Hyperbranched Sulfonated Polydiphenylamine as a Novel Self-Doped Conducting Polymer and Its pH Response

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ABSTRACT: A synthesis strategy for a hyperbranched sulfonated polydiphenylamine was developed. First, a hyperbranched polyvinylbenzoxylamine (H-PVBPA) was prepared by controlled atom transfer radical copolymerization of an amino-protected vinylbenzoxylamine (4-VBPA-^{t}BOC) and 4-chloromethyl styrene followed by deprotection. Second, H-PVBPA was reacted with sodium diphenylamine sulfonate under acidic conditions to generate hyperbranched sulfonated polydiphenylamine (H-PSDA). The H-PSDA exhibited conductivities of 3.7×10^{-2} and 1.2×10^{-2} S/cm in HCl-doped and self-doped states, respectively. The microstructure of H-PSDA in aqueous solutions was found to be sensitive to the pH. In the dedoped state (at pH $\geq$ 7), AFM identified nanoscale particles of uniform size around 40 nm. The self-doped H-PSDA aggregated at pH = 7 via intermolecular doping interaction, generating large and irregular particles (>200 nm). When the pH was decreased below 5, the aggregates could be dispersed as smaller particles of about 120 nm because of the replacement of the intermolecular self-doping by the external-doping interaction caused by the small molecules of HCl.

Introduction

In the past decade, dendrimers have been extensively studied as materials with novel physical properties.[1,2] They have a very compact structure and can be highly functionalized. They can be prepared by the step-growth polycondensation of AB_n monomers. However, the step-growth synthesis requires strict experimental conditions and even intermediate purifications. In contrast, the synthesis of hyperbranched polymers can provide dendritic molecules in a single, one-pot reaction. The self-condensation vinyl polymerization (SCVP) is a new synthesis method, which can be employed to prepare hyperbranched (co)polymers.[3] An initiator-monomer ("inimer") with the general structure AB*, in which A is a double bond and B* is a functional group, was employed. B* can be transformed to an active center which initiates the polymerization of the double bonds. This general approach was applied to various kinds of living polymerizations, i.e., ionic,[3] radical,[4−6] group transfer,[7] and even ring-opening polymerization,[8] because the B* group can be transformed into a cationic, radical, or anionic active center. In recent years, the SCVP synthesis concept was used to prepare hyperbranched polymers in a single, one-pot controlled radical polymerization. Three controlled (living) radical polymerizations, namely the stable free radical polymerization (SFRP),[9] the atom transfer radical polymerization (ATRP),[10] and the reversible addition−fragmentation chain transfer polymerization (RAFT),[11] have been developed. A radical SCVP of styrene was carried out in the presence of vinyl-functionalized 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) by the SFRP method.[6,12] Matyjaszewski et al. developed an ATRP method, which allowed the controlled radical polymerization of some vinyl-functionalized inimers.[13] The 4-chloromethylstyrene (CMS) inimer was homopolymerized to hyperbranched polystyrene (H-PS) and also copolymerized with styrene by the ATRP method.[14] Yang et al. reported an inimer which could be copolymerized with styrene by the RAFT method.[15] Furthermore, Mueller et al.[16] synthesized the macroinimer acryoyl-functionalized poly(*tert*-butyl acrylate), which has a polymerizable double bond at one end and a bromine atom at the other end that can act as initiator in the ATRP method.

As an important conjugated polymer, polyaniline (PANI) was extensively studied in the past decades.[17−20] PANI was easily prepared from aniline via an acid-mediated radical mechanism. Its poor processability and solubility in common solvents were caused by the stiffness of its backbone and the inter-hydrogen bonding interaction with the amino moieties of the adjacent chains. To improve the solubility of PANI in organic compounds and its processability, many approaches have been employed, such as the copolymerization of aniline with its derivatives[21] and substitutions on the emeraldine base, either at the N sites or on the phenyl rings of the PANI backbone.[22] Synthesis methods through modifications of the PANI backbone were also employed to produce water-soluble polyaniline.[23,24]

In the present paper, a hyperbranched sulfonated polydiphenylamine was prepared. First, a styryl-substituted aniline macromonomer, namely 4-(4-vinylbenzoxyl)(*N*-*tert*-butoxycarbonyl) phenylamine (4-VBPA-^{t}BOC), was prepared by reacting 4-aminophenol with di*tert*-butoxyl dicarbonate followed by the substitution with 4-vinylbenzyl chloride. The amino-protected 4-VBPA-^{t}BOC was subjected to atom radical copolymerization with CMS, which acted as an inimer. The subsequent deprotection with trifluoroacetic acid (TFA) produced hyperbranched poly(4-(4-vinylbenzoxyl) phenylamine) (H-PVBPA) containing pendent amine moieties. Second, the H-PVBPA was reacted with a water-soluble monomer, sodium diphenylamine sulfonate (SDAS) to generate hyperbranched sulfonated polydiphenylamine (H-PSDA). The conductivities of the final H-PSDA self-doped or HCl-doped were determined by

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the four-point method, and the electromagnetic shielding effectiveness (EMI SE) of the self-doped copolymer over a frequency range from 10 to 10^3 MHz was also measured. The behavior of the H-PDA in aqueous solutions at various pH values was characterized by UV, AFM, and SEM. Furthermore, the oxidation levels of these copolymers at various doping states were examined by X-ray-photoelectron spectroscopy (XPS).

Experimental Section

Materials. 4-Aminophenol (98+ wt%), sodium diphenylamino-4-sulfonic, hydrochloric acid (37 wt%), aniline (99 wt%), di*tert*-butyldicarbonate (97 wt%), trifluoroacetic acid (TFA, 97 wt%), ammonium persulfate (98 wt%), 4-choromethyl styrene (97 wt%), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, 98 wt%), triethylamine (97 wt%), CuCl (99+ wt%), ethyl-2-chloropropionate (EPNCl, 97 wt%), and potassium carbonate (99 wt%) were purchased from Aldrich and used without further purification. The solvents, dimethylformamide (DMF), tetrahydrofuran (THF), and dichloromethane (DCM), purchased from Aldrich, were of HPLC purity. An H^+-type ion-exchange resin (H^+-type AMBERJET 1200 H resin) was purchased from Aldrich (Trademark of Rohm and Haas Co.).

N-*tert*-butoxylcarbonyl-4-aminophenol (4-AP-^{t}BOC) and 4-(4-vinylbenzoxyl) (*N*-*tert*-butoxycarbonyl) phenylamine) (4-VBPA-^{t}BOC) were prepared as described in refs 25 and 26, respectively.

ATRP of 4-VBPA-^{t}BOCA in the Presence of CMS. 4-VBPA-^{t}BOC (7.5 mmol), 0.25 mmol of CMS, 0.25 mmol of CuCl, and 0.375 mmol of PMDETA were introduced into a 50 mL flask containing 10 mL of THF. The system was degassed three times using thaw−freeze cycles, and then the temperature was raised to 60 °C and the reaction allowed to proceed for 48 h more under a dry nitrogen atmosphere. The increase with time of the viscosity indicated the start of polymerization. Small samples were taken out periodically for NMR determinations. After reaction, 30 mL of THF was introduced to dilute the viscous paste in the flask. To remove the PMDETA and CuCl, the THF solution was passed through a neutral Al_2O_3 column. The light yellow solution obtained was first concentrated by removing the THF using a rotary evaporator and then subjected to precipitation in a mixture of methanol/water (5:1, v/v). Further purification was achieved by dissolution in THF followed by precipitation in the above nonsolvent mixture. A light yellow precipitate, hyperbranched PVBPA-^{t}BOC (H-PVBPA-^{t}BOC), was obtained and dried under vacuum for at least 24 h at room temperature with a yield of 46 wt%. FTIR (cm^{-1}): 3300−3150 (−NH), 2900 (phenyl), 1750−1670 (−C=O in ^{t}BOC). ^{1}H NMR (ppm): 7.4−6.7 (m, 8H), 6.34(s, 1H), 5.05 (s, 2H), 2.75 (m, 1H), 1.90 (m, 2H), 1.53 (m, 9H).

