

Synthesis of polyaniline in organic solvents

Hiromasa Goto, Kyoka Komaba, Takuya Yonehara, Ryo Miyashita & Reiji Kumai

To cite this article: Hiromasa Goto, Kyoka Komaba, Takuya Yonehara, Ryo Miyashita & Reiji Kumai (2022): Synthesis of polyaniline in organic solvents, *Polymer-Plastics Technology and Materials*, DOI: [10.1080/25740881.2022.2075270](https://doi.org/10.1080/25740881.2022.2075270)

To link to this article: <https://doi.org/10.1080/25740881.2022.2075270>



Published online: 24 May 2022.



Submit your article to this journal



Article views: 15



View related articles



CrossMark

View Crossmark data



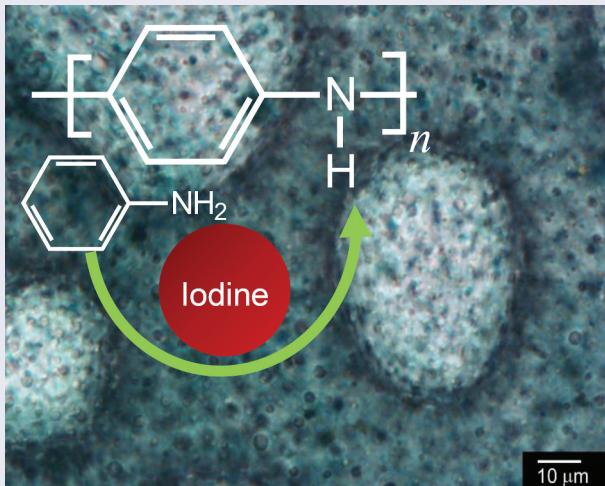
Synthesis of polyaniline in organic solvents

Hiromasa Goto ^a, Kyoka Komaba^a, Takuya Yonehara^a, Ryo Miyashita^a, and Reiji Kumai ^b

^aDepartment of Material Science, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Japan; ^bPhoton Factory, Institute of Materials Structure Science (IMSS), High Energy Accelerator Research Organization (KEK), Tsukuba, Japan

ABSTRACT

In organic solvents, a simple method to prepare polyaniline (PANI) was found. PANI was oxidatively synthesized using a small amount of iodine as an auxiliary agent for polymerization in organic solvents such as ethanol, dichloromethane, chloroform, hexane, and toluene. The chemical structure of the resultant PANI was confirmed with infrared absorption spectroscopy measurements. The electrical conducting function of the resulting PANI was examined using 4-point probe method. In the polymerization process, PANI-based polymer alloys with non-conjugated polymers can be prepared via polymerization in organic solvents with iodine.



ARTICLE HISTORY

Received 27 December 2021

Revised 3 May 2022

Accepted 5 May 2022

KEYWORDS

Charge carriers; conductivity; organic solvents; emeraldine; polyaniline

1. Introduction

Polyaniline (PANI) is a promising conductive polymer. PANI has recently been used to develop nanocomposites^[1–8] and functional composites^[9–11] for obtaining new organic conductive polymer composite materials. PANI has been applied to batteries,^[12] gas sensors,^[13] electromagnetic shielding materials,^[14] catalysts,^[15] and separation materials.^[16,17] The synthesis of PANI is generally performed in water under acidic conditions using ammonium persulfate (APS) as the oxidant. However, the low solubility of PANI in most common solvents limits the industrial applications of this technique. Therefore, the synthesis of soluble PANI,^[18] processability improvements,^[19] and the

combination of PANI with carbon^[20] or film-like^[21] products have been studied. The electrical conductivity of PANI has also been improved via secondary doping.^[22,23]

The processability of PANI could be achieved by dedoping of the doped state via ammonia treatment and subsequently converting it to a PANI-emeraldine base (PANI-EB). Then, PANI-EB is dissolved in a high-boiling-point solvent, *N*-methyl-2-pyrrolidone (NMP), and casted on a metal or glass substrate. The solvent is finally evaporated to obtain PANI-EB film as an insulator. The film is treated with hydrochloric acid or sulfuric acid to obtain PANI-emeraldine salt (PANI-ES) film as a conductive product. The synthesis of PANI in low-boiling-point solvents would conveniently produce

PANI films or plastics following the evaporation of the solvent in the PANI solution cast in a substrate or a mold. This approach could reduce the number of processing steps and create conductive films and plastic ingots.

PANI was previously synthesized using 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in a small amount of tetrahydrofuran and chloroform (CHL).^[24] However, owing to its strong electron-withdrawing properties, DDQ is an expensive reagent and must be handled with care. Aniline polymerization in water/toluene could be conducted without DDQ, but it requires interfacial polymerization in a bilayer system or the use of surfactants.^[25]

Using the polarons (radical cations) of PANI-ES in the doped state could produce radical polymerization of styrene.^[26] This study showed that PANI is not only a conductive material but also a polymerization initiator. The polarons of conductive polymers are charge carriers of these polymers and present unique functions, such as coloration, one-dimensional movement along the main chain, and magnetism. In this study, we report the generation of polarons in the initial stage of the polymerization reaction by using iodine to enable the synthesis of PANI in various organic solvents. PANI was effectively synthesized in various solvents, including ethanol (EtOH) and hexane. We also demonstrate that the polymerization of aniline in organic solvents containing resins could produce polymer alloys via a one-pot synthesis strategy.

2. Experimental

2.1. Polymerization of aniline sulfate in organic solvents in the presence of iodine

Aniline sulfonic acid and iodine were dissolved in EtOH or dichloromethane (DCM) at 0°C. After 30 min of stirring, APS was added to the solution and stirred for another 24 h. The solution was then filtered and washed with a considerable amount of water, acetone, and methanol before being dried under reduced pressure (entries 1 and 2 in Table 1). Although the polymerization of the aniline sulfate as a monomer with APS in EtOH solution without iodine gave no preferable product, the polymerization for 3 days at room temperature yielded black and infusible material. However, using APS with iodine in EtOH solution to polymerize aniline sulfate resulted in emerald green PANI. This result indicated that the synthesis of PANI-ES in organic solvents requires a small amount of iodine (Scheme 1).

2.2. Synthesis of polyaniline in organic solvents in the presence of organic sulfonic acid and iodine

First, to synthesize PANI in an organic solvent, camphor sulfonic acid (CSA),^[27] benzene sulfonic acid (BSA), methane sulfonic acid (MSA), or dodecylbenzene sulfonic acid (DBSA) was added to aniline (Scheme 2). Aniline formed the aniline sulfate. A small amount of iodine was added to the solution, and the stirring continued. The mixture was cooled to 0°C, and then APS was added. After further stirring, a dark green PANI product was formed in the solution. The crude product was washed with a substantial amount of water, acetone, and methanol. Products are obtained through filtration and drying under reduced pressure. As shown in Table 1, polymerization was successful when toluene (entry 3), *n*-hexane (entry 4), EtOH (entry 5), dichloromethane (DCM) (entries 6–8), and CHL (entries 9–12) were used as solvents. Polymerization of aniline in *m*-cresol, NMP, and *N,N*-dimethyl formamide (DMF) yielded no desired products. The reaction provided low synthetic yield in DCM at room temperature (~25°C) (entry 6).

Polymerization using sulfuric acid in DCM resulted in a dark-colored material; however, the reaction did not proceed to completion, and infrared (IR) absorption measurements showed that the products contained no PANI structure. These findings may be attributed to the inability of aniline to form salts with sulfuric acid in organic solvents, which is required for the polymerization reaction.

2.3. Polyaniline from aniline dimers

Toluene was used as a solvent to polymerize 4-aminodiphenylamine sulfate (ADA_{sul}), a dimeric aniline monomer (Scheme 3). First, sulfuric acid was added to 4-aminodiphenylamine (ADA) in water. ADA_{sul} was produced via recrystallization and dried under reduced pressure. Since ADA_{sul} does not dissolve in toluene, it was finely ground in a mortar and added in a form of powder to toluene. Exactly 0.3 g of the ADA_{sul} powder was dispersed in 6 mL toluene, and 0.02 to 0.1 g iodine and 1.6 g APS were added to the mixture (Table 2). The reaction was performed for 24 h at 0°C. As shown in Figure 1, the optimum amount of iodine added to the monomer was approximately 17 wt%. In the figure, the resultant polymer is abbreviated as P(ADA)_{TOL}I_{2n}-APS, where *n* is the quantity of iodine added (in grams).

Table 1. Polymerization of aniline in the presence of iodine.

