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Self-doped polyaniline derived from poly(2-methoxyaniline-5-phosphonic acid) and didodecyldimethylammonium salt†

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Salt formation of poly(2-methoxyaniline-5-phosphonic acid) (PMAP) with didodecyldimethylammonium bromide (DDDMABr) was performed to give the organic solvent soluble self-doped polyaniline, PMAP–DDDMA. The UV-vis-NIR absorption and ESR spectra clearly support the self-doping. This is in sharp contrast to the corresponding ammonium salt of poly(2-methoxyaniline-5-sulfonic acid), where dedoping was suggested. The drop-cast film of PMAP–DDDMA exhibited its conductivity.

1. Introduction

Polyaniline is one of the promising conducting polymers because of its availability, environmental stability and practical applicability.[1–6] The emeraldine base (half-oxidized) form of polyaniline can be doped *via* simple protonation to lead to a conducting polysemiquinone radical cationic (polaronic) state.[7] Thus, polyaniline generally requires a strong protonic acid such as sulfonic acid, hydrochloric acid and sulfuric acid to exhibit its conductivity. However, such protonic acid dopants are potentially corrosive materials and have a risk of their leakage into the environment. Toward the latter issue, self-doped conducting polyanilines having acid moieties attached through covalent bonds[8–14] can give one of the solutions. Such self-doped conducting polyanilines usually exhibit water solubility. This property is useful for film forming *via* coating with an aqueous solution. On the other hand, self-doped conducting polyanilines which are soluble in organic solvents have been very little studied so far.[15] Development of such self-doped conducting polyanilines which are soluble or dispersed in organic solvents can expand the utility of the self-doped polyanilines. In this context, we focused on phosphonic acid as the protonic acid moiety of the self-doped polyanilines because it does not only show enough acidity for doping but also is a dibasic acid. So, two acidic protons are available in phosphonic acid. The second acid moiety not used for doping would provide features, such as salt formation while keeping the doping state. Recently, we have successfully synthesized and characterized poly(2-methoxyaniline-5-phosphonic acid) (PMAP, Fig. 1a),[16–18] which is the first example of polyaniline bearing phosphonic acid directly attached to its backbone.[16]

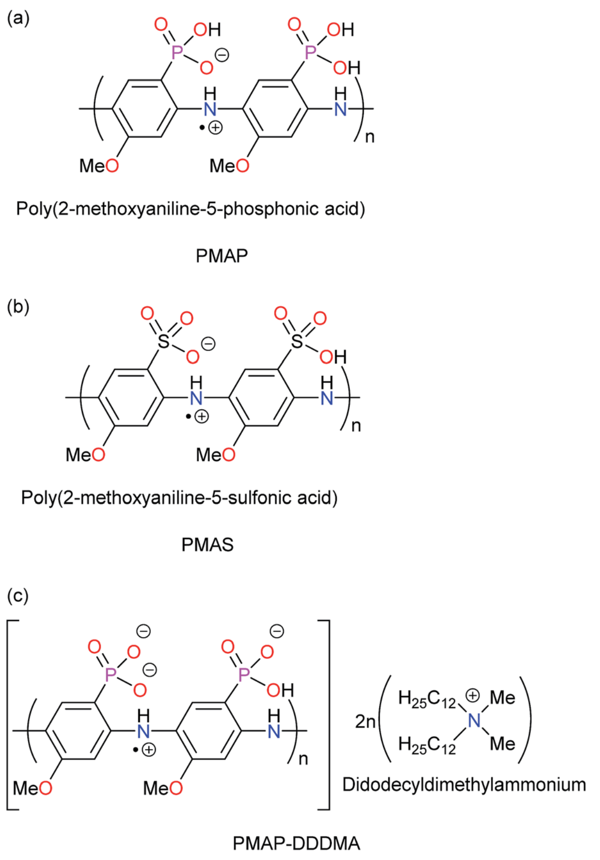

Fig. 1 Structures of (a) PMAP, (b) PMAS and (c) PMAP–DDDMA.