A controlled linear PVBPA-^{t}BOC was prepared using the same procedure but replacing CMS with EPNCl.

General Procedure of Deprotection of H-PVBPA-^{t}BOC. H-PVBPA-^{t}BOC (2.4 g) was dissolved in 60 mL of DCM in a 100 mL flask. TFA (4.0 g) was added and the system subjected to intensive stirring. The system was sealed in a dry nitrogen atmosphere, the temperature was raised with a slight reflux to about 60 °C, and the reaction was allowed to proceed for 6 h. Two layers were formed, and the DCM and the excess of TFA were removed under vacuum. Then, triethylamine (3.0 g) and 100 mL of DCM were introduced to precipitate the salt. The DCM was washed with 50 mL of water until neutral and dried with Na_2SO_4. After the DCM was removed using a rotary evaporator, a red solid, PVBPA, was obtained with a yield of 90 wt%. FTIR (cm^{-1}): 3350−3250 (−NH_2), 2900 (phenyl), 1610 (C−NH, def). ^{1}H NMR (ppm): 7.4−5.8 (m, 8H), 4.95 (s, 2H), 2.38 (s, 1H), 1.46 (m, 2H).

Copolymerization of Hyperbranched PVBPA and Sodium Diphenylamine Sulfonate (SDAS). H-PVBPA (0.133 g), 1.14 g of $(NH_4)_2S_2O_8$, and 2.7 g of SDAS were introduced into a 50 mL flask containing 30 mL of 1.2 N HCl. The system was subjected to intensive stirring and cooled to 5 °C. After 8 h, the copolymer was separated by centrifugation at 3500 rpm for 30 min in a super-speed centrifuge (RC-5B, Dupont) and the precipitate was washed three times with water/ethanol (10:1, v/v) until a colorless supernatant was obtained. The precipitate was neutralized with a 1.0 N ammonium aqueous solution and the neutralized copolymer was further purified by dialysis. The neutralized solution of 0.01 g/L could be passed through the PTFE filter membrane with a pore size of 250 nm. The dialysis bag (Fisherbrand, Nominal MWCO 60,000, which separates the linear and low-molecular-weight homopolmyers or copolymers), containing a neutralized copolymer aqueous solution (the copolymer was dissolved in 50 mL of water), was kept in a 0.01 N ammonium aqueous solution for 7 days until no colored supernatant was detected. This was followed by dialysis in water for additional 7 days for the solution to become neutral. A self-doping copolymer solution was prepared by passing the obtained solution through an H^+ ion-exchange column containing an IR 1200 H resin by ion exchanging NH_4^+ with H^+.[27]

Characterization. Proton (^{1}H) NMR, UV−vis absorption, and FTIR measurements were carried out on a 500 MHz INOVA-500, a Thermo Spectronic Genesys-6, and a Perkin-Elmer-FTIR 1760 spectrometer, respectively. The solutions for NMR were prepared by dissolving the polymer in deuterated DMF, deuterated chloroform, deuterated DMSO, or deuterated water. Gel permeation chromatography (GPC, Waters) was used to evaluate the molecular weights of the polymers on the basis of a polystyrene calibration curve. The GPC was equipped with three 30 cm long columns filled with Waters Styragel, a Waters HPLC 515 pump, and a Waters 410 RI detector. The GPC measurements were carried out at 60 °C using DMF as eluent at a flow rate of 1.0 mL/min and 1.0 cm/min chart speed. The elemental analysis of the polymer samples was carried out on a Perkin-Elmer Model 2400 C, H, N analyzer. The chlorine and sulfur contents were determined by the oxygen flask method. The room-temperature conductivities of the compressed pellets of the self-doped and HCl-doped hyperbranched copolymers were determined using the conventional four-point probe method. The electromagnetic shielding effectiveness (EMI SE) was determined over a frequency range from 10 to 10^3 MHz using the coaxial cable method. The setup consisted of an Elgal (Israel) SET 19 A shielding effectiveness tester with its input and output connected to a HP 8510A network analyzer. An HP APC-7 calibration kit was used to calibrate the system. The EMI SE values, expressed in dB, were calculated from the ratio of the incident to transmitted power of the electromagnetic wave using the following equation:

$$\mathrm{SE} = 10 \log [P_1/P_2] \quad \text{(decibels, dB)}$$

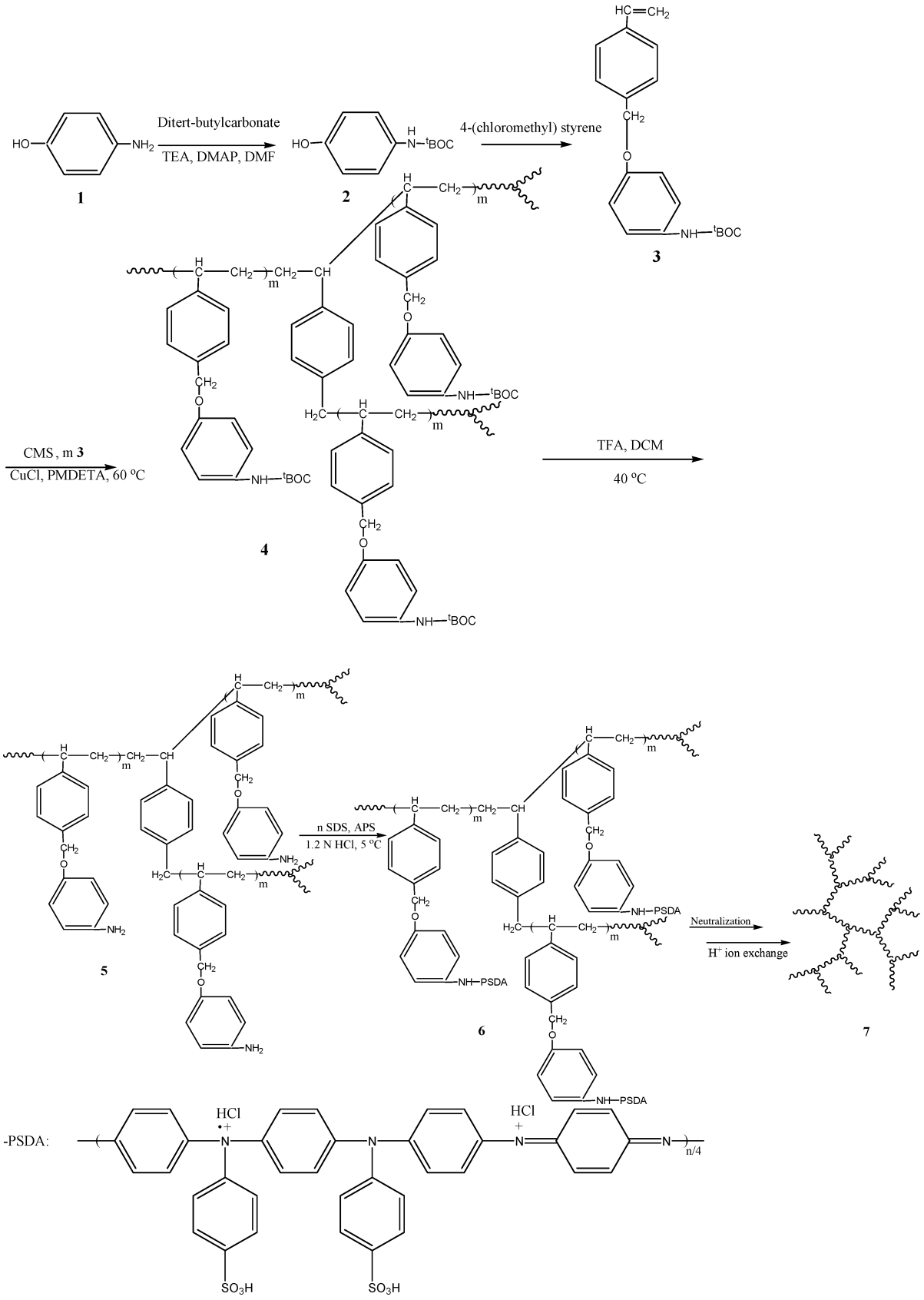
where P_1 and P_2 are the incident power and the transmitted power, respectively.

