b,635)	MS (g)	IS	IS
70:30	SS	PS (bg,550)	PS (g,614)	MS (b,636)	MS (g,787)	IS	IS
50:50	SS	SS	PS (g)	MS (b,632)	MS (g,520)	MS (p,554)	PS (y,612)
30:70	SS	SS	PS (g,562)	MS (b,628)	S (dg,515)	S (y,543)	MS (dg,713)
10:90	SS	SS	SS	MS (b,483)	S (dg,470)	S (g)	S (g)
0:100	SS	SS	SS	MS (p,477)	S (dg,460)	S (g,390)	S (v,480)

[a] Solubility: IS=insoluble; MS=mainly soluble; PS=partially soluble; S=soluble; SS=slightly soluble.
[b] Solution color: b=blue; bg=bluish green; dg=dark green; g=green; p=purple; v=viridian; y=yellow.
[c] The data is an estimated value based on the polarity index and dielectric constant of acetic acid.

The sulfonic group should be responsible for the significant variation of the solubility. Additionally, a certain dependence of the solubility in NH_4OH and water on the AN/SDP ratio provides evidence that the polymerization products are indeed copolymers containing both monomer units rather than a simple mixture of two homopolymers.

Solvatochromism and thermochromism: As listed in Table 3, the solution color of the virgin doped AN/SDP copolymers depends on the solvents used. The copolymer solutions are blue in NMP and become green in DMF, DMSO, and formic acid. The UV-visible maximum absorption wavelength of the AN/SDP (100:0 and 70:30) polymer solutions increases steadily when changing the solvents from DMF, DMSO, and NMP to formic acid. This signifies that the copolymers exhibit solvatochromic properties, as the copolymer chains may have different conformations in different solvents and therefore different conjugation lengths.^[8,15] In addition, the maximum UV-visible absorption wavelength of the copolymer solutions depends significantly on the AN/SDP ratio, regardless of a slight variation of solution color. The wavelength of the polymer solutions in NMP and formic acid exhibits a maximum at the AN/SDP molar ratio of 70:30. However, there is no clear relationship between the color and maximal absorption wavelength of the solutions. Besides the solvatochromism, the copolymers also exhibit interesting reversible thermochromism.^[31] Figure 12

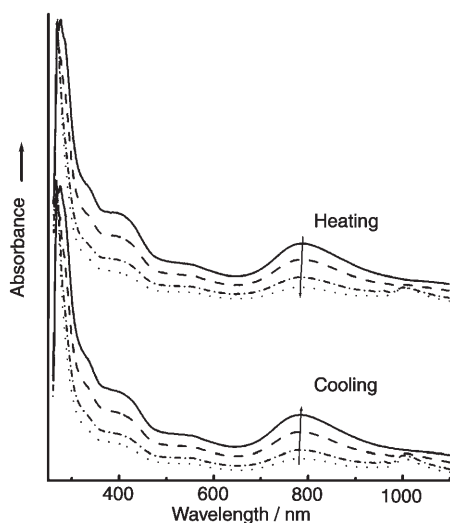


Figure 12. Typical reversible variation of UV-visible absorption spectra of the AN/SDP (70:30) copolymer salt in formic acid with temperature: — = 25, --- = 40, - · - · = 70, and · · · · = 90 °C.

shows a representative temperature dependence of UV-visible spectra of the AN/SDP (70:30) copolymer in formic acid. An almost completely reversible variation of the maximal absorption wavelength of the spectra, from 787, 786, and 785 to 784 nm, took place with heating or cooling the polymer solution between 25 and 90 °C. However, the solution color did not seem to change much, as observed by the

naked eye, indicating that the variation of copolymer structure with temperature is reversible. That is to say, on heating the polymer solution from 25 to 90 °C, the absorbance at 784–787 nm, which is mainly related to the conjugated structure, steadily decreases. On the contrary, the absorbance at 784–787 nm becomes stronger on cooling from 90 to 25 °C.