Entry	Polym. ¹	Mon. (g)	APS(g)	T (°C)	I ₂ (g)	Solvent ² (mL)	Acid ³ (g)	Q ⁴ (g)
1	PANI _{EtOH} -APS	Aniline sulfate (0.5)	0.5	0	0.08	EtOH (50)	–	0.17
2	PANI _{DCM} -APS	Aniline sulfate (0.5)	0.5	0	0.08	DCM (50)	–	0.09
3	PANI _{TOL} -(-)-CSA-APS	Aniline (0.3)	0.5	0	0.02	Toluene (6)	(-) CSA (0.3)	0.29
4	PANI _{Hex} -(-)-CSA-APS	Aniline (0.3)	0.5	0	0.02	Hexane (6)	(-) CSA (0.3)	0.17
5	PANI _{EtOH} -(-)-CSA-APS	Aniline (0.3)	0.5	0	0.02	EtOH (6)	(-) CSA (0.3)	0.083
6	PANI _{DCM} -(-)-CSA-APS-25C	Aniline (0.3)	0.5	25	0.02	DCM (6)	(-) CSA (0.3)	trace
7	PANI _{DCM} -(-)-CSA-APS	Aniline (0.3)	0.5	0	0.02	DCM (6)	(-) CSA (0.3)	0.086
8	PANI _{DCM} -(-)-CSA	Aniline (1)	–	0	0.05	DCM ⁴ (20)	(-) CSA (1)	0.53
9	PANI _{DCM} -(+)-CSA	Aniline (1)	–	0	0.05	CHL (20)	(+) CSA (1)	0.23
10	PANI _{CHL} -BSA	Aniline (0.3)	–	0	0.02	CHL (12)	BSA (0.3)	0.1
11	PANI _{CHL} -MSA	Aniline (0.3)	–	0	0.02	CHL (12)	MSA (0.3)	0.05
12	PANI _{CHL} -DBSA	Aniline (0.3)	–	0	0.02	CHL (12)	DBSA (0.3)	0.07

¹Unless otherwise indicated, polymerization was conducted at 0°C.²PANI_{DCM}-(-)-CSA-APS-25C (entry 6) was obtained by polymerization at 25°C. CHL: Chloroform.³BSA: Benzene sulfonic acid. MSA: Methane sulfonic acid. DBSA: Dodecylbenzene sulfonic acid. CSA: Camphor sulfonic acid.⁴Q: Quantity of the resultant in grams.

3. Results and discussion

3.1. Ultraviolet-visible spectroscopy

Figure 2 shows the ultraviolet-visible absorption spectra of NMP-soluble fractions of PANI_{CHL}-(+)-CSA and P(ADA)_{TOL}I₂(0.1)-APS. An absorption peak due to the π-π* transition of the main chain of PANI_{CHL}-(+)-CSA was observed at 339 nm. PANI_{CHL}-(+)-CSA showed a polaron band at 630 nm, and P(PDA)_{TOL}I₂(0.1)-APS showed a polaron band at 600 nm. The PANI obtained using (+)-CSA and (-)-CSA did not exhibit circular dichroism. After converting PANI-ES to PANI-EB with ammonia/water and adding optically active CSA, optically active CSA-doped PANI can be obtained.

3.2. Infrared spectroscopy

Infrared (IR) spectroscopy showed that all of the PANIs synthesized in toluene, *n*-hexane, EtOH, DCM, and CHL exhibit similar IR absorption patterns. The IR spectra of PANIs synthesized in EtOH and DCM (PANI_{EtOH}-APS and PANI_{DCM}-APS) are shown in Figure 3. Table 3 shows the assignment of the signals for PANI_{EtOH}-APS and PANI_{DCM}-APS. The absorption of benzenoid structures appears at 1562 or 1560 cm⁻¹, whereas that of quinonoid structures appears at 1492 or 1483 cm⁻¹. The absorption peak at 1300 or 1301 cm⁻¹ is due to ν_{C-N} in secondary aromatic amines, while that at 1244 or 1241 cm⁻¹ reflects ν_{C-N}⁺ in the polaron lattice of PANI, that at 1108 or 1121 cm⁻¹ reflects δ_{C-H}, and

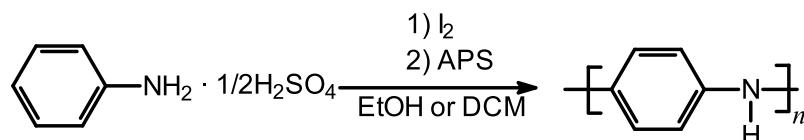
that at 800 or 816 cm⁻¹ indicates γ_{C-H} absorption (ν: stretching vibration, δ: in-plane bending vibration, γ: out-of-plane deformation).

Figure 4 depicted the IR absorption spectra of PANIs prepared from aniline in the presence of (-)-CSA and iodine. Table 4 shows the assignment of IR signals for PANI synthesized with APS (PANI_{DCM}-(-)-CSA-APS-25C) and no use of APS (PANI_{DCM}-(-)-CSA). The signals show the same tendency in the IR, indicating aniline can be polymerized using iodine in organic solvent. Here, the IR spectrum of PANIDCM-(-)-CSA-APS-25C was obtained from the trace amount of the sample for possible measurement.

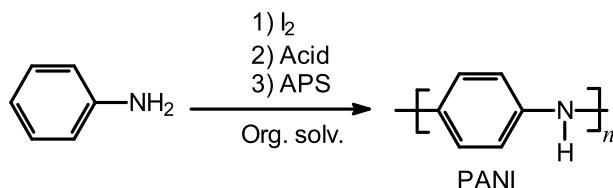
Figure 5 shows the IR absorption spectra of PANI prepared from ADA_{sul} in toluene solution with different amounts of iodine. Assignment of IR signals for P(ADA)_{TOL}I₂(0.02)-APS, P(ADA)_{TOL}I₂(0.04)-APS, P(ADA)_{TOL}I₂(0.06)-APS, P(ADA)_{TOL}I₂(0.08)-APS, and P(ADA)_{TOL}I₂(0.1)-APS is summarized in Table 5. The chemical structures of the as-prepared products were identical despite changes in the iodine amount.

3.3. Electron spin resonance spectroscopy

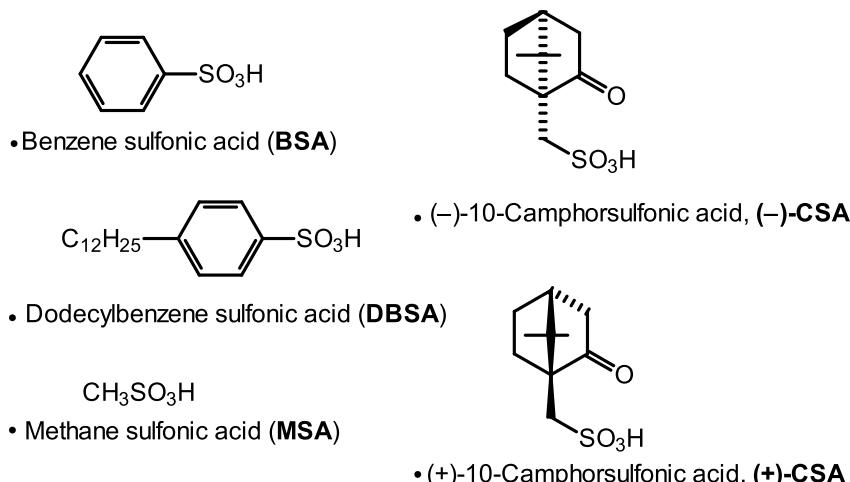
Table 6 summarizes the electron spin resonance (ESR) results and electrical conductivity measurements of the PANI samples. The signal at approximately g = 2.004 was attributed to nitro radicals. Figure 6 shows a representative ESR spectrum of PANI prepared in EtOH solution from aniline sulfate in the presence of



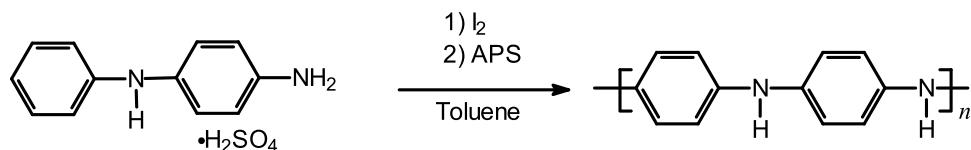
Scheme 1. Polymerization of aniline sulfate in organic solvents with the aid of iodine. APS: Ammonium persulfate. Organic solvent: Ethanol (EtOH) or dichloromethane (DCM).



Acid



Scheme 2. Polymerization of aniline in organic solvents with the aid of iodine and organic sulfonic acids. Organic solvent: EtOH, toluene, *n*-hexane, DCM, and chloroform (CHL). CSA: Camphor sulfonic acid.



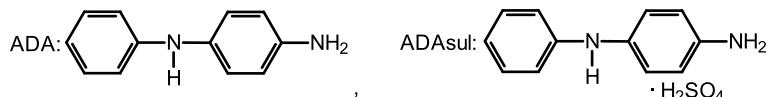
Scheme 3. Polymerization of 4-aminodiphenylamine sulfate (ADA_{sul}) in toluene solution.

Table 2. A series of polymerizations of 4-aminodiphenylamine sulfate in toluene solution in the presence of iodine.

Polyaniline	Mon ² (g)	APS (g)	T (°C)	I ₂ (g)	Solvent (mL)
P(ADA) _{TOL} I ₂ <i>n</i> -APS ¹	ADA _{sul} (0.3)	1.6	0	0.02–0.1	TOL (6)

¹P(ADA)_{TOL}I₂*n*-APS: Poly(4-aminodiphenylamine) prepared in toluene (TOL), *n* = 0.02, 0.04, 0.06, 0.08, and 0.1 g (*n* denotes I₂ quantity in grams).