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† Electronic supplementary information (ESI) available: Details for calculation of the composition, Fig. S1, structure of the mixture including PMAP–DDDMA; Fig. S2, pictures of PMAP–DDDMA before and after washing in various solvents and Fig. S3, photos of the spin-coated film of PMAP–DDDMA before and after washing on a glass substrate. See DOI: 10.1039/c5ra18468a

Poly(2-methoxyaniline-5-phosphonic acid monoethyl ester) (PMAPE) was synthesized as well.[19] The conductivity of various amine complexes of PMAP was investigated and the charge dissipation properties of some PMAP/amine complexes using electron-beam lithography were reported.[20] We also found that PMAP exhibits deprotonation-induced efficient delocalization of polarons.[21] On the other hand, there still remains the issue of developing organic solvent soluble self-doped polyanilines in our studies. In this context, we conceived that the salt formation of the second acid moiety of the dibasic acid with long-chain alkyl quaternary ammonium should give the self-doped conducting polyanilines solubility in organic solvents. As a related work, long-chain alkyl quaternary ammonium salt formation of poly(2-methoxyaniline-5-sulfonic acid) (PMAS,[22] Fig. 1b) which has a sulfonic acid moiety which is a monobasic acid was reported.[15] However, we expected PMAP bearing the phosphonic acid moiety to form a sufficient amount of quaternary ammonium salt while keeping the self-doping state because phosphonic acid is a dibasic acid. Such salt formation of the excess acid moiety for doping is also expected to lower the acidity resulting in reducing the potential corrosive risk in the application. Here, we report the preparation of organic solvent soluble self-doped conducting polyaniline *via* salt formation of PMAP and didodecyldimethylammonium bromide (DDDMABr) (PMAP–DDDMA, Fig. 1c), and its characterization including solubility, thermostability, absorption in solution and spin-coated film, electron spin resonance (ESR) and conductivity.

2. Experimental section

2.1 General

PMAP was prepared according to the previously reported procedures.[16,17] The molecular weight (M_w) of PMAP is 2.0×10^3 (see ref. 16 and 17 for details). PMAS was kindly provided by Mitsubishi Rayon Co. Other reagents and solvents were purchased from commercial sources. Elementary analysis was performed on a J-SCIENCE LAB Co., Ltd MICRO CORDER (JM-10). Quantification of bromine was conducted on an integrated automated combustion ion chromatography analyzer system (Mitsubishi chemical analytech, XS2100-H). ICP-AES analysis was made on a SHIMADZU ICPS-8100. Thermogravimetry analysis (TGA) was recorded on an SII TG/DTA6200 analyzer. UV-vis-NIR spectra were recorded on a JASCO V-670 spectrophotometer. Dynamic light scattering was measured on a Photal OTSUKA ELECTRONICS ELSZ. ESR spectra were taken on a JEOL X-band spectrometer (JES-RE1XE).

2.2 Preparation of PMAP–DDDMA

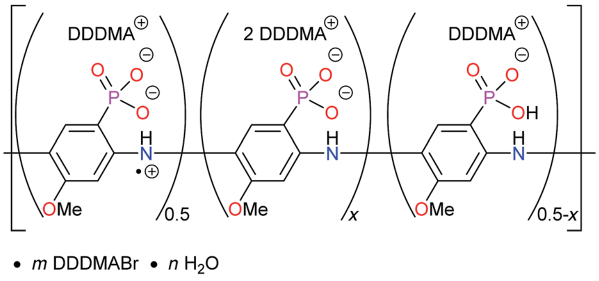
PMAP (100 mg, 0.5 mmol based on an aniline unit) was dissolved with 2.5 M aqueous pyridine solution (122 μL, 1.5 mmol) at room temperature, and the solution was diluted with water (400 mL) and toluene (400 mL). To the two-phase mixture was added DDDMABr (352 mg, 0.75 mmol). The mixture was gently stirred for 15 min at room temperature. The mixture was moved to a separatory funnel, where 50 mL of toluene was used to wash it. The mixture was stood at least overnight until the layers were separated. The toluene layer was collected (almost 80–90% of the toluene layer was carefully taken to avoid mixing with the water layer), and evaporated. The residue was further dried under a reduced pressure at 50 °C for 6 h and at room temperature overnight to give PMAP–DDDMA as a black solid (315 mg, 37% yield based on a PMAP aniline unit). The obtained solid includes DDDMABr and water as shown in Table 1. To decrease the amount of DDDMABr, the mixture (31.9 mg) was washed with a 2 mL solution of hexane and ethyl acetate (1 : 1) with sonication (1 min). The PMAP–DDDMA was collected by filtration with a membrane filter under a reduced pressure. The main residue was dried under a reduced pressure at 60 °C for 3 h. A partial residue adhered on the filter was extracted with dichloromethane after washing with ethyl acetate. The filtrate was concentrated under a reduced pressure. This residue was combined with the main one, and they were dried together as described above. The PMAP–DDDMA after washing (13.1 mg, 72% yield based on a PMAP aniline unit) was obtained.