Crystallinity: The wide-angle X-ray diffractograms for the HCl-doped AN/SDP copolymers in Figure 13 suggest that

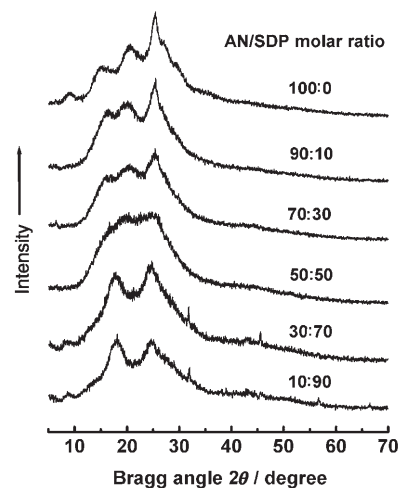


Figure 13. X-ray diffraction patterns for the copolymer HCl salts with the AN/SDP molar ratios from 100:0 to 10:90.

the copolymers are substantially amorphous. PAN shows four peaks at the Bragg angle (2θ) of 9.2, 16.1, 20.6, and 25.4°.^[32] The two strongest peaks centered at 20.6 and 25.4° can be ascribed to the periodicity parallel and perpendicular to the polymer chains.^[33] With increasing SDP content, three of the peaks gradually merge into two peaks. In particular, the intensity of the peak at 25.4° becomes weaker and shifts to a lower Bragg angle. At the same time, a new peak appears around 17.7° and becomes the strongest. Note that the AN/SDP (50:50) copolymer exhibits the broadest peak. Consequently, it can be concluded that the crystalline structure significantly varies with the SDP content, with the lowest crystallinity at a SDP content of 50 mol % because of its most disordered chain structure. The variation of the crystallinity indicates that the AN/SDP polymers prepared by this method are real copolymers rather than a mixture of two homopolymers.

Conducting nanocomposite films: As shown in Figure 14, highly transparent, flexible, and conductive nanocomposite films of CDA containing a small amount of the AN/SDP (50:50) copolymer nanoparticles do not show any well-defined percolation threshold. However, the data have been fitted to the scaling law of percolation theory.^[33] This method yields a percolation threshold value of 0.10 % and a critical exponent of 1.96. The critical exponent value is in good agreement with the predicted universal critical expo-

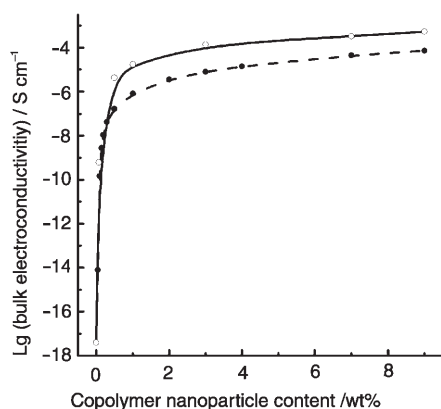


Figure 14. Effect of AN/SDP copolymer salt nanoparticle content on the bulk electrical conductivity of the nanoparticles-CDA composite films cast from *m*-cresol (○) and acetone (●).

ment of 2 for PAN/(camphor sulfonic acid-PMMA) composite films.^[34] It seems that the percolation threshold for the copolymer nanoparticles/HCl-CDA system in this study is significantly lower than the percolation threshold (4.0 or 0.84%) for the composite films from PAN/camphor sulfonic acid-unplasticized or -plasticized CDA.^[35] It is worth noting that the copolymer nanoparticles/CDA composite films have similar electroconductivity to 2 nm-sized polypyrrole nanoparticles/polycarbonate composite films.^[36] It is interesting to note that films cast from *m*-cresol exhibit a ten times higher conductivity than that from acetone, because the *m*-cresol, as a secondary dopant, induces an expanded conformation and longer conjugation length of the chains in the nanoparticles in the film.^[37]