Scanning electron microscopy (SEM) was used to examine the surface morphology. The polymer samples were prepared through spin-coating polymer aqueous solutions of 0.1 g/L on freshly cleaned mica plates at 1000 rpm for 1 min followed by sputter-coating with carbon (to prevent sample-charging) and examined using a Hitachi S-4000 Field Emission Scanning Electron Microscope operated at 20 keV. The atomic force microscope (AFM, Quesant Scan Atomic Company) was used to investigate the molecular conformation of the macromolecules and the structure of the aggregates. Polymer aqueous solutions (0.1 g/L) at various pH values were spin-coated for 1 min onto freshly cleaned silicon wafers at 1000 rpm, and subsequently examined under AFM in the tapping mode. The XRD of the polymer particles was recorded on a SIEMENS, D5000, X-ray diffractometer with Cu Kα radiation of 1.5406 Å wavelength operated at a maximum of 30 MA and 40 KVP.

Results and Discussion

Synthesis and Characterization. A hyperbranched sulfonated polydiphenylamine (**7**) was prepared via the six successive steps presented in Scheme 1. The vinyl-functionalized monomer, 4-VBPA-^{t}BOC (**3**), was first

Scheme 1. Synthesis Strategy of Hyperbranched PSDA



obtained via the amino-protected reaction of 4-aminophenol with ^{t}BOC to generate ^{t}BOC-protected aminophenol (4-AP-^{t}BOC, **2**). This reaction was followed by the substitution reaction of 4-chloromethyl styrene to the hydroxide moiety of 4-AP-^{t}BOC (**2**). Further, 4-VBPA-^{t}BOC (**3**) was subjected to ATRP copolymerization using CMS as inimer. The active site, the chloride moiety, initiated the polymerization of 4-VBPA-^{t}BOC, generating branching and thus forming a hyperbranched PVBPA-^{t}BOC (**4**). After deprotection with TFA, a hyperbranched PVBPA (**5**) was obtained by removing the ^{t}BOC moieties. Then, sodium diphenylamine sulfonate

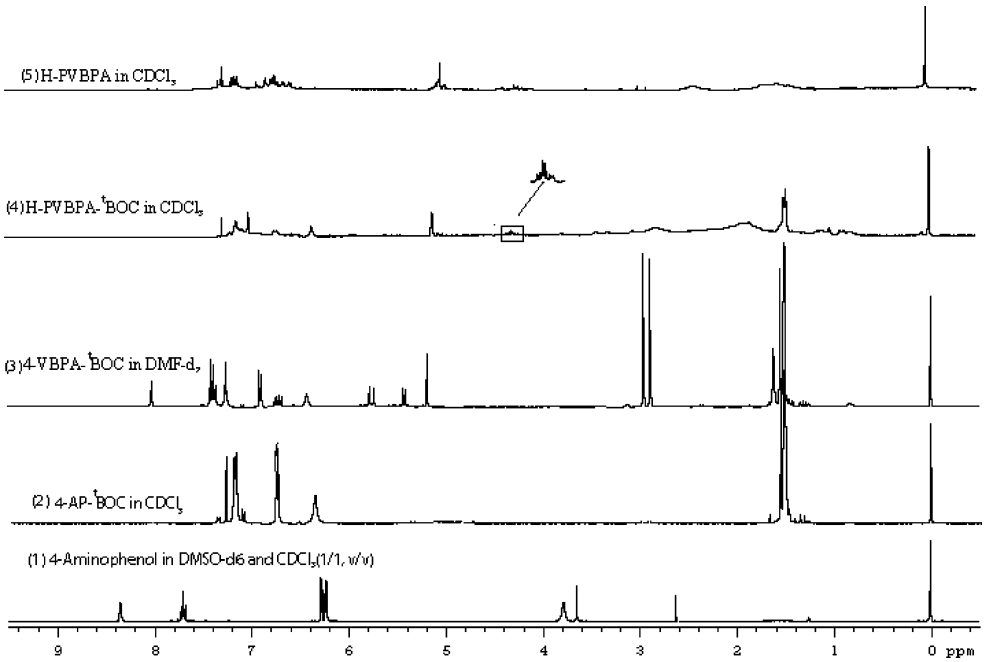


Figure 1. NMR spectra of 4-aminophenol (**1**), 4-AP-^{t}BOC (**2**), VBPA-^{t}BOC (**3**), H−PVBPA-^{t}Boc (**4**), and H-PVBPA (**5**).

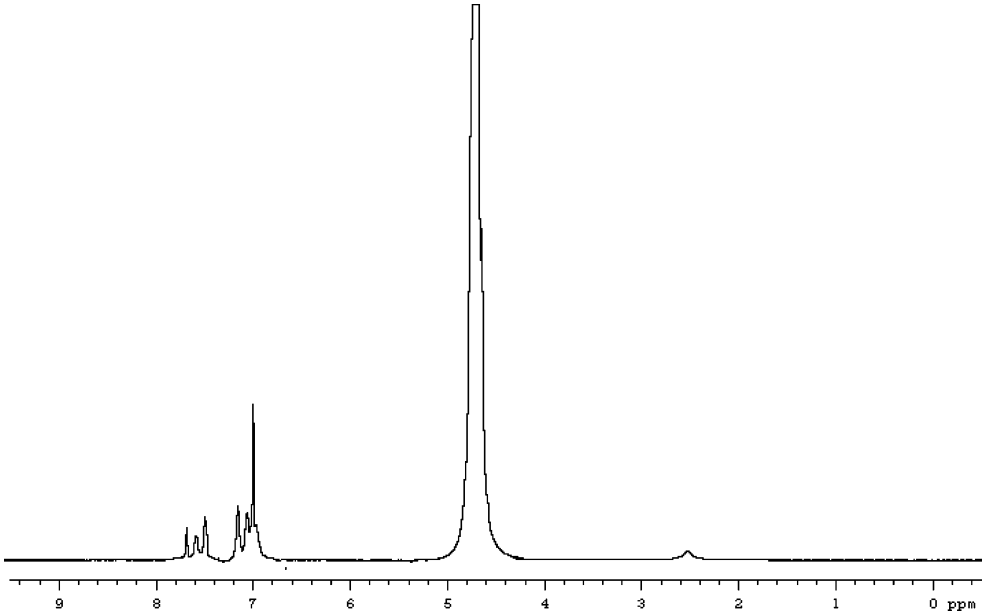


Figure 2. NMR spectra of self-doped H-PSDA (**6**) in deuterated water.

was allowed to react with the amine moieties of H-PVBPA to generate a hyperbranched poly(sodium diphenylamine sulfonate) (**6**). Finally, the ion-exchange reaction between **6** and the H^+ of an ion-exchange resin resulted in an acidified hyperbranched H-PSDA (**7**). Figure 1 presents the ^{1}H NMR spectra of compounds **2**, **3**, **4**, and **5**. After the ^{t}BOC protection, the proton signal of the amino moiety of **2** was shifted to a lower field, 6.34 ppm, because of the shielding due to the ^{t}BOC. For compound **3**, the proton signals which can be assigned to the vinyl moiety are located at 6.67, 5.6, and 5.2 ppm, respectively (deuterated DMF as solvent). The signals due to the amino and methyl moieties of ^{t}BOC are still present at 6.41 and 1.56 ppm, respectively, and the signal due to hydroxide moiety at 7.48 ppm disappeared, indicating that the styrene moiety was successfully attached to aminophenol. The vinyl-functionalized monomer (**3**) was copolymerized with CMS by the ATRP method (the polymerization kinetics will be discussed later). The broad signals of the obtained hyperbranched PVBPA (**4**) at 7.4−6.7 ppm can be assigned to the substituted phenyl moieties of **4** and CMS, and the signals at 2.75 and 1.90 can be assigned to methylene and methane of the ethylene originated from the vinyl moiety (**3**). The other signals at 6.34 and 1.53 ppm can be assigned to ^{t}BOC, indicating that the polymerization did not destroy the ^{t}BOC protection. The weak and broad signals at 4.2−4.7 ppm can be assigned to the methylene adjacent to the chloride end group, indicating a well-carried-out ATRP. After deprotection, the signals at 6.34 and 1.53 ppm assigned to ^{t}BOC could be hardly identified (see the spectrum of **5** in Figure 1).