²Mon: monomer.; polymerization temperature = 0°C.



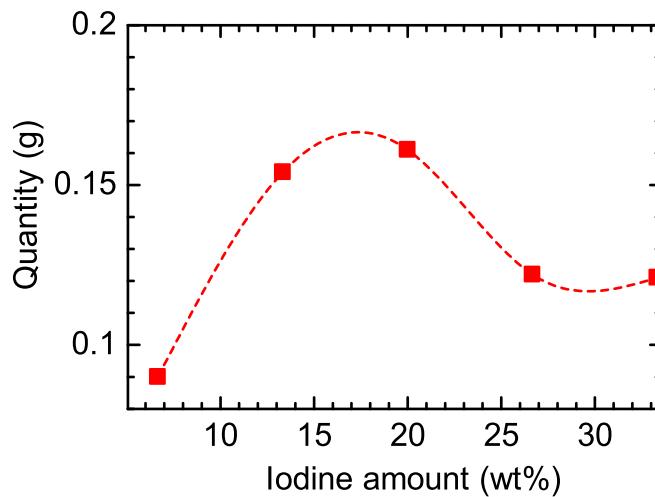


Figure 1. Product quantity (in grams) as a function of iodine amount (wt%) versus the monomer in toluene solution. Monomer: ADA_{sul} (0.3 g). APS: 1.6 g. Reaction temperature: 0°C.

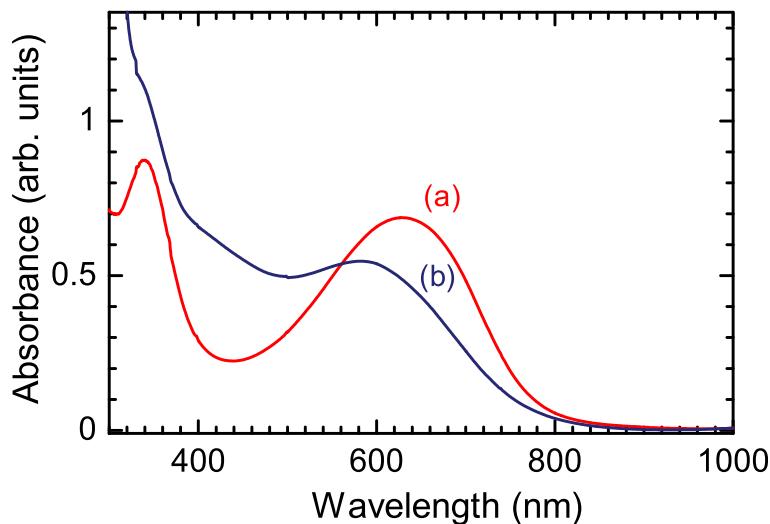


Figure 2. UV-vis optical absorption of $\text{PANI}_{\text{CHL}}\text{-}(+)\text{-CSA}$ (a) and $\text{P}(\text{ADA})_{\text{TOLI}_2(0.1)}\text{-APS}$ (b) in *N*-methylpyrrolidone (NMP) solution.

iodine ($\text{PANI}_{\text{EtOH}}\text{-APS}$). The ESR line shape was Lorentz type. The peak-to-peak width (ΔH_{pp}) and the peak-to-peak intensity (I_{pp}), and g value are obtained with the measurement.

Figure 7 shows the ESR results of a series of $\text{P}(\text{ADA})_{\text{TOLI}_2n}\text{-APS}$. ΔH_{pp} value remained constant despite changes in the iodine amount for the polymerization because the mobility of carrier polarons in the main chain is maintained regardless of the spin concentration (Table 6, Figure 7). The electrical conductivity of the PANI synthesized from the aniline monomer was in the range of 2.5×10^{-3} to 2.79 S/cm. Among the samples obtained, the PANI synthesized in hexane ($\text{PANI}_{\text{Hex}}\text{-}(-)\text{-CSA-APS}$) exhibited the highest electrical conductivity. Increasing the iodine amount in the polymerization reaction of ADA_{sul}

increased the electrical conductivity of the resulting polymer because of an increase in the iodine quantity that enhanced the concentration of radical cations (polarons) as charge carriers of PANI (Table 7). However, further addition of iodine in the polymerization resulted in decrease of conductivity. This may be due to the fact that excess amount of iodine is the cause of decrease of synthetic yield and main chain length as conduction path.

3.4. Thermal analysis

Figure 8 shows dynamic scanning calorimetry (DSC), thermogravimetric (TG) analysis, and differential thermal analysis (DTA) measurement results of the normal PANI (traditional PANI prepared using the general

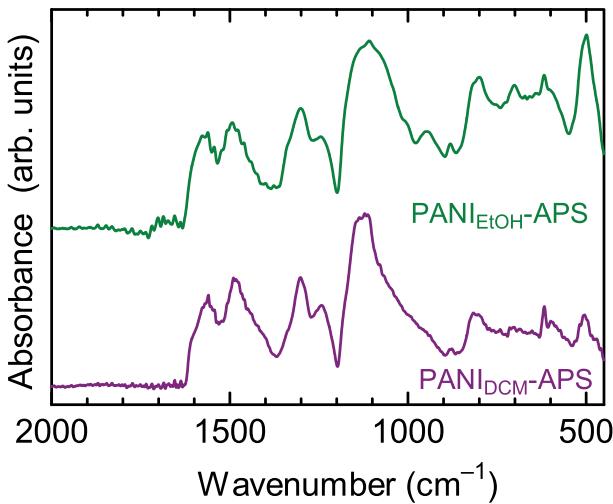


Figure 3. Infrared (IR) absorption spectra of polyaniline (PANI) prepared from aniline sulfate in the presence of iodine in EtOH and DCM solution. PANI_{EtOH}-APS (green line). PANI_{DCM}-APS (purple line).

Table 3. Assignment of IR signals¹ for PANI_{EtOH}-APS and PANI_{DCM}-APS.

	v _B	v _Q	v _{C-N}	v _{C-N} ⁺	δ _{C-H}	γ _{C-H}
PANI _{EtOH} -APS	1562	1492	1300	1244	1108	800
PANI _{DCM} -APS	1560	1483	1301	1241	1121	816

v: Stretching vibration, δ: In-plane bending vibration, γ: Out-of-plane deformation.

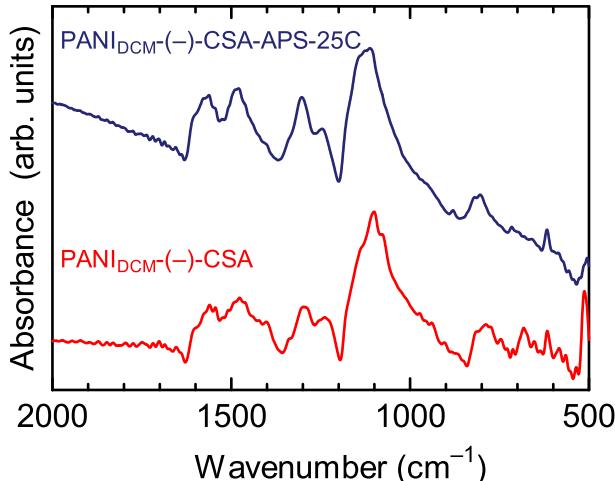


Figure 4. IR absorption spectra of polyaniline (PANI) prepared from aniline in the presence of iodine in DCM solution. PANI_{DCM}(-)CSA-APS-25C (dark blue line). PANI_{DCM}(-)CSA (PANI prepared with no use of APS, red line).

method), and PANI_{CHL}-BSA, P(ADA)_{TOL}I₂(0.1)-APS. The DSC results showed that no phase change occurred for these samples at < 230°C (Figure 8(a,c,e)).

Table 4. Assignment of IR signals¹ for PANI_{DCM}(-)CSA-APS-25C and PANI_{DCM}(-)CSA.

	v _B	v _Q	v _{C-N}	v _{C-N} ⁺	δ _{C-H}	γ _{C-H}
PANI _{DCM} (-)CSA-APS-25C	1562	1480	1302	1245	1112	804
PANI _{DCM} (-)CSA	1561	1477	1297	1240	1101	788

v: Stretching vibration, δ: In-plane bending vibration, γ: Out-of-plane deformation.