PMAS–DDDMA was prepared similarly in half the scale, but where pyridine was not added because the PMAS–DDDMA was not sufficiently extracted with toluene in the presence of pyridine.

2.3 ICP-AES analysis

The precisely weighed sample (PMAP–DDDMA before washing: 1.9068 mg, after washing: 2.1865 mg) was diluted with concentrated nitric acid in a measuring flask to 20 mL in total. Quantification was carried out using the calibration curve, which was prepared using four points of the diluted phosphorus standard solution (0, 5, 10 and 50 ppm of P). The results for PMAP–DDDMA before and after washing were 1.75 and 3.50 ppm, respectively.

Table 1 Structure of the mixture including PMAP–DDDMA and the coefficients *m*, *n* and *x*, and the molecular formula for PMAP–DDDMA before and after washing[a,b]



PMAP–DDDMA	m	n	x	Molecular formula
Before washing	1.85	4.70	0.43	$C_{92.32}H_{199.22}N_{4.28}O_{8.70}P_{1.00}Br_{1.85}$
After washing	0.66	3.10	0.07	$C_{51.81}H_{109.14}N_{2.72}O_{7.10}P_{1.00}Br_{0.66}$

[a] The presumption is given that the PMAP in PMAP–DDDMA is the half-oxidized form based on a previous report.[18] [b] See the ESI for details of the calculation.

2.4 TGA

The sample was put in an open aluminum pan and measured under a nitrogen atmosphere (rate of temperature increase 5 °C).

2.5 Investigation of solubility

PMAP–DDDMA before or after washing (*ca.* 0.5 mg each, which was measured using a precision balance for elementary analysis) was mixed with 0.5 mL of the solvent in a sample tube at room temperature. After 1 min of sonication of the sample, the solubility was checked by visual observation.

2.6 Film formation by a spin-coating method

The glass substrate was pretreated as follows: (1) washing ultrasonically with solvents in the order of acetone, ethanol and desalted water, (2) drying with an air duster, (3) cleaning by UV-O_3 treatment (12 W low pressure mercury lamp, flowing air) for 1 min. Toluene (150 μL) was added to PMAP–DDDMA before or after washing (7.5 mg each), which was sonicated. 100 μL of the sample was dropped on the glass substrate. The substrate was spun to form the film (1000 rpm, 20 s), which was baked at 100 °C for 2 min under air. The film thickness was measured by a surface profiler (Kosaka Laboratory Ltd., surfcorder ET200).

2.7 ESR measurement

To an ESR tube was added a 4.3 or 4.9 g L^{-1} toluene solution of PMAP–DDDMA before or after washing, resulting in some precipitation in both samples. They were used as is for the ESR measurements. The spectra for PMAP–DDDMA before and after washing were recorded at room temperature under non-saturating microwave-power conditions (0.995 and 0.998 mW) operating at 9.4522 and 9.4188 GHz, respectively.