After the reaction between H-PVBPA and sodium diphenylamine sulfonate, the obtained copolymer (**6**) became water soluble. The NMR spectrum of **6** in deuterated water (Figure 2) exhibited broad signals at

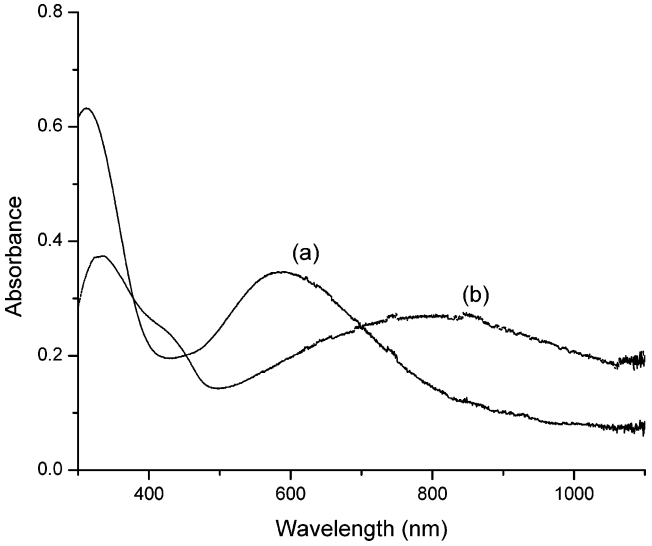


Figure 3. UV spectra of (a) dedoped and (b)self-doped H-PSDA in aqueous solution.

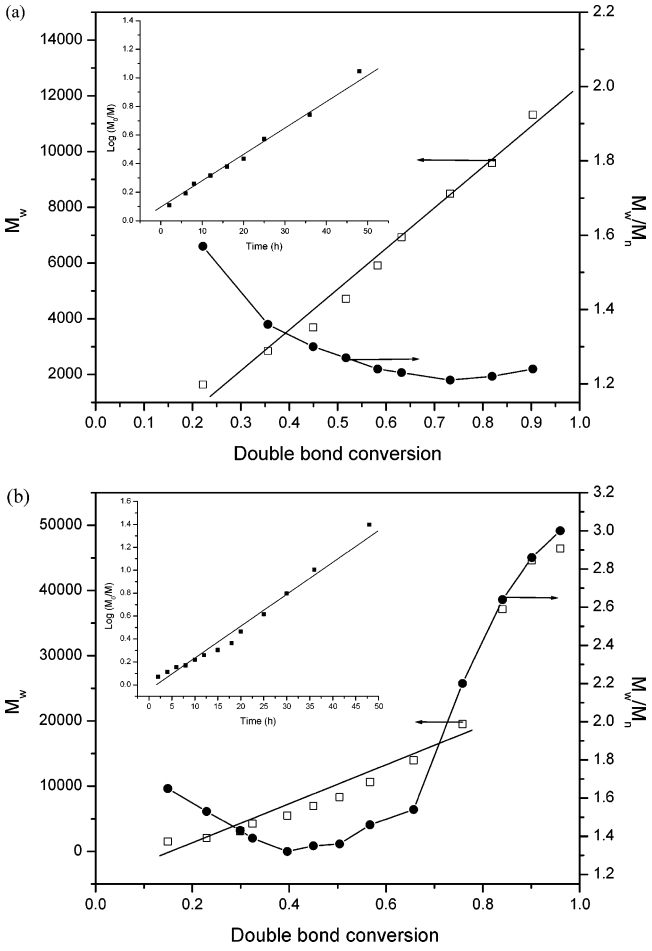


Figure 4. Dependence of M_w and PDI for (a) homopolymerization of 4-VBPA-^{t}BOC and (b) copolymerization with CMS on the reaction time during the ATRP processes. (a) [4-VBPA-^{t}BOC]/[EPNCl]/[CuCl]/[PMDETA] = 30:1:1:1.5, 60 °C, and (b) [4-VBPA-^{t}BOC]/[CMS]/[CuCl]/[PMDETA] = 30:1:1:1.5, 60 °C.

6.5−8.0 ppm, which can be assigned to the phenyl rings of the branched side chains of polysodium diphenylsulfonate (PSDAS). The signals assigned to the polyethylene main chain could hardly be identified because, being hydrophobic, they were not exposed to water; as a result, the signals became very broad or even unidentifiable.

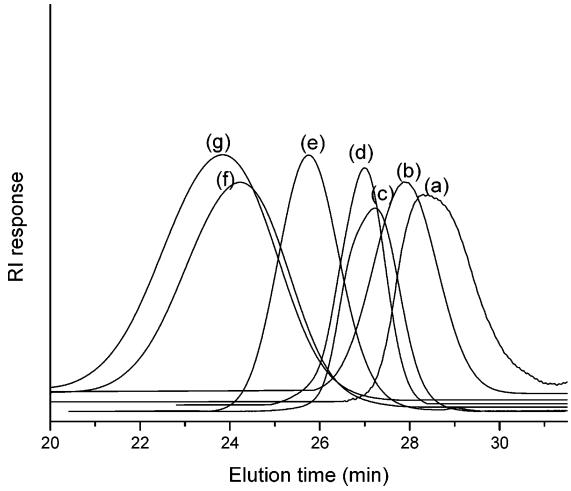


Figure 5. GPC traces of the prepolymers during the ATRP process of 4-VBPA-^{t}BOC in the presence of CMS as a function of the reaction time: (a) 2, (b) 6, (c) 10, (d) 12, (e) 18, (f) 25, and (g) 36 h. Reaction conditions are the same as those in Figure 4b.

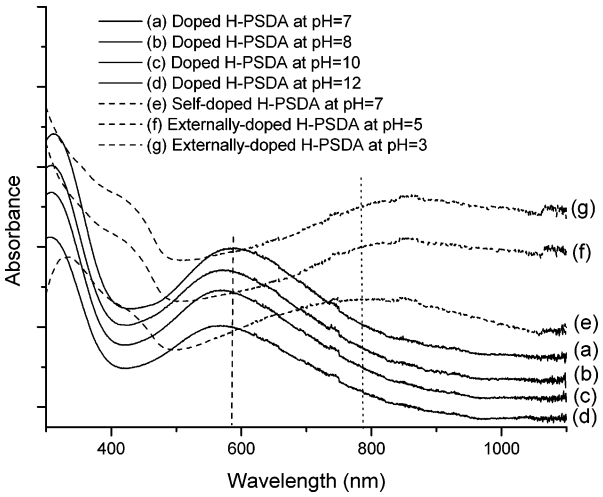


Figure 6. UV spectra of the H-PSDA aqueous solutions at various pH values.

The UV spectrum (Figure 3a) of dedoped **6** in aqueous solution exhibited two absorbance peaks around 310 and 590 nm, which can be assigned to the $\pi-\pi^*$ transition of the benzenoids and exciton transition of the quinoid rings, respectively. The relatively high peak of the latter suggests the existence of a long conjugation. Furthermore, after acidification with H^+ by ion exchange between NH_4^+ and H^+, the peak of the self-doped copolymer was shifted above 800 nm (see Figure 3b) in aqueous solution, indicating the formation of polaron structures which contribute to the conductivity. It should be noted that the spectrum of the self-doped polymer (Figure 3b) is very similar to the spectrum of the doped oligoaniline in the semi-oxidized state, consistent with the chemical nature of the hyperbranched product.