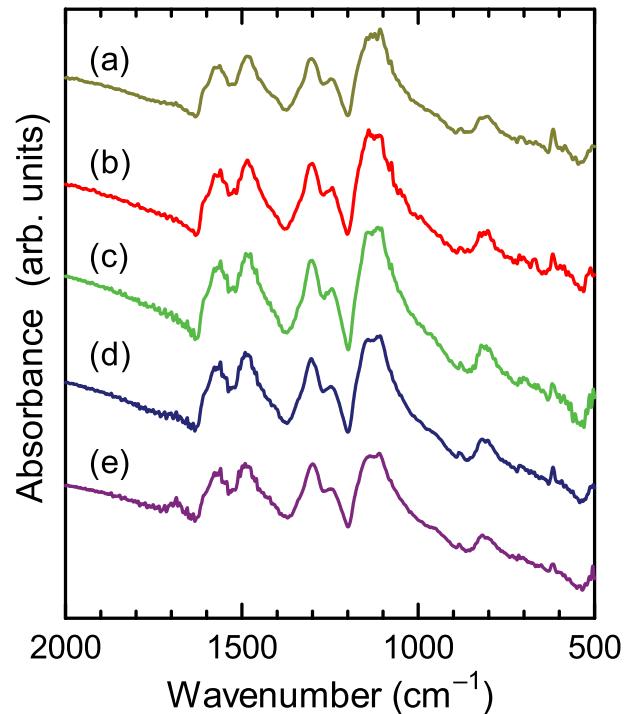


Figure 5. IR absorption spectra of PANI prepared from ADA_{sul} in toluene. (a) P(ADA)_{TOL}I₂(0.02)-APS. (b) P(ADA)_{TOL}I₂(0.04)-APS. (c) P(ADA)_{TOL}I₂(0.06)-APS. (d) P(ADA)_{TOL}I₂(0.08)-APS. (e) P(ADA)_{TOL}I₂(0.1)-APS.

Table 5. Assignment of IR signals¹ for P(ADA)_{TOL}I₂(0.02)-APS, P(ADA)_{TOL}I₂(0.04)-APS, P(ADA)_{TOL}I₂(0.06)-APS, P(ADA)_{TOL}I₂(0.08)-APS, and P(ADA)_{TOL}I₂(0.1)-APS.

	v _B	v _Q	v _{C-N}	v _{C-N} ⁺	δ _{C-H}	γ _{C-H}
P(ADA) _{TOL} I ₂ (0.02)-APS	1577	1484	1302	1247	1133	803
P(ADA) _{TOL} I ₂ (0.04)-APS	1561	1484	1300	1243	1139	814
P(ADA) _{TOL} I ₂ (0.06)-APS	1560	1488	1300	1244	1135	821
P(ADA) _{TOL} I ₂ (0.08)-APS	1561	1490	1303	1247	1142	818
P(ADA) _{TOL} I ₂ (0.1)-APS	1560	1490	1298	1243	1136	817

v: Stretching vibration, δ: In-plane bending vibration, γ: Out-of-plane deformation.

TG was used to measure the weight losses upon heating. Similarities of the samples in the result were observed for the inflection point at approximately 280°C (Figure 8(b,d,f)). All the samples were carbonized with heating at 550°C (Figure 8(b,d,f)). The signals in the DTA are observed for normal PANI (443°C and 493°C),

Table 6. ESR results and electrical conductivity of PANI prepared in the presence of iodine.

Polymer ¹	ESR		Conductivity σ (S/cm)
	ΔH_{pp} (mT)	g value	
PANI _{EtOH} -APS	0.436	2.00472	1.3×10^{-2}
PANI _{DCM} -APS	0.623	2.00467	2.5×10^{-3}
PANI _{TOL} (-) CSA-APS	0.242	2.00449	0.92
PANI _{Hex} (-) CSA-APS	0.315	2.00411	2.79
PANI _{EtOH} (-) CSA-APS	0.304	2.00445	0.13
PANI _{DCM} (-) CSA-APS-25C ²	0.44	2.00416	0.70
PANI _{DCM} (-) CSA-APS	0.44	2.00436	0.28
PANI _{DCM} (-) CSA	0.476	2.00425	3.0×10^{-2}
PANI _{DCM} (+) CSA	0.696	2.00442	0.15
PANI _{CHL} -BSA	0.374	2.00455	1.95
PANI _{CHL} -MSA	0.242	2.00448	0.90
PANI _{CHL} -DBSA	0.242	2.00448	0.82
PMMA-PANI ³	0.414	2.00503	1.5×10^{-5}
HPC-PANI ⁴	0.104	2.00509	< 10^{-9}
PS-PANI ⁵	0.341	2.00454	5.3×10^{-2}

¹Unless otherwise indicated, polymerization was conducted at 0°C.

²PANI_{DCM}(-) CSA-APS-25C was prepared at 25°C.

³PMMA: Poly(methyl methacrylate).

⁴HPC: Hydroxypropyl cellulose.

⁵PS: Polystyrene.

PANI_{CHL}-BSA (433°C and 496°C), and P(ADA)_{TOL}I₂ (0.1)-APS (441°C and 538°C). These results indicate that P(ADA)_{TOL}I₂(0.1)-APS prepared from a dimer of aniline has relatively good thermal stability compared with other samples.

3.5. Synchrotron XRD analysis

Figure 9(a,b) shows the synchrotron X-ray diffraction (XRD) results for normal PANI, PANI_{CHL}-DBSA, PANI_{DCM}(-)CSA, and polystyrene-PANI (PS-PANI) as examples. Normal PANI shows diffraction signals at 3.5 and 4.4 Å. PANI_{DCM}-DBSA showed a clear signal at 5.9 Å in addition to the signals at 4.4 and 3.3 Å, implying higher crystallinity. Further, PANI_{DCM}(-)CSA exhibited diffractions at 3.3, 3.5,

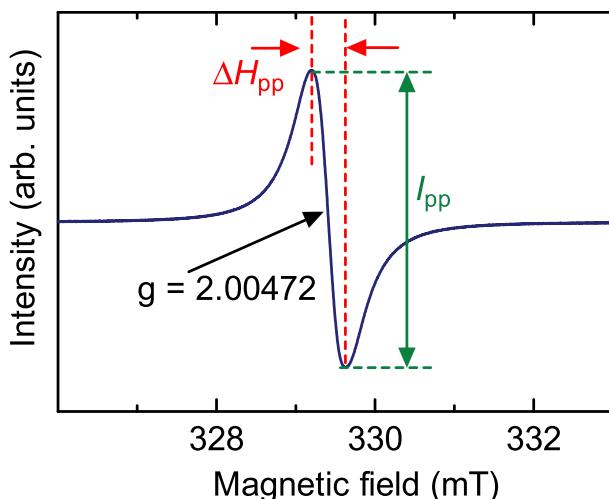


Figure 6. Electron spin resonance (ESR) of PANI_{EtOH}-APS.

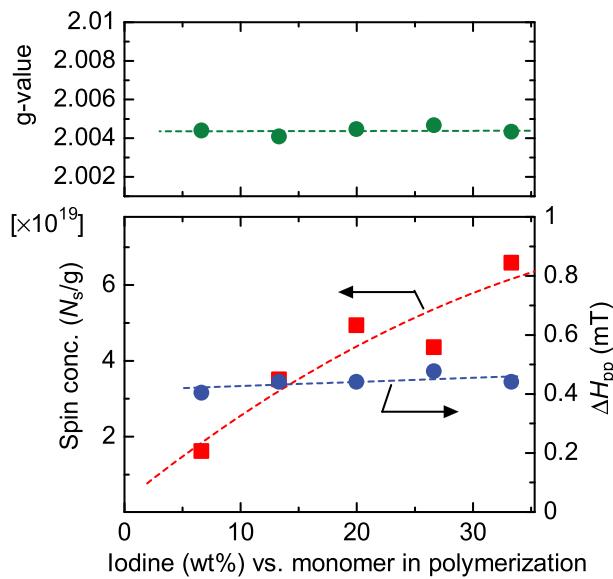


Figure 7. g-value, spin concentration, and peak-to-peak width (ΔH_{pp}) as a function of the amount of iodine added in the polymerization to obtain P(ADA)_{TOL}I_{2n}-APS.

Table 7. ΔH_{pp} in ESR, conductivity, and quantity of the series of P(ADA)_{TOL}I_{2n}-APS.

P(ADA) _{TOL} I _{2n} -APS ¹	ΔH_{pp} (mT)	Conductivity (S/cm)	Q ² (g)
n = 0.02 (6.7 wt% vs. mon.)	0.404	9.8×10^{-3}	0.09
n = 0.04 (13.3 wt% vs. mon.)	0.440	2.1×10^{-2}	0.154
n = 0.06 (20.0 wt% vs. mon.)	0.440	2.2×10^{-1}	0.161
n = 0.08 (26.7 wt% vs. mon.)	0.476	3.0×10^{-2}	0.122
n = 0.1 (33.3 wt% vs. mon.)	0.440	3.2×10^{-2}	0.121

¹n in grams, mon. = 0.3 g.

²Q: Quantity of the resultant in grams.

4.2, and 6.2 Å (Figure 9(a)). The diffraction patterns of the sample depicted circles that form as non-orientation (Figure 9(b)). This result shows that PANI synthesized in organic solvents with the aid of iodine forms a linear structure with high crystallinity, which is comparable to normal PANI prepared in water.

Polymerization with cooling can suppress the occurrence of side reactions to yield a linear form of PANI. Propagation in the ortho-position and formation of phenazine cycles as side reactions depress electrical conductivity. However, a series of PANIs prepared in this study showed moderate electrical conductivity. After polymerization, low-molecular-weight fractions as side-reaction products can be removed via the purification process. Synchrotron X-ray diffraction results indicated that the products in this study are comparable to PANI prepared using the general method. The PANI prepared in organic solvents with an aid of iodine can be determined as PANIs having a one-dimensional structure.