2.8 Electrical conductivity measurement

A platinum interdigitated array electrode composed of 65 pairs (width between electrodes = 3 μm, length = 2.4 mm, see Fig. 2) [IDA electrode (Pt) from ALS Co., Ltd, see also http://www.als-japan.com/support-ida.html] was used to measure the sheet resistance by a direct-current method. The solution of PMAP–DDDMA before or after washing (*ca.* 50 g L^{-1} toluene suspension), or PMAP–pyridine (1 : 2 based on an aniline unit) (10 g L^{-1} aqueous solution) was dropped onto the electrode, which was dried at 100 °C for 2 min. The measurement of the electrical resistance for a two-probe method was conducted under environmental conditions.

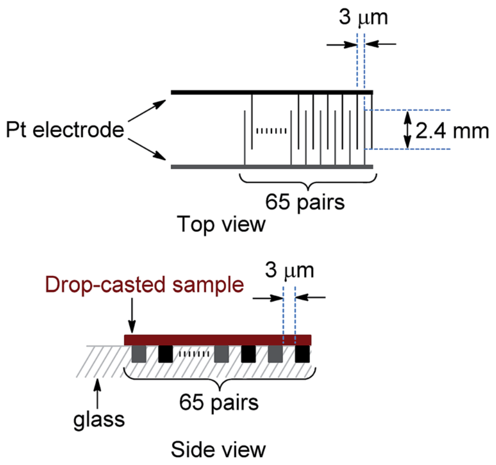


Fig. 2 Schematic view of a platinum interdigitated array electrode.

3. Results and discussion

3.1 Preparation of PMAP–DDDMA and its composition

PMAP–DDDMA was prepared by just mixing of PMAP–pyridine and DDDMABr in water and toluene. The black toluene layer was collected and evaporated to give a black solid mixture. The black colour suggests the presence of PMAP. The structure of the obtained mixture in this experiment can be obtained as shown in Table 1,[23] where the presumption is made that the PMAP in PMAP–DDDMA is in a half-oxidized form based on a previous report.[18] The composition of the mixture was investigated by ICP-AES analysis for phosphorus, ion chromatography analysis for bromine and elementary analysis for carbon, hydrogen and nitrogen (Table 1). The percentage of weight for oxygen was calculated by subtracting the sum of the percentages of weight for carbon, hydrogen, nitrogen, phosphorus and bromine from 100 wt%. Using the values of the percentage of weight for phosphorus, bromine and oxygen, the coefficients m, n and x, and the molecular formula were determined (Table 1). The details of the calculation are shown in the ESI.† The molar ratio of the phosphonate moiety and DDDMA is 1 : 1.43, showing sufficient salt formation. However, a certain amount of DDDMABr is included in the obtained mixture (molar ratio of the phosphonate moiety and DDDMABr is 1 : 1.85). To remove the unwanted DDDMABr, the mixture was washed with the mixed solution of hexane and ethyl acetate (1/1). The coefficients m, n and x, and the molecular formula after washing are summarized in Table 1. The washing worked to some extent to reduce the amount of DDDMABr (m = 1.85 to 0.66). The molar ratio of the phosphonate moiety and DDDMA is 1 : 1.07, showing the almost one to one salt formation. Table 2 summarizes the percentages of weight for the mixture before and after washing. The differences between the calculated values and the ones from elementary analysis for carbon, hydrogen and nitrogen are at most 0.21. Such a good agreement ensures the accuracy of the estimated component content.

Other ammonium salts such as dodecyltrimethylammonium bromide, tetrahexadecylammonium bromide and tetradodecylammonium bromide were employed instead of DDDMABr. In the case of dodecyltrimethylammonium bromide and tetrahexadecylammonium bromide, the toluene layer was not coloured, and the aqueous layer was black. These observations suggest that the ammonium salts of PMAP were not extracted with toluene. When tetradodecylammonium bromide was used, both the toluene and aqueous layers were black. These findings revealed that DDDMABr is the most suitable for the salt formation among them.