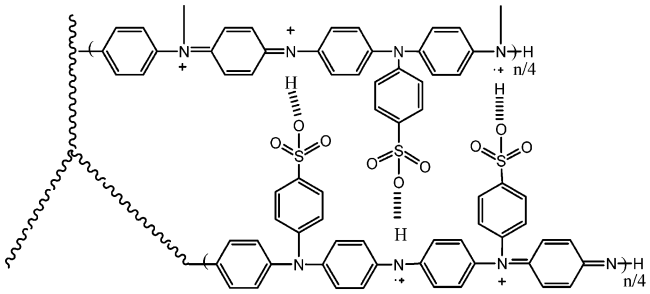
Atom Transfer Radical Copolymerization between 4-VBPA-^{t}BOC and CMS. As noted above, 4-VBPA-^{t}BOC can be polymerized via the ATRP method. The polymerization was followed by NMR and GPC. The signals which can be assigned to the vinyl moiety decreased with increasing reaction time. The conversion (α) of the double bonds was calculated using the expression $\alpha = (A^0_{5.6}/A^0_{6.34}\text{-}A^t_{5.6}/A^t_{6.34})/(A^0_{5.6}/A^0_{6.34})$, where $A^0_{5.6}$,

Table 1. Elemental Analysis of a Typical H-PSDA Copolymer in Various Doping States by XPS

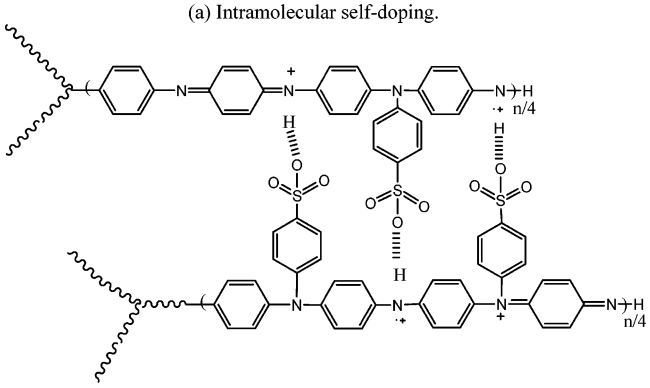
element (orbital)	possible components	binding energy (eV)	(fwhm (eV)[a], component concentration(%))		
			dedoped	self-doped	externally doped
N 1s	=N−	398.20	2.4, 45.6	1.1, 5.5	1.2, 2.6
	−NH−	399.41	1.6, 54.4	1.68, 52.1	1.81, 38.1
	$=N^+-$	400.83		1.49, 39.8	2.53, 45.0
	$-N^+H-$	402.31		0.92, 2.6	2.15, 14.3
S 2p	$-SO_3^-$	167.88	2.41, 94.2	1.55, 43.4	1.16, 20.7
	$-SO_3H$	168.80	1.14, 5.8	1.52, 56.6	2.11, 79.3

[a] fwhm means the full widths at half-maximum of the fitted peaks.

Scheme 2. Self-doped Mechanism of Hyperbranched PSDA



(a) Intramolecular self-doping.

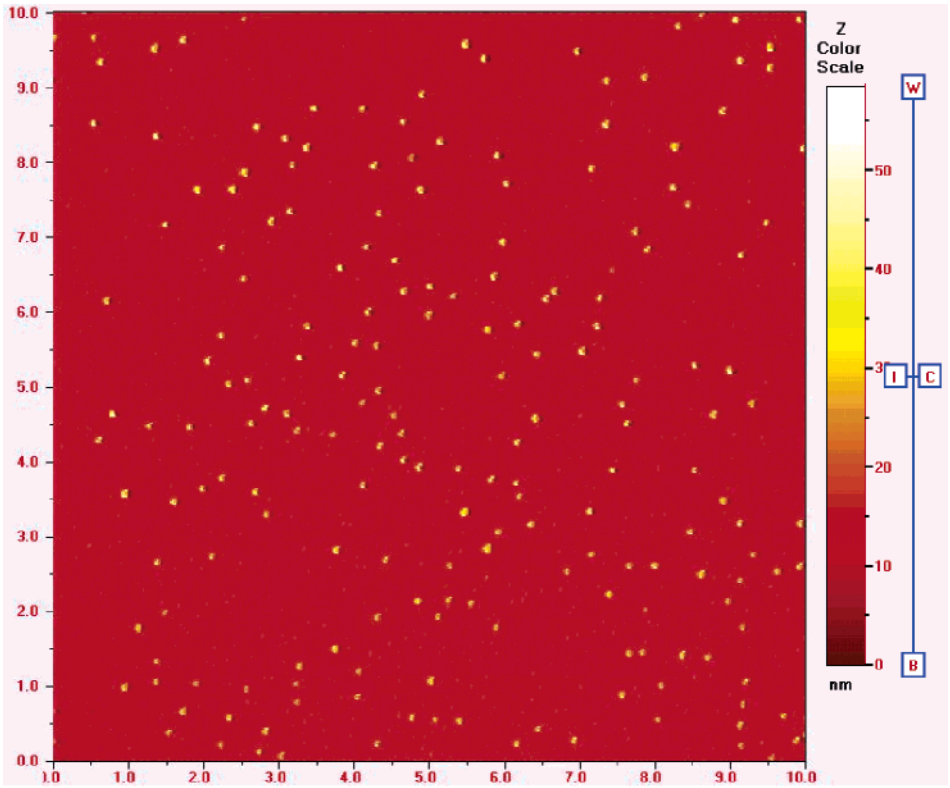


(b) Intermolecular self-doping.

$A^0_{6.34}$ and $A^t_{5.6}$, $A^t_{6.34}$ are the integral areas of the signals at 5.6 (vinyl proton) and 6.34 ppm (amino proton) at times $t = 0$ and t, respectively.[14−16] The kinetic results are plotted in Figure 4. In the absence of CMS, the weight-average molecular weight increased linearly with the double-bond conversion and the polydispersity of the molecular-weight distribution became as low as PDI = 1.2 (Figure 4a). Consequently, the homopolymerization of 4-VBPA-^{t}BOC proceeded in a living manner. However, in the presence of CMS, the molecular weight increased almost linearly with the conversion only for conversion smaller than 70%, consistent with a linear "living" polymerization process (see Figure 4b). It appears that the growing polymer chains are not significantly incorporated into each other until later during polymerization, when a significant deviation from the above behavior occurs. CMS has a double bond and a chloride atom. The latter atom can initiate the polymerization of 4-VBPA-^{t}BOC, and as a result, the growing PVBPA chains have a double bond at the chain end. This double bond can be incorporated into another growing macromonomer, generating a branching. The growing chain can either include additional monomer units or other chains of polystyrene. As a result, the molecular weight of the hyperbranched copolymer increased dramatically. The polydispersity of the hyperbranched copolymer became broad with a PDI up to 3.0 after 48 h (see Figure 4b). Figure 5 presents GPC traces of the intermediate copolymers as a function of time. The molecular weight increased dramatically in the late stages of copolymerization in the presence of CMS, becoming even 45 000 after 48 h, thus deviating from the homopolymerization linearity (see Figure 4a).

pH Response of H-PSDA. The UV spectra of the hyperbranched PSDA at various pH values are presented in Figure 6. In the dedoped state, the absorption peak around 590 nm was slightly blue-shifted with increasing pH. The sulfonic moieties no longer self-doped the nitrogens at high pH values. As already mentioned, in the self-doped state, the absorption occurred around 800 nm due to the polaron formation. The self-doping can be caused by intra- or intermolecular interactions between the sulfonic acid moieties and the nitrogens, as shown in Scheme 2. At pH values <7, the peak around 800 nm was red-shifted. The HCl external doping can overwhelm the self-doping because of the weak connection in the latter case. The smaller HCl molecules can easily replace the sulfonic moieties in the doping process.