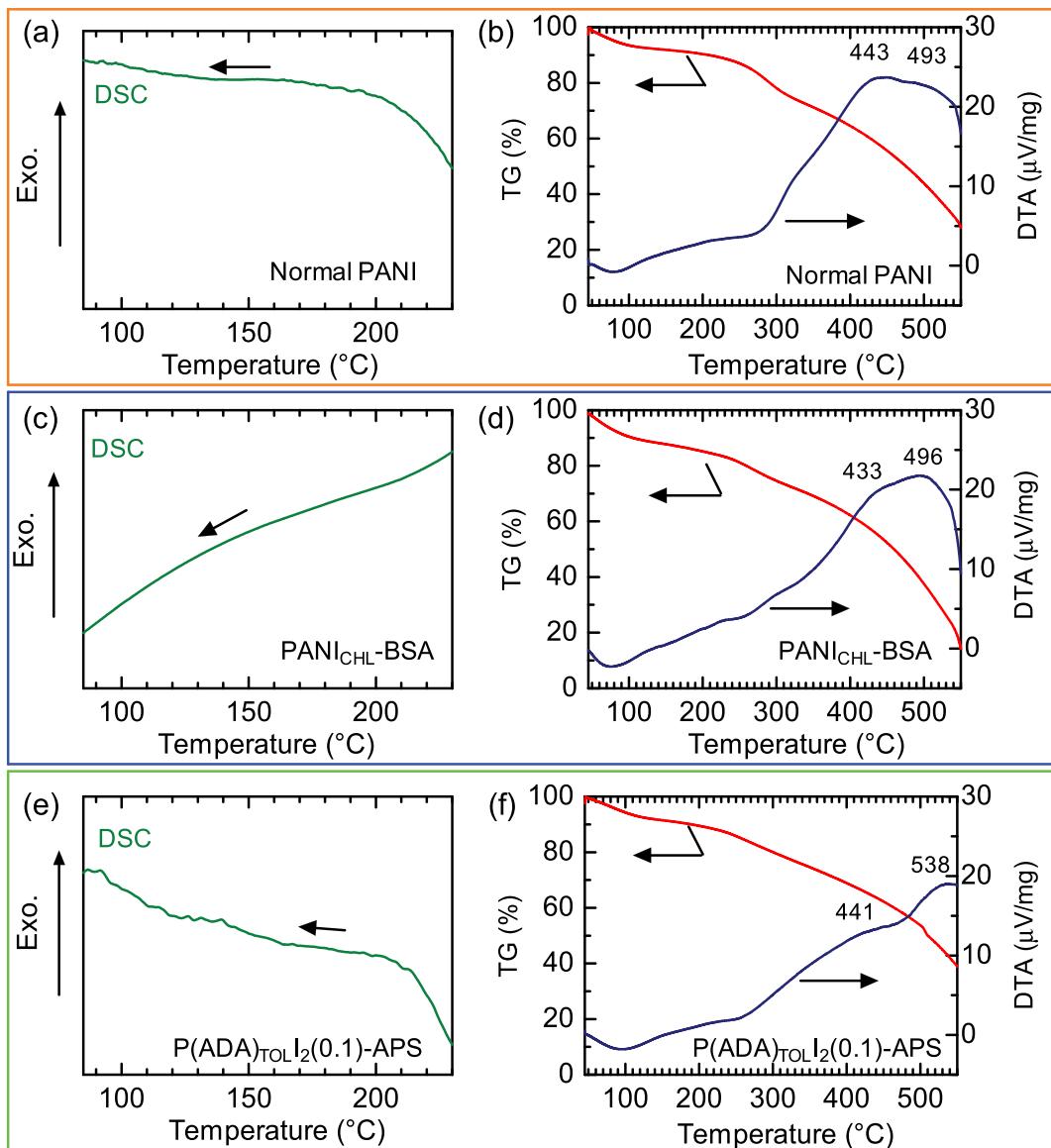


Figure 8. Dynamic scanning calorimetry (DSC), thermogravimetric (TG) analysis, and differential thermal analysis (DTA) measurement results of the normal PANI (traditional PANI prepared using the general method), PANI_{CHL}-BSA, and P(ADA)_{TOL}I₂(0.1)-APS.

3.6. Applications for preparation of polymer alloys

Preparation of PANI in high-boiling-point solution, such as NMP, DMF, and *m*-cresol, is required for the production of PANI-based polymer composites for blending. Here, the dedoped state of PANI with no electrical conductivity is required because doped PANI has no solubility. Furthermore, the infusibility of PANI prevents the melt method from producing polymer alloys. However, the synthesis of PANI in organic solution containing another synthetic polymer allows us to produce PANI-based polymer alloys using a combination of synthetic polymers in a single step. This convenient method can improve the production of PANI-based polymer alloys. In this section, the one-pot

preparation of acryl resin-PANI (polymethyl methacrylate-PANI (PMMA-PANI), polystyrene-PANI (PS-PANI), and hydroxypropyl cellulose-PANI (HPC-PANI) alloy was performed with polymerization of the monomers in low-boiling-point solvents (Table 8). This method is referred to as the “preparation of polymer alloy via polymerization reaction” (PAPR). The PANI-based polymer alloys can be prepared from both aniline and ADA_{Sul}. In this experiment, productions of PANI-based polymer alloys are carried out as an example for applications. PMMA-PANI was prepared as follows. PMMA (4 g) was dissolved in DCM (10 mL). Then, aniline (0.5 g), iodine (0.028 g), and APS (1 g) were added to the solution and stirred at 0°C. After 24 h,

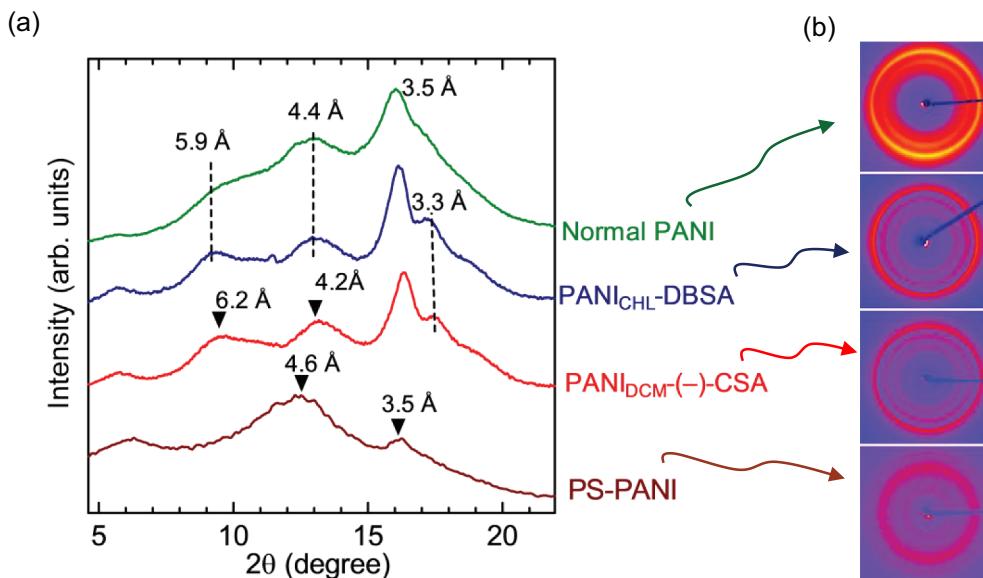


Figure 9. Synchrotron X-ray diffraction (XRD) results for normal PANI, PANI_{CHL}-DBSA, PANI_{DCM}(-)CSA, and PS-PANI.

the emerald green solution was cast on a glass substrate and dried naturally to obtain PMMA–PANI alloy, in a film form. The electrical conductivity of this film was 1.5×10^{-5} S/cm (Table 6). The PMMA–PANI displayed a Lorentz-type symmetrical ESR signal with $g = 2.0503$ and $\Delta H_{pp} = 0.414$ mT (Table 6). Since DCM, with a low-boiling point, was used as the solvent in this method, the polymer alloy film could be made by painting the as-prepared solution on a glass substrate after the polymerization reaction. Figure 10(a,b) shows the optical micrographs of PMMA–PANI; fine spherical PANI is clearly dispersed in the PMMA matrix. Thus, PMMA–PANI alloys could be conveniently prepared by PAPR. This approach offers a new route for the preparation of paints that have moderate conductivity.

The HPC–PANI alloy was prepared as follows. HPC (80 g) was dissolved in CHL (100 mL). Aniline (2 g), (–)CSA (3 g), iodine (0.05 g), and APS (4 g) were then added to the solution, and stirring was conducted at a low speed (16 rpm) using a mechanical stirrer for 12 h at 0°C. The mixture transformed into a rubbery mass, and the resultant product was abbreviated as HPC–PANI. HPC–PANI had a surface hardness of 4.5 HA after the solvent evaporated, as measured using a durometer. The HPC–PANI alloy shows no electrical conductivity due to the small amount of the PANI component in the HPC matrix. The HPC–PANI displayed a Lorentz-type symmetrical ESR signal with $g = 2.0509$. A narrow ΔH_{pp} value of 0.104 mT indicated that the charge carrier of the PANI component in the polymer alloy is delocalized along the main chain

because of a form of expanded coil in the HPC liquid crystal matrix, corresponding to secondary doping (Table 6). Therefore, the polymerization of aniline, secondary doping, and formation of alloy with HPC may simultaneously occur in the organic solvent. The polarizing optical microscopy image indicated that the polymer alloy showed birefringence derived from the cholesteric liquid crystal form of HPC (Figure 10(c)).