Table 2 The percentages of weight (wt%) for the mixture before and after washing[a]

PMAP–DDDMA		Percentage of weight (wt%)				
		C	H	N	P[c]	Br[d]
Before washing	Calculated values[b]	65.71	11.90	3.55	1.84	8.76
	Values from elementary analysis	65.58	11.88	3.70	—	—
After washing	Calculated values[b]	64.32	11.37	3.94	3.20	5.43
	Values from elementary analysis	64.38	11.16	4.09	—	—

[a] The presumption is made that the PMAP in PMAP–DDDMA is in a half-oxidized form based on a previous report.[18] [b] See the ESI for details of the calculation. [c] The value was obtained from the ICP-AES analysis. [d] The value was obtained from the ion-chromatography (before and after washing: 8.76 and 5.43 wt%, respectively).

3.2 Thermal stability

TGA was conducted to investigate the thermal stability of PMAP–DDDMA. The TGA curves for PMAP–DDDMA before and after washing under a nitrogen atmosphere are shown in Fig. 3. A significant loss of mass was observed from around 200 °C in both experiments. This is considered to be derived from the loss of the ammonium moiety. A relatively smaller loss at around 200 °C was observed after washing, which is consistent with the decrease of the ammonium moiety in the mixture by washing.

3.3 Solubility in organic solvents

The solubility of PMAP–DDDMA before and after washing was investigated by the preparation of a 1.0 g L^{-1} solution using various solvents, where the solubility was checked by visual observation. The results are summarized in Table 3. The pictures are shown in Fig. S2.† Alcohols (ethanol and 2-propanol) and dichloromethane dissolved PMAP–DDDMA both before and after washing well. Toluene dissolved them moderately. The colour of all the soluble solutions shown above was blackish dark brown. On the other hand, DMSO, acetone, diethyl ether and hexane are poor solvents for PMAP–DDDMA both before and after washing. In particular, hexane almost did not dissolve them.

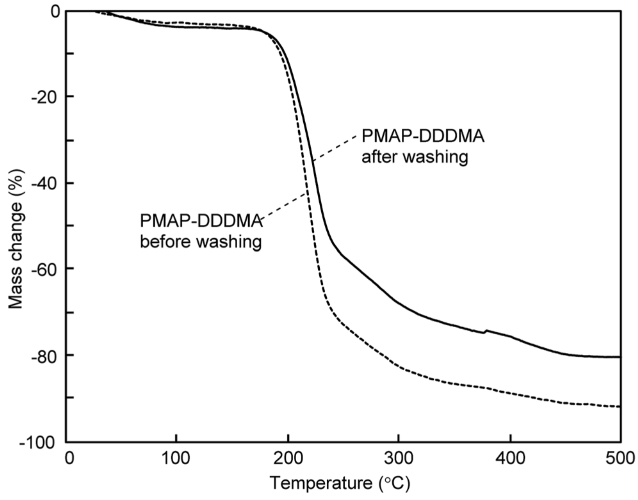


Fig. 3 TGA curves for PMAP–DDDMA before and after washing under a nitrogen atmosphere.

Particles were not found in the toluene solution of PMAP–DDDMA both before and after washing (0.1 g L^{-1}) by a dynamic light scattering measurement. But, precipitation from this toluene solution was observed after standing overnight.

3.4 Electronic absorption

Electronic absorption of PMAP–DDDMA was investigated in a solution and spin-coated film. Fig. 4a shows the UV-vis-NIR absorption spectra of PMAP–DDDMA before and after washing and PMAS–DDDMA in toluene. PMAS–DDDMA was prepared in a similar way to PMAP–DDDMA for comparison. The shape of the spectra for PMAP–DDDMA before and after washing is similar, but PMAP–DDDMA after washing exhibited a larger peak than that of the sample before washing because these spectra were measured based on weight/volume concentration. The peak at around 470 nm and the steadily increasing peak from 1000 nm were observed in PMAP–DDDMA before and after washing, and should be attributed to a polaron band and a free carrier tail arising from the delocalization of electrons, respectively.[24] These are characteristic in conducting polyanilines. These observations also indicate that the self-doping is maintained after the salt formation. On the other hand, PMAS–DDDMA did not show the typical peaks for the conducting polyanilines. The dedoping is suggested to take place after the

Table 3 Solubility of PMAP–DDDMA before and after washing (1.0 g L^{-1} solution in various solvents)

	Solubility of PMAP–DDDMA[a]	
Solvents	Before washing	After washing
Ethanol	Good	Good
2-Propanol	Good	Good
Dichloromethane	Good	Good
Toluene	Moderate	Moderate
THF	Good	Moderate
DMSO	Bad	Bad
Ethyl acetate	Bad	No
Acetone	Bad	Bad
Diethyl ether	Moderate	No
Hexane	No	No

[a] Good: no precipitation was observed. Moderate: a small amount of precipitation was observed. Bad: a large amount of precipitation was observed. No: the solvent was not coloured at all.