The pH response of the H-PSDA conformation in aqueous solutions was investigated using AFM and SEM (see Figures 7 and 8). For the dedoped H-PSDA, the particle size decreased slightly with increasing pH from 7 to 10 from about 40 to about 28 nm (see Figure 7a and b). However, during the self-doping at pH = 7, the particle sizes became nonuniform, attaining an average of about 250 nm (Figure 7c), because the self-doping involves intermolecular interactions (Scheme 2) which lead to aggregation. When the pH was decreased to 3, the external doping by the HCl molecules could easily replace, for thermodynamic reasons (the free energy becoming smaller), the sulfonic acid moieties' doping; as a result, the aggregation decreased from an average of about 250 nm to about 120 nm. As shown in Figure 8, at pH = 7, the aggregates of the self-doped H-PSDA increased with storage time, as also observed via SEM. Irregular particles with sizes from 120 to 300 nm were identified after 1 day of storage (see Figure 8a); however, larger particles of about 350 nm were formed after one week of storage (Figure 8b). As shown in Scheme 2, self-doping occurs via intermolecular interactions between the sulfonic acid moieties and the nitrogens, and as a result, the aggregates are large. The aggregates were found to decrease to around 40 nm when the solution was neutralized with 0.1 N ammonium hydroxide solution. However, the sulfonic acid moieties which were not doped remained exposed to water, and for this reason, the aggregates were soluble in water. Furthermore, the self-doped and externally doped H-PSDAs were in an amorphous state, as shown in Figure 9. The pH response of the H-PSDA was reversible. Therefore, this pH sensitivity can have potential applications in biosensors.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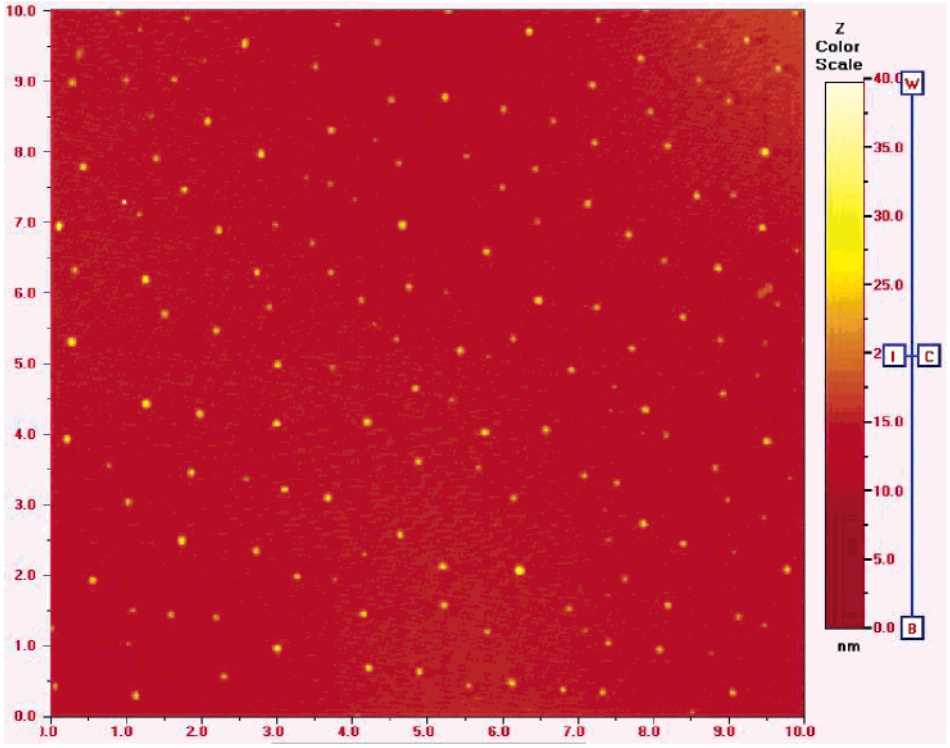
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(b)

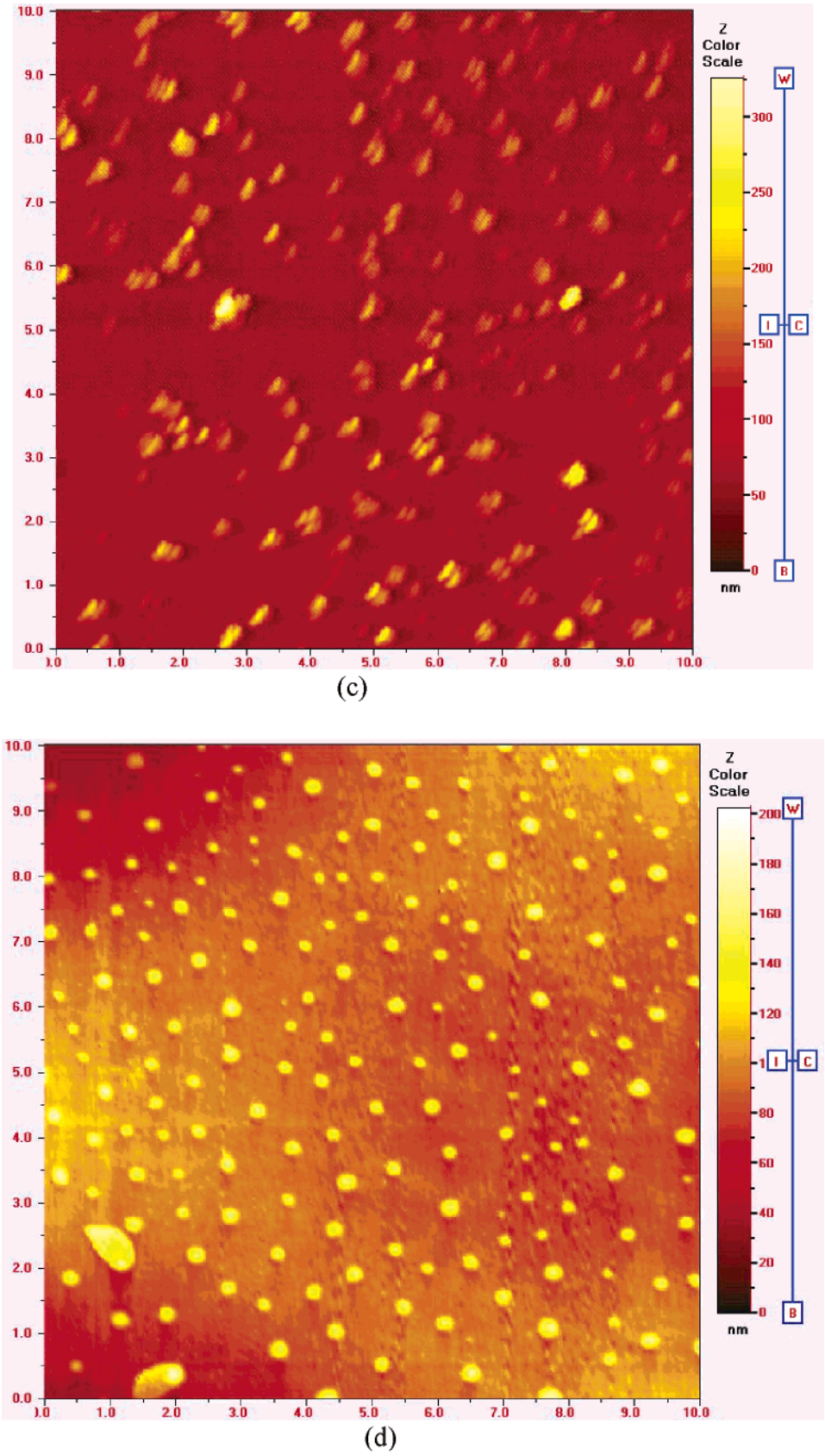

Figure 7. AFM images of the H-PSDA obtained via spin-coating on mica plates with a concentration of 0.1 g/L at various pH values: (a) dedoped PSDA at pH = 7, (b) dedoped PSDA at pH = 10, (c) self-doped PSDA at pH = 7, and (d) externally doped PSDA at pH = 3.