The PS–PANI alloy was prepared as follows (PS–PANI, Table 8). PS (0.1 g) was dissolved in toluene (6 mL). Then, ADA_{sul} (0.3 g) and iodine (0.1 g) were added to the solution. The mixture was stirred for 12 h using a magnetic stirrer at 0°C. The mixture was washed with a substantial amount of water and methanol. Filtration followed by drying under reduced pressure provided 0.248 g of the desired powdery polymer alloy. The product was abbreviated as PS–PANI, and its electrical conductivity was 5.3×10^{-2} S/cm. The PS–PANI alloy showed the ESR signal ($\Delta H_{pp} = 0.341$ mT,

Table 8. Polymerization of anilines in polymer solutions using iodine to prepare PANI-based polymer alloys.

Composite	Resin (g)	Mono. (g)	T (°C)	Iodine (g)	Solvent (mL)	APS (g)	Acid (g)
PS–PANI ¹	PS (0.1)	ADA _{sul} ⁴ (0.3)	0	0.1	Toluene (6)	0.6	–
PMMA–PANI ²	PMMA (4)	Aniline (0.5)	0	0.028	DCM (10)	1	(–)CSA (1 g)
HPC–PANI ³	HPC (80)	Aniline (2)	0	0.05	CHL (100)	4	(–)CSA (3 g)

¹PS: Polystyrene.

²PMMA: Poly(methyl methacrylate) resin.

³HPC: Hydroxypropyl cellulose.

⁴ADA_{sul}: 4-Aminodiphenylamine sulfate.

$g = 2.00454$), Table 6. PS-PANI shows synchrotron XRD signals at 3.5 and 4.6 Å derived from PANI component in the alloy. The signal at 4.6 Å can be overlap with a signal from PS (Figure 9(a,b)).

The IR spectra of PS, PMMA, and HPC as the host polymer; normal PANI, PS-PANI, PMMA-PANI, and HPC-PANI are shown in Figure 11. The benzenoid structure (1562 cm^{-1}), quinonoid structure (1490 cm^{-1}), and ν_{CH} (2923 and 2854 cm^{-1}) absorptions of PS could

be observed in the spectra of PS-PANI (Figure 11(a)). This finding indicates that PS-PANI simultaneously presents the structures of PS and PANI. PMMA-PANI showed absorption at 2923 and 2854 cm^{-1} , which is derived from ν_{CH} of PMMA, and at 1721 cm^{-1} , which is due to $\nu_{\text{C=O}}$, as shown in Figure 11(b). However, the absorptions of benzenoid and quinonoid structures in PANI could not be clearly observed likely because the signals of this structure overlap with a large portion of the absorption of PMMA in the alloy. HPC-PANI showed mainly IR absorptions of HPC component. The IR signals from PANI in the alloy overlap with a large portion of the absorption of HPC (Figure 11(c)). Assignment of the IR signals are summarized in Table 9.

4. Possible mechanism

We propose a possible mechanism for aniline polymerization in the presence of iodine with reference from a previous report.^[28] Scheme 4 shows a possible mechanism of the polymerization of aniline with iodine. First, the radical on the nitrogen and benzene are coupled via homolysis to form $=\text{NH}_2^+$ and a radical in the ring (Step 1). A quinonoid is formed when the radical in the ring moves to the *p*-position (Step 2). Another aniline sulfate is coupled with the radical at the *p*-position of the quinonoid to form an aniline dimer (Step 3). The proton on the amine is moved to form the neutral form of the aniline dimer (Step 4). Then, iodine accepts an electron from the benzene ring of the aniline dimer and the generation of a radical on the *p*-position and a cation in the ring (Step 5). The cation moves to the *ipso*-position to form a quinonoid structure (Step 6). Another aniline sulfate molecule is coupled with the radical with the removal of the proton on the quinonoid ring (Step 7). The proton on the amine is eliminated to form a neutral form of aniline (Step 8). Sequential reactions from Step 1 to Step 8 as propagation yield polyaniline. Iodine could help APS serve as an oxidant for the polymerization in the organic solvent.

Scheme 5 shows a possible mechanism of the polymerization of ADA_{sul} with iodine. First, the radical on the nitrogen moves to the *p*-position of the benzene ring to form a quinonoid structure (Step 1). Then, the radicals are coupled with another ADA molecule to form an aniline tetramer (Step 2). The proton on the amine is eliminated, the proton on the quinonoid structure is removed, and the quinonoid structure is changed to the benzenoid structure (Step 3). Iodine accepts an electron from

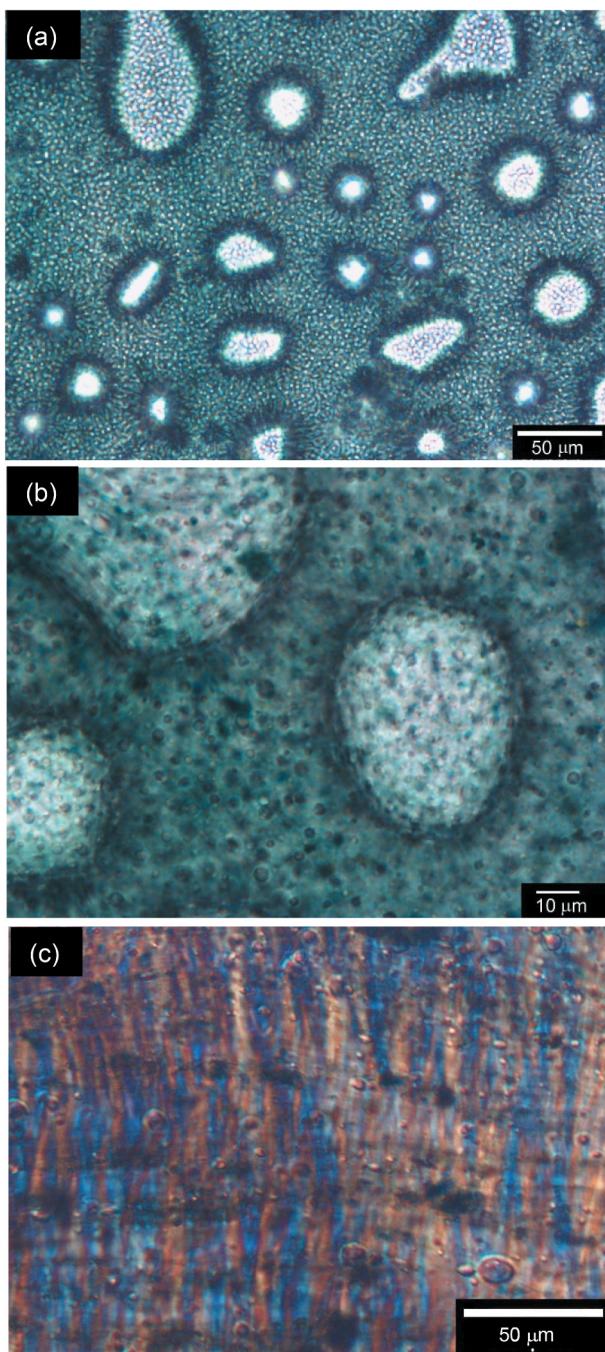


Figure 10. (a) Optical microscopic image of PMMA-PANI. (b) Magnified image of (a). (c) Polarizing optical microscopy image of HPC-PANI.

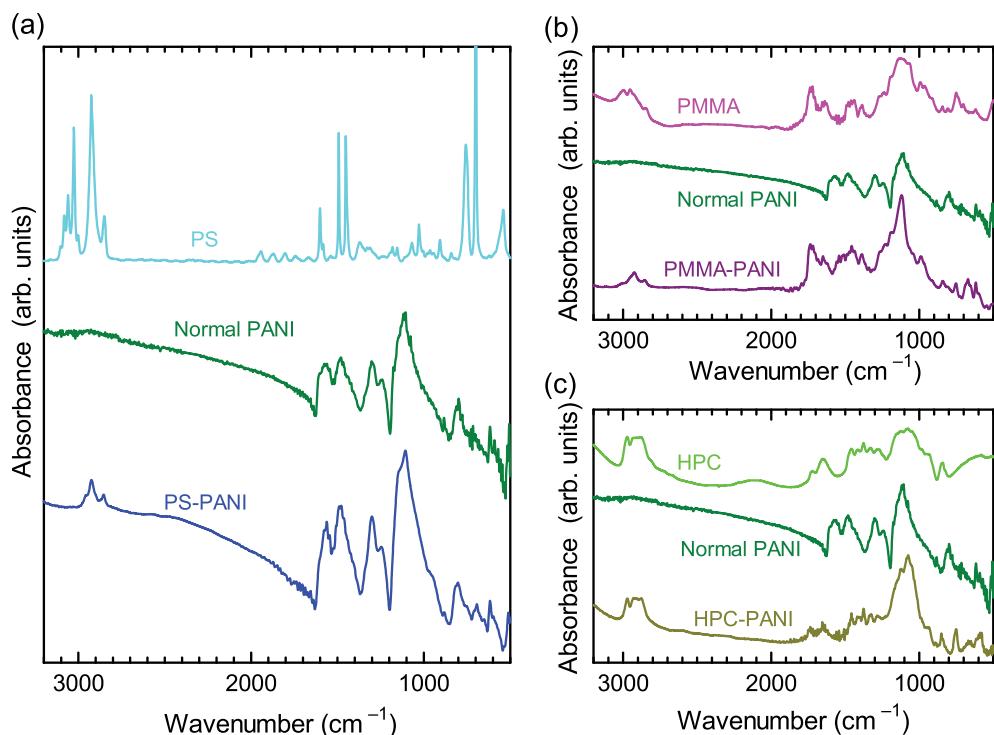


Figure 11. Infrared absorption spectra of polymer alloys. (a) PS, normal PANI, and PS–PANI alloy. (b) PMMA, normal PANI, and PMMA–PANI alloy. (c) HPC, normal PANI, and HPC–PANI alloy. Normal PANI (traditional PANI) was the standard for comparison.