In particular, the nanocomposite films of AN/SDP copolymer nanoparticles in CDA at the percolation threshold (0.10 wt%) exhibit a slightly lower transparency (88%) and tensile strength (142 MPa) than those of pure CDA films (with a transparency and strength of 90% and 151 MPa, respectively). In other words, the nanocomposite film retains 98% of the transparency^[36] and 94% of the strength of the matrix film but exhibits 5×10^7 times the conductivity of the matrix film. Note that a uniform, transparent, and flexible nanocomposite film with a conductivity of $5.4 \times 10^{-4} \text{ S cm}^{-1}$ could be fabricated, even at a high nanoparticle content of 9.0 wt%. This result signifies that the low processability of the AN/SDP copolymers could be resolved by simply blending with traditional processable polymers as the matrix.

Conclusion

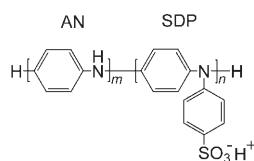
Copolymer nanoparticles were successfully synthesized by the oxidative polymerization of AN and SDP monomers in acidic aqueous media in the absence of any external emulsifier or stabilizer. The polymerization yield, size, morphology, and conductivity of the copolymer particles significantly depend on the comonomer ratio, oxidant/monomer ratio, polymerization time and temperature, monomer concentration, acidic medium, and oxidant species. These key synthe-

tic parameters have therefore been optimized for the formation of small copolymer nanoparticles with optimal properties. The copolymers are mainly or completely soluble in NMP and formic acid. In particular, the copolymers containing more than 50 mol% SDP units are partly or totally soluble in water and NH_4OH . A variation of the particle size, spectra, and properties of the polymers with the comonomer ratio suggests that the polymers obtained are real copolymers rather than a simple mixture of two homopolymers. The presence of sulfonic groups on the SDP units is vital for the facile synthesis of nanoparticles as small as 50 nm by means of the precipitation copolymerization of AN with SDP monomers. The negatively charged sulfonic side groups act as a unique internal stabilizer and can engender strong electrostatic repulsion between the as-formed particles and further efficiently stabilize them. Nanocomposite films were facilely fabricated by blending the AN/SDP copolymer nanoparticles with CDA. The films have a low percolation threshold of 0.10 wt% nanoparticles. The nanocomposite films at the percolation threshold possess 98% of the transparency, 94% of the tensile strength, and 5×10^7 times the conductivity relative to pure CDA film. The nanocomposite film containing 9 wt% copolymer nanoparticles exhibits conductivity of about $5.4 \times 10^{-4} \text{ S cm}^{-1}$, which is very close to the values obtained for the copolymer nanoparticles alone. In particular, the electrical and other properties of the nanocomposite films could be optimized by simply changing the nanoparticle content. Furthermore, it could be speculated that the nanoparticles could be used as a novel support for enzyme immobilization due to their very large surface-to-volume ratio. In addition, they possess large amounts of sulfonic and imino groups that present very simple, mild, and time-saving possibilities for enzyme immobilization.^[38]

Experimental Section

Reagents: Aniline (AN), sodium diphenylamine-4-sulfonate (SDP), cellulose diacetate (CDA), ammonium peroxydisulfate, *N*-methylpyrrolidone (NMP), formic acid, dimethyl sulfoxide (DMSO), and other solvents were commercially obtained and used as received.

Synthesis of the AN/SDP copolymer nanoparticles: The AN/SDP copolymer nanoparticles were prepared by chemically oxidative polymerization in an aqueous HCl medium under different polymerization conditions without any external stabilizers. A representative procedure for the preparation of the AN/SDP (50:50) copolymer nanoparticles is as follows: HCl (1.0 M, 25 mL) was added to AN (0.455 mL, 5 mmol) and SDP (1.356 g, 5 mmol) in a 250 mL glass flask in a water bath and stirred vigorously for half an hour. In a separate container, ammonium peroxydisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.571 g, 2.5 mmol) was dissolved in HCl (1.0 M, 25 mL) to prepare an oxidant solution. The oxidant solution was then added dropwise to the monomer solution at a rate of one drop every 3 s at 25°C over a period of 30 min. The reaction mixture was then continuously stirred by using a magnetic stirrer for 24 h in a water bath at 25°C. After the reaction, the virgin HCl salt copolymer particles formed were isolated from the reaction mixture by filtration or centrifugation and washed with an excess of distilled water to remove the oxidant and oligomers. The salt particles of the copolymers in the corresponding solutions were analyzed directly by LPA, AFM, and TEM before filtration. A dark green powder was left to dry under an infrared lamp for one