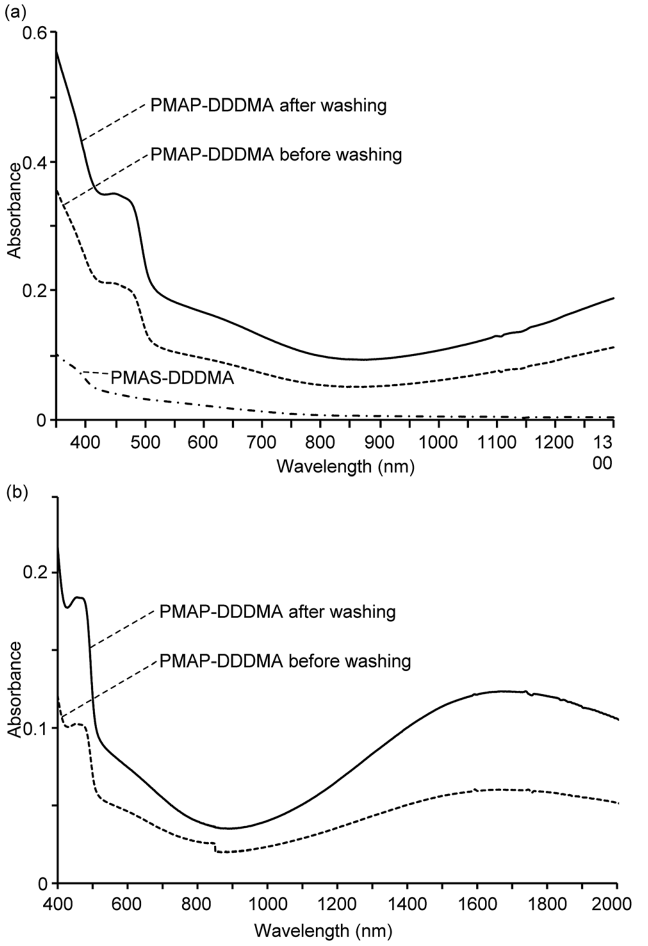


Fig. 4 UV-vis-NIR absorption spectra: (a) PMAP–DDDMA before and after washing and PMAS–DDDMA in a 0.1 g L^{-1} toluene solution and (b) spin-coated film of PMAP–DDDMA before and after washing on a glass substrate.