Table 9. Assignment for IR signals¹ of the polymer alloys.

	ν_{CH}	$\nu_{\text{C=O}}$	ν_{B}	ν_{Q}	$\nu_{\text{C-N}}$	$\nu_{\text{C-N+}}$	$\delta_{\text{C-H}}$	$\gamma_{\text{C-H}}$
Normal-PANI	–	–	1561	1480	1302	1249	1117	798
PS	2925	–	–	–	–	–	–	–
	2849							
PS-PANI	2923	–	1562	1490	1300	1246	1106	803
	2854							
PMMA	2952	1721	–	–	–	–	1124	–
	2846							
PMMA-PANI	2923	1735	–	–	–	–	1118	–
	2854							
HPC	2924	–	–	–	–	–	1076	–
HPC-PANI	2922	–	–	–	–	–	1075	–

¹v: Stretching vibration, δ: In-plane bending vibration, γ: Out-of-plane deformation.

the benzene ring. In the ring, the formation of a radical cation occurred (Step 4). The cation moves to the *ipso*-position to form a quinonoid structure (Step 5). Another ADA sulfate molecule is coupled with the radical with the removal of the proton on the quinonoid ring (Step 6). The proton on the amine is eliminated (Step 7). Sequential reactions from Step 1 to Step 7 as propagation yield polyaniline. Iodine could help APS serve as an oxidant for the polymerization in organic solvents.

These proposed mechanisms can be a way to prepare PANI because the fundamental mechanism of the formation of PANI is still unclear. Furthermore, the resulting PANI has combinations of benzenoid, quinonoid,

neutral, and radical cation to form several PANI structures, such as emeraldine salt, emeraldine base, pernigraniline, and leucoemeraldine.^[29]

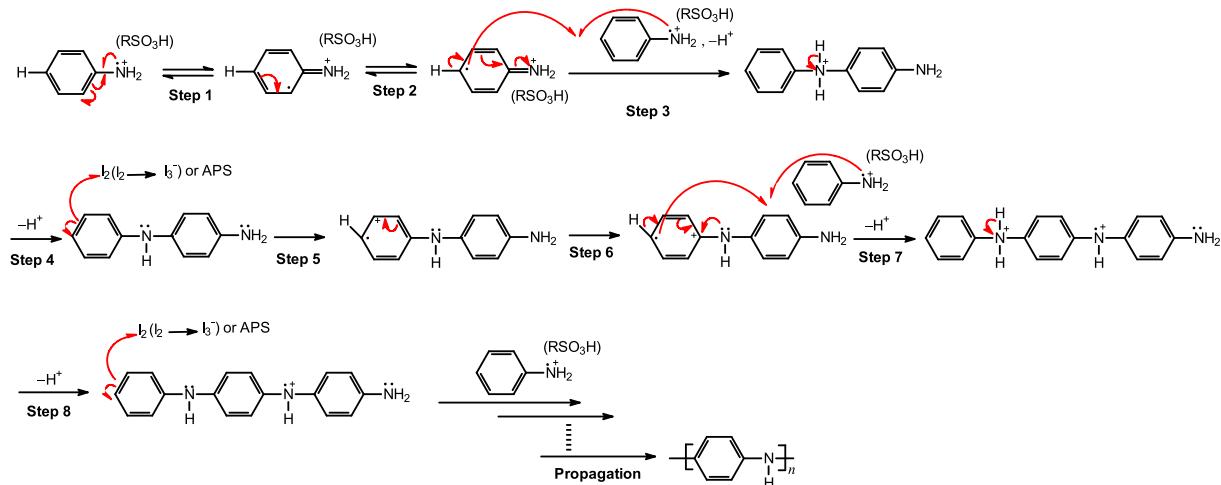
5. Conclusions

PANI could be obtained in organic solvents with iodine. However, no polymerization reaction occurs in *m*-cresol, NMP, and *N,N*-dimethylformamide. The addition of alkyl sulfonic acids, such as CSA and DBSA, promoted the synthesis of PANI in organic solvents; however, the addition of sulfuric acid did not yield the desired product. A combination of aniline sulfate, iodine, and APS yielded PANI in the organic solvents.

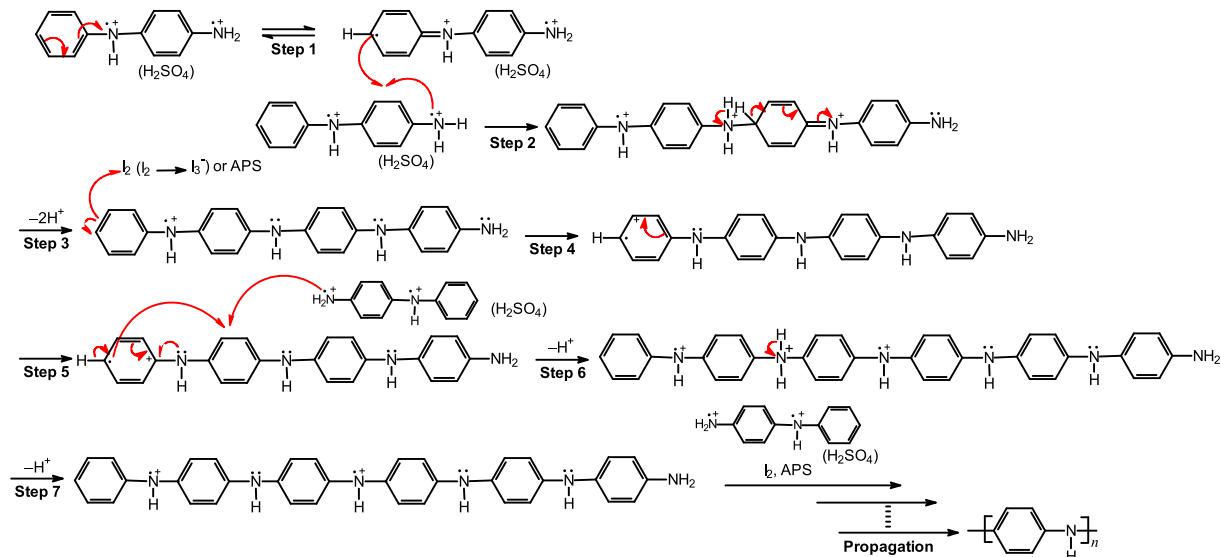
Iodine promotes electron-acceptor doping in aniline and the aniline dimer, resulting in localized radical cations. The propagation for polymerization occurs when radical-bearing aniline molecules react with intact aniline via a chain reaction. The polarons (radical cation) generated by iodine in the initial stage of polymerization appear to be the key to promoting the polymerization reaction in organic solvents.

6. Chemicals

Aniline (Fujifilm Wako Pure Chemical Corporation, Tokyo) was purified by distillation. *N*-methylpyrrolidone (NMP) (Tokyo Chemical Industry Co. Ltd., TCI, Tokyo),



Scheme 4. Possible polymerization mechanism of aniline with the aid of iodine. RSO_3H denotes organic sulfonic acid.



Scheme 5. Possible polymerization mechanism of 4-aminodiphenylamine sulfate with an aid of iodine.

4,4'-diaminodiphenylamine sulfate (TCI), methane sulfonic acid (TCI), benzene sulfonic acid (TCI), dodecylbenzene sulfonic acid (TCI), (+)-camphor sulfonic acid (TCI), (-)-camphor sulfonic acid (TCI), ammonium persulfate (APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$) (Yoneyama Yakuhin Kogyo, Osaka), EtOH (Nacalai Tesque, Inc., Kyoto), *n*-hexane (Nacalai), toluene (Nacalai), chloroform (Nacalai), dichloromethane (Nacalai), iodine (Sigma-Aldrich, St. Louis) were used as received. Normal PANI was prepared by general method. A solution of aniline (1 g), H_2SO_4 (1 g), APS (1 g) in the water (200 mL) was stirred for 12 h at 0°C. The crude product was washed with a large volume of water, methanol, and acetone in this order followed by filtration. Reduced pressure for the product gave dark emerald powder as PANI emeraldine salt (PANI-ES).