Surface Elemental Analysis by XPS. Figure 10 presents the wide-scale XPS spectra of the HCl-doped, self-doped, and dedoped copolymers. They exhibit binding energies around 168, 284, 398, and 533 eV, which can be assigned to S 2p, C 1s, N 1s, and O 1s, respectively. The integral area ratios between two peaks, which are due to S 2p and N 1s, respectively, are about 1:2, 1:1, and 1:1 for the dedoped, self-doped,

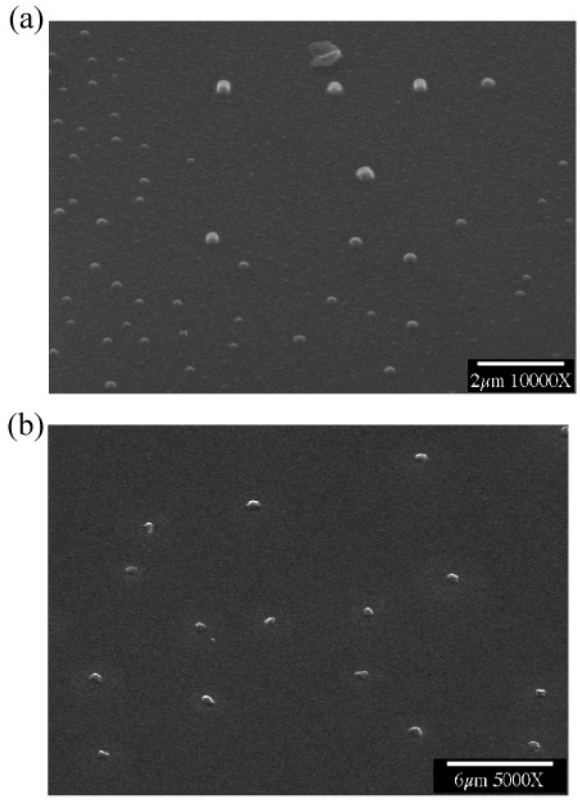

Figure 8. SEM pictures of self-doped H-PSDA obtained via spin-coating on mica plates with a concentrations of 0.1 g/L at pH = 7 as a function of the storage time: (a) 1 day of storage and (b) one week of storage.

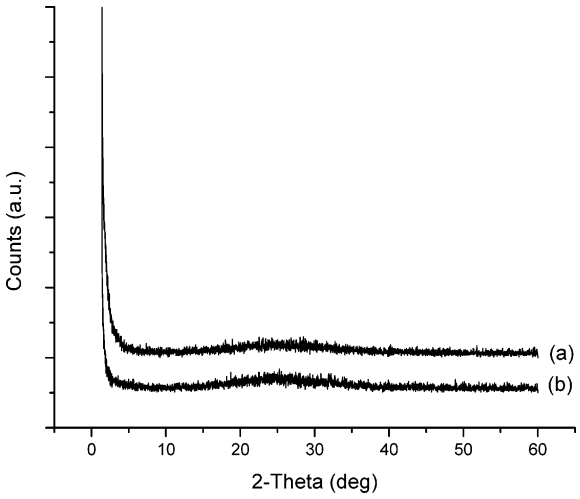

Figure 9. XRD profiles of the (a) self-doped and (b) externally doped H-PSDA copolymers.

and externally doped copolymers, respectively. The peaks due to Cl 2p at 199 eV could be hardly identified in the dedoped and self-doped copolymers, indicating that the chloride ions have been completely removed. Of course, the chloride peak appeared for the externally doped copolymer because of HCl doping. The interpretation for the C 1s and O 1s is not pursued because the surface contamination during XPS experiments cannot be avoided.

The N and S cores can be present upon doping or dedoping in several energetic states involving different components.[23,28] The oxidation and doping levels of the copolymers can be determined by analyzing the N 1s and S 2p core levels (see Table 1 and Figure 11a−c and

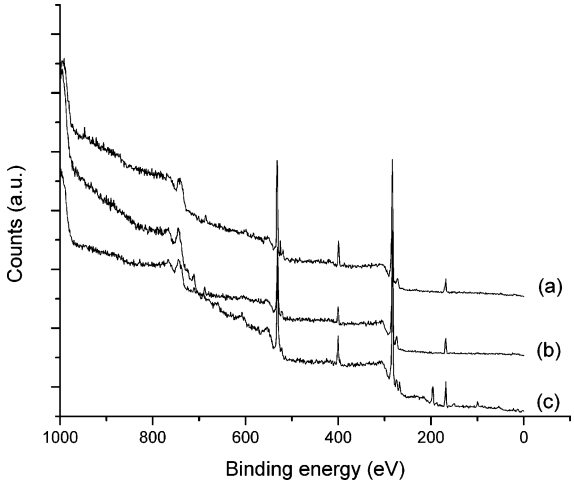

Figure 10. XPS spectra of H-PSDA copolymers: (a) dedoped, (b) self-doped, and (c) externally doped.

a′−c′). The N 1s core has four fitted components with binding energies (BEs) at 398.20, 399.41, 400.83, and 402.31 eV, respectively (see Figure 11a−c). They can be assigned to the undoped imine and amine, doped imine, and positively charged amine, as listed in Table 1. The oxidation levels for the self-doped and externally doped copolymer are 45.3 and 47.6%, respectively, close to that for the copolymer in the dedoped state (its total oxidation level being about 45.6%). The doping levels attained in the former two cases are 42.3 and 59.3%, respectively, the higher value for the externally doped copolymer, being due to the additional doping by HCl on the nitrogens of the amine moieties.

The S 2p spectra could be fitted using two components with BEs of 167.88 and 168.80 eV, respectively (see Figure 11a′−c′). The former, with the lower BE, originates from the sulfur of the sulfonic acid moieties that protonates the nitrogens of the amine or the imine moieties. The latter, with the higher BE, can be assigned to the sulfur in the $-SO_3H$ moieties because the sulfur in the $-SO_3^-$ has a higher electron density than that in the $-SO_3H$. In the dedoped state, 94.2% of the sulfur cores were present in the $-SO_3^-$ anions. In the self-doped state, most of the ammonium moieties could be replaced with H^+ via the ion exchange. Consequently, there are 43.4% of $-SO_3H$ moieties protonating the nitrogens of the amine or imine moieties via inter- or intramolecular doping interaction. However, that value decreased to 20.7% after external doping. As mentioned above, a doping level as high as 59.3% was attained in the case of HCl doping. The external doping even partially replaced the self-doping.

Conductivity and Electromagnetic Shielding Effectiveness (SE). The conductivities determined on various compressed H-PSDA pellets by the four-point probe method were below 10^{-1} S/cm, much lower than that of PANI. This can be attributed to the sulfonic withdrawing effect and to the steric constrain of the aromatic substituent at the N sites. The conductivities of the self-doped and externally doped H-PSDA were 1.2×10^{-2} and 3.7×10^{-2} S/cm, respectively, which are slightly larger than those of the linear PSDAS reported in a previous paper.[29] For the conductivities being in the semiconducting range, 10^{-1}−10^{-4} S/cm, the obtained materials can be used for EMI shielding.[30] The SE values of the self-doped copolymer over a frequency range from 10 to 10^3 MHz, presented in Figure 12, are