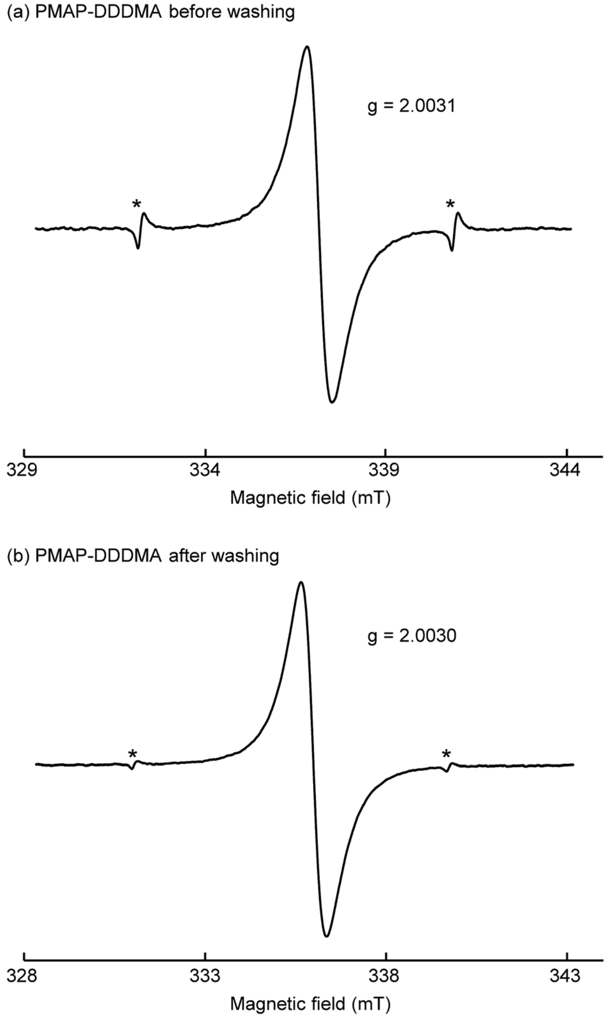


Fig. 5 ESR spectra of PMAP–DDDMA (a) before and (b) after washing in toluene at room temperature. The asterisks denote Mn^{2+} markers.

salt formation. Fig. 4b shows the UV-vis-NIR absorption spectra for the spin-coated films of PMAP–DDDMA before and after washing. The spin-coating was conducted on a glass substrate. The pictures are shown in Fig. S3.† The colour of the films was pale brown. The absorption spectra are similar to those observed in a solution. The thickness and transmittance at 455 nm of the films were 293 nm and 79% for PMAP–DDDMA before washing and 337 nm and 65% for PMAP–DDDMA after washing.

3.5 ESR property

Fig. 5 shows ESR spectra of PMAP–DDDMA before and after washing in toluene, where a single resonance line centered on around $g = 2.003$ without hyperfine coupling was observed in both spectra. The obtained spectra are characteristic of conducting polyanilines,[25] indicating that the self-doping is maintained after the salt formation. The peak-to-peak line width ΔH_{pp} was 0.69 and 0.71 mT for PMAP–DDDMA before and after washing, respectively. These values are larger than those of PMAP/pyridine (1 : 2) ($\Delta H_{\text{pp}} = 0.20$ mT) and PMAPE/pyridine (1 : 1) ($\Delta H_{\text{pp}} = 0.46$ mT) in water, suggesting that the polaron of PMAP–DDDMA is less delocalized than the others.[25]

3.6 Conductivity

The conductivity was investigated in terms of the sheet resistance of the drop-cast film. A platinum interdigitated array electrode (Fig. 2) was used to measure the sheet resistance by a direct-current method. The *ca.* 50 g L^{-1} toluene suspensions of PMAP–DDDMA before and after washing were drop-casted on the electrode. The sheet resistances of PMAP–DDDMA before and after washing were 2.5×10^{11} and 2.0×10^{8} $\Omega\ \square^{-1}$, respectively. Three orders of magnitude decrease of the sheet resistance was observed after washing. As compared to that of PMAP/pyridine (1 : 2 based on an aniline unit) (2.5×10^{7} $\Omega\ \square^{-1}$, which was obtained using a similar method to those of PMAP–DDDMA), the value after washing is still larger. DDDMA cations and/or DDDMABr are likely to interfere with efficient conduction, which might be due to inefficient carrier hopping between the polymers in the bulk conditions. As shown in the ESR experiments, less delocalization of the polaron in PMAP–

DDDMA than that in PMAP/pyridine (1 : 2) also might be reflected in the conductivity.

4. Conclusions

In conclusion, the salt formation of PMAP with DDDMABr was performed to give the organic solvent soluble self-doped polyaniline, PMAP–DDDMA. The UV-vis-NIR absorption and ESR spectra clearly supported self-doping. This is in sharp contrast to the corresponding ammonium salt of polyaniline sulfonic acid, PMAS–DDDMA, where dedoping was suggested. The drop-cast film of PMAP–DDDMA exhibited moderate conductivity. The application of PMAP–DDDMA, for example, as a charge dissipation material, is expected by utilizing its high solubility with various organic solvents.[26] From an expanded perspective, not only solubility but also structure and other properties would be controlled by designing the conducting polymer salt, as the ionic structure within polymers is considered to result in unique functions.

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