Scheme 1. A nominal macromolecular chain structure of aniline (AN) and sulfodiphenylamine (SDP) copolymers.

(NH₄)₂S₂O₈/monomer ratio of 0.25 in 1.0 M HCl at 25 °C. The virgin HCl-doped nanoparticles were sedimented by centrifugation and washed with 1.0 M HCl aqueous solution. After drying at 60 °C in an oven for 48 h, the 10–30 μm-thick film was peeled off the glass substrate to form a free-standing film for performance evaluation.

Measurements: The copolymerization was followed by analysis by the OCP technique, by using a saturated calomel electrode (SCE) as reference electrode and a Pt electrode as working electrode. IR spectra were recorded on a Nicolet FTIR Nexus 470 spectrophotometer using KBr pellets. UV-visible spectra were obtained on a Lambda 35 UV-visible spectrophotometer from Perkin–Elmer in a wavelength range of 190–1100 nm. Samples consisted of either homogeneous solutions of the copolymers for the molecular structure evaluation, or nanocomposite films of the copolymer particles in CDA for transparency characterization. Wide-angle X-ray diffractograms for virgin HCl-doped particles of the AN/SDP copolymers were obtained by using a D/max 2550 model X-ray diffractometer (Rigaku, Japan) with CuK_α radiation at a scanning rate of 10 ° min⁻¹ in the reflection mode over a 2θ range from 5 to 70°. The size and size distribution of the water-washed copolymer particles were analyzed in aqueous medium or NaCl aqueous solution on a Beckman Coulter LS230 laser particle-size analyzer (LPA) by using a static scattering laser with a wavelength of 750 nm. AFM measurements of particle size were carried out by using a SPA-300HV AFM instrument (Seiko SII instrument, Japan) in the standard tapping mode in a scan range of 20 μm in the *xy* direction and 2 μm in the *z* direction. The resolution in the *xy* and *z* directions was 0.2 and 0.01 nm, respectively. The AFM samples were prepared by dropping an aqueous suspension of the particles onto a cover glass, followed by drying in air at 20 °C. AFM observation of the particle size distribution was performed by using a Multimode IIIa Instrument, Digital Instrument USA, in the standard tapping mode with a scan range of 125 × 125 mm² in the *xy* direction and 5 mm in the *z* direction at a scanning rate of 1.606 Hz with a magnification of 1000000. The resolution in the *xy* and *z* directions was 0.1 and 0.01 nm, respectively. Samples for high-resolution TEM (Jeol TEM-2010) were prepared by dropping a suspension of the particles onto copper grids. The solubility of the copolymers was evaluated by using the following method: Dried polymer powders (5 mg) were added to the solvent (1 mL) and dispersed thoroughly. After the mixture was shaken continuously for 24 h at room temperature, the solubility of the polymers and solution color were characterized. The bulk electrical conductivity of a pressed disk with a thickness of 10–100 μm for the AN/SDP copolymers and the nanocomposite films were measured by a two-probe method at 20 °C. The mechanical properties of the films were measured by using an Electronic Pulling Tester.

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week. The AN/SDP copolymers exhibit the nominal structure as presented in Scheme 1.

Preparation of the nanocomposite films: The nanocomposite films were prepared by ultrasonically dispersing preformed AN/SDP (50:50) copolymer nanoparticles in acetone or *m*-cresol solutions of CDA for 2.0 h, followed by solution casting onto a glass plate. The ellipsoidal copolymer nanoparticles were prepared with an

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