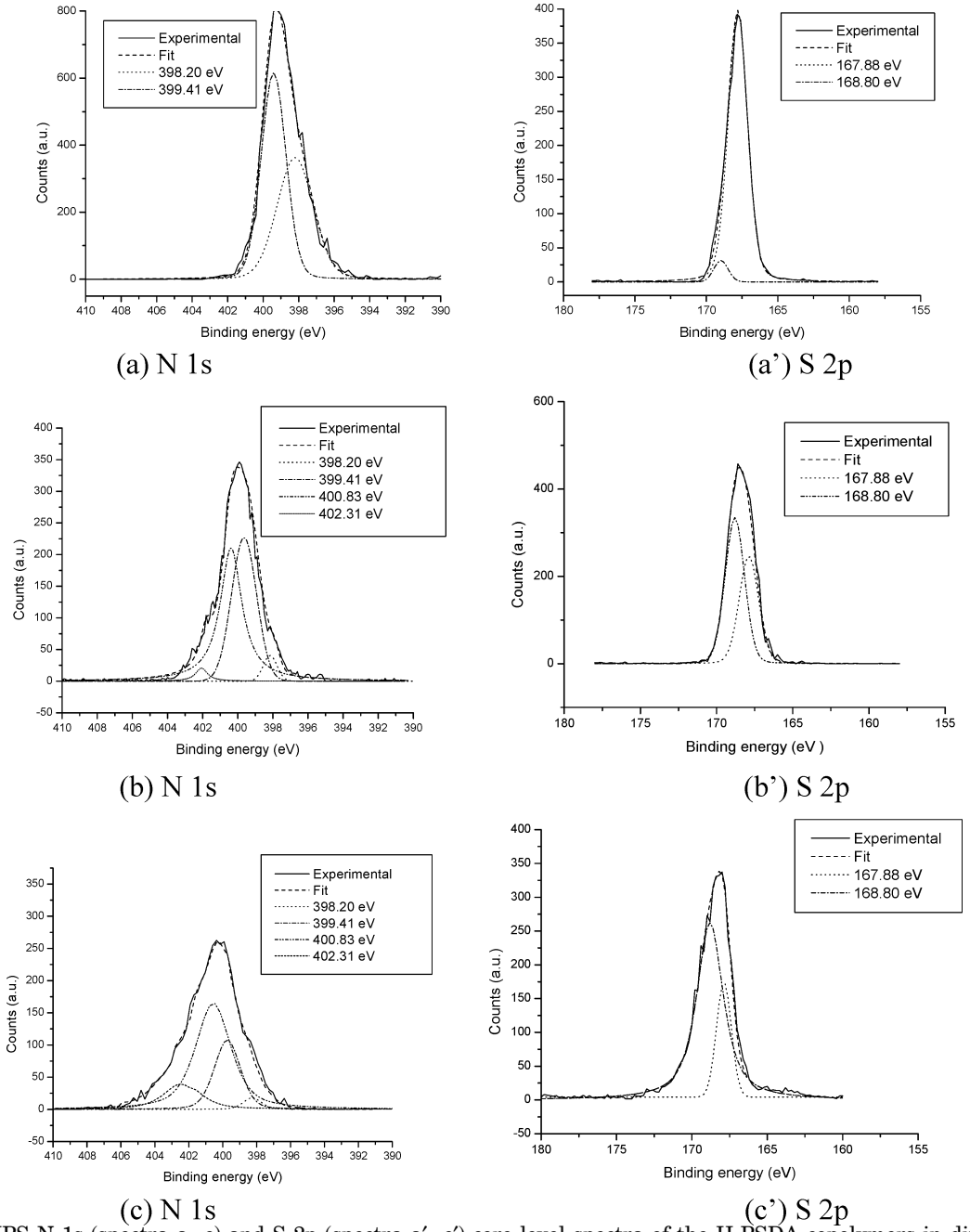

Figure 11. XPS N 1s (spectra a−c) and S 2p (spectra a′−c′) core level spectra of the H-PSDA copolymers in different doping states: (a) dedoped, (b) self-doped, and (c) externally doped.

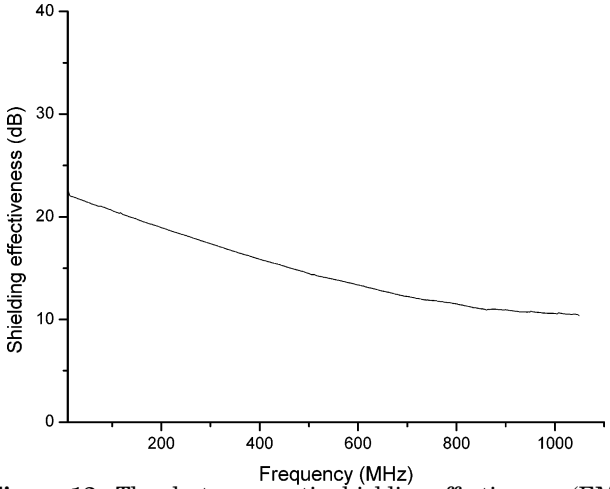

Figure 12. The electromagnetic shielding effectiveness (EMI SE) of the self-doped H-PSDA as a function of frequency.

above 10 dB. The hyperbranched copolymers and their nanoscale-size aggregates have potential applications as EMI materials.

Conclusion

A synthesis methodology to prepare a hyperbranched sulfonated polydiphenylamine as a novel conducting polymer was developed. The obtained hyperbranched sulfonated polydiphenylamine (H-PSDA) is water soluble. The morphology of the H-PSDA in aqueous solutions is dependent on the pH. In the dedoped state, at pH values above 7, the aggregates of the polymeric particles had almost a uniform diameter around 40 nm. In the self-doped sate at pH = 7, the aggregates acquired nonuniform sizes with an average of about 250 nm because of the intermolecular doping interactions. However, at lower pH values (<5), the external HCl doping became

dominant and the aggregates acquired smaller sizes of about 120 nm.

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(25) ***N-tert*-butoxylcarbonyl-4-aminophenol (4-AP-^{t}BOC).** 4-Aminophenol (5.4 g) and 11.0 g of di*tert*-butyldicarbonate were dissolved into a 55 mL mixture of THF/DMF (1:1, v/v) in a 100 mL flask. The mixture was cooled at 0 °C. Triethylamine (5.1 g) was introduced dropwise within 1 h. The system was kept at 0 °C for 4 h, the temperature was raised to room temperature, and the reaction was continued for 12 more h. Further, the solvent was evaporated under vacuum, 300 mL of DCM and 100 mL of water were added, and two layers were formed. The pH of the water layer was carefully adjusted with a 1.0 N HCl aqueous solution until neutral and extracted twice with 50 mL of DCM each time. The combined DCM solution was washed with water three times (50 mL each) and dried using Na_2SO_4. The DCM was removed using a rotary evaporator under vacuum. A light-yellow solid, 4-AP-^{t}BOC, was obtained with a yield of 86 wt%. FTIR (cm^{-1}): 3550−3200 (−NH and −OH), 2900 (phenyl), 1750−1670 (−C═O in ^{t}BOC). ^{1}H NMR (ppm): 7.18 (d, 2H), 6.71 (d, 2H), 6.34 (s, 1H), 1.53 (m, 9H). ESI MS $(Na + M)^+$: 232.1.
(26) **4-(4-Vinylbenzoxyl)(*N-tert*-butoxycarbonyl)phenylamine) (4-VBPA-^{t}BOC).** 4-AP-^{t}BOC (2.09 g), 1.38 g of K_2CO_3 and 1.52 g of 4-vinylbenzyl chloride were mixed with 15 mL of acetone in a 50 mL flask. The system was heated with intensive stirring under a slight reflux and allowed to react under a nitrogen atmosphere. The reaction was followed using TLC plates. After the 4-AP-^{t}BOC was consumed, 1.0 g of triethylamine was introduced and the reaction continued at 60 °C. After the 4-vinylbenzyl chloride (or 4-choromethylstyrene, CMS) was consumed, 300 mL of DCM and 100 mL of water were added and two liquid layers were generated. The water layer was extracted twice with 50 mL of DCM each time. The combined DCM phases were washed three times with 50 mL of water each time until neutral and dried using Na_2SO_4. Further purification was achieved by passing through an inhibitor remover disposable column (Aldrich, Catal. 30631−2) to eliminate the excess of 4-AP-^{t}BOC (which inhibits the radical homopolymerization of 4-VBPA-^{t}BOC). DCM was removed using a rotary evaporator under vacuum. A light-red solid, 4-VBPA-^{t}BOC, was obtained with a yield of 83 wt%. FTIR(cm^{-1}): 3300−3150 (−NH), 2900 (phenyl), 1750−1670 (−C═O in ^{t}BOC), 957 (−CH═CH_2). ^{1}H NMR (DMF-9, ppm): 7.3−6.8 (m, 8H), 6.67 (m, 1H), 6.41 (s, 1H), 5.6 (m, 2H), 5.2 (s, 2H), 1.56 (m, 9H). ESI MS $(Na + M)^+$: 348.0.
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