7. Instruments

The IR absorption spectra of the PANIs were obtained with a FT-IR 4600 (JASCO, Tokyo) instrument by the KBr method except for polystyrene film. Surface hardness of HPC-PANI was measured with a durometer (OBEST, Guangdong). The IR spectra of polystyrene was obtained with the neat film. UV-vis optical absorption spectroscopy measurement was carried out with a V-630 UV-vis optical absorption spectrometer (JASCO). A powder sample was pressed into a pellet, and the conductivity was measured by the four-point probe method with a Mitsubishi Chemical Analytech LORESTA-GP MCPT610. ESR measurements of the solid sample packed into a 5 mm quartz tube were performed using a JES TE-200 (JEOL, Tokyo) spectrometer in X-band. TG/DTA measurements were carried out by

TG/DTA7300 (Hitachi High-Tech Science Corporation, Tokyo). DSC measurements were carried out with X-DSC7000 (Hitachi High-Tech Science Corporation). Optical texture observations were conducted using a high-resolution polarizing microscope (ECLIPS LV 100, Nikon) with an LU Plan Fluor lens and a CFIUW lens (Nikon, Tokyo). Synchrotron XRD measurements were carried out at BL-8B beamline of the Photon Factory (PF), High Energy Accelerator Research Organization (KEK). The measurements were performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2019G005, 2021G503).

Acknowledgments

We would like to thank the OPEN FACILITY, Research Facility Center for Science and Technology, University of Tsukuba for DSC, TG, and DTA measurements. This research was supported by Japan Society for the Promotion of Science (JSPS), Grants-in-Aid for Scientific Research (No. 20K05626).

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by the Japan Society for the Promotion of Science (JSPS, Grants-in-Aid for Scientific Research (KAKENHI) [20K05626].

Notes on contributors

Hiromasa Goto received his PhD with a focus on liquid crystalline conjugated polymer from University of Tsukuba under supervision of Prof. Hideki Shirakawa (2000 Nobel Prize laureate). H. Goto has continued the research on polymer liquid crystals and synthetic metals. He developed electrochemical and chemical polymerization in liquid crystal, and crystal.

Kyoka Komaba is currently PhD student in Goto laboratory at University of Tsukuba. She received Tsukuba Alumni Association Award from Prof. Dr. Leo Esaki (1973 Nobel Prize laureate) in 2019.

Takuya Yonehara is currently PhD student in Goto laboratory at University of Tsukuba.

Ryo Miyashita is currently PhD student in Goto laboratory at University of Tsukuba.

Reiji Kumai received his Ph.D. degree from the University of Tokyo in 1995. He was a research scientist at the Joint Research Center of Atom Technology (1995 – 1999) and joined the National Institute of Advanced Interdisciplinary Research (1999 – 2001) as a researcher. In 2001, his institute was reorganized as National Institute of Advanced Industrial Science and Technology (AIST). In 2011, he moved to

Institute of Material Structure Science, High Energy Accelerator Research Organization (KEK) as a professor. His research is now focused on the structural science of condensed matter by using quantum beams.

ORCID

Hiromasa Goto  <http://orcid.org/0000-0003-4276-735X>

Reiji Kumai  <http://orcid.org/0000-0002-5320-0028>

References

- [1] Bera, S.; Kundu, S.; Khan, H.; Jana, S. Polyaniline Coated Graphene Hybridized SnO₂ Nanocomposite: Low Temperature Solution Synthesis, Structural Property and Room Temperature Ammonia Gas Sensing. *J. Alloy. Comp.* **2018**, *744*, 260–270. DOI: [10.1016/j.jallcom.2018.02.034](https://doi.org/10.1016/j.jallcom.2018.02.034).
- [2] Moradian, M.; Nasirian, S. Structural and Room Temperature Gas Sensing Properties of Polyaniline/Titania Nanocomposite. *Org. Elec.* **2018**, *62*, 290–297. DOI: [10.1016/j.orgel.2018.08.006](https://doi.org/10.1016/j.orgel.2018.08.006).
- [3] AlMashrea, B. A.; Abla, F.; Chehimi, M. M.; Workie, B.; Han, C.; Mohamed, A. A. Polyaniline Coated Gold-Aryl Nanoparticles: Electrochemical Synthesis and Efficiency in Methylene Blue Dye Removal. *Synth. Met.* **2020**, *269*, 116528. DOI: [10.1016/j.synthmet.2020.116528](https://doi.org/10.1016/j.synthmet.2020.116528).
- [4] Packiaraj, M.; Kumar, K. K. S. Preparation of Novel Flexible Freestanding Conducting Polyaniline Nanocomposite Films Using Recent Generation Polycarboxylate Ether. *Synth. Met.* **2021**, *281*, 116897. DOI: [10.1016/j.synthmet.2021.116897](https://doi.org/10.1016/j.synthmet.2021.116897).
- [5] Rehman, A.; Houshyar, S.; Reineck, P.; Padhye, R.; Wang, X. Multifunctional Smart Fabrics through Nanodiamond-Polyaniline Nanocomposites. *ACS Appl. Polym. Mater.* **2020**, *2*(11), 4848–4855. DOI: [10.1021/acsapm.0c00789](https://doi.org/10.1021/acsapm.0c00789).
- [6] Zhu, X.; Zhao, Q.; Zhang, T.; Pang, X. Electrorheological Response of Novel polyaniline-Fe₂O₃ Nanocomposite Particles. *Polym. Plast. Tech. Mater.* **2019**, *58*, 573–577. DOI: [10.1080/03602559.2018.1493118](https://doi.org/10.1080/03602559.2018.1493118).
- [7] Anum, R.; Zahid, M.; Siddique, S.; Shakir, H. M. F.; Rehan, Z. A. PVC Based Flexible Nanocomposites with the Incorporation of Polyaniline and Barium Hexa-Ferrite Nanoparticles for the Shielding against EMI, NIR, and Thermal Imaging Cameras. *Synth. Met.* **2021**, *277*, 116773. DOI: [10.1016/j.synthmet.2021.116773](https://doi.org/10.1016/j.synthmet.2021.116773).
- [8] Kornberg, A. B.; Thompson, M. R.; Zhu, S. Flexible Conductive Substrate Incorporating a Submicrometer Co-continuous Polyaniline Phase within Polyethylene by Controlled Crazing. *ACS Appl. Polym. Mater.* **2021**, *3*(4), 1880–1889. DOI: [10.1021/acsapm.0c01416](https://doi.org/10.1021/acsapm.0c01416).
- [9] Ashwini, I. S.; Pattar, J.; Anjaneyulu, P.; Prakash Babu, D.; Sreekanth, R.; Manohara, S. R.; Nagaraja, M. Synthesis and Electrical Properties of Polyaniline-Cerium Oxide Composites. *Synth. Met.* **2020**, *270*, 116588. DOI: [10.1016/j.synthmet.2020.116588](https://doi.org/10.1016/j.synthmet.2020.116588).
- [10] Cruz-Medina, R.; Vega-Rios, A.; Hernández-Escobar, C. A.; Estrada-Monje, A.; Rodríguez-Sánchez, I.; Zaragoza-Contreras, E. A. Polystyrene-Polyaniline

- Core-Shell Composite Particles Using a Bifunctional Selectively Polymerizable Monomer as the Interfacial Linkage. *Synth. Met.* **2020**, *265*, 116402. DOI: [10.1016/j.synthmet.2020.116402](https://doi.org/10.1016/j.synthmet.2020.116402).
- [11] Kumar, A.; Kumar, V.; Awasthi, K. Polyaniline–Carbon Nanotube Composites: Preparation Methods, Properties, and Applications. *Poly. Plast. Tech. Eng.* **2018**, *57*(2), 70–97. DOI: [10.1080/03602559.2017.1300817](https://doi.org/10.1080/03602559.2017.1300817).
- [12] Wu, K.; Huang, J.; Tu, J.; Xu, X.; Huang, H.; Liu, Y.; Li, L.; Yao, J. Reinforced Polyaniline-dodecyl Benzene Sulfonate Hydrogel with Well-aligned Fibrous Morphology as Durable Electrode Materials for Zn-ion Battery. *Synth. Met.* **2021**, *274*, 16721. DOI: [10.1016/j.synthmet.2021.116721](https://doi.org/10.1016/j.synthmet.2021.116721).
- [13] Alharthy, R. D.; Saleh, A. A Novel Trace-Level Ammonia Gas Sensing Based on Flexible PAni-CoFe₂O₄ Nanocomposite Film at Room Temperature. *Polymers*. **2021**, *13*(18), 3077. DOI: [10.3390/polym13183077](https://doi.org/10.3390/polym13183077).
- [14] Zhang, Y.; Yang, Z.; Yu, Y.; Wen, B.; Liu, Y.; Qiu, M. Tunable Electromagnetic Interference Shielding Ability in a One-Dimensional Bagasse Fiber/Polyaniline Heterostructure. *ACS Appl. Polym. Mater.* **2019**, *1*(4), 737–745. DOI: [10.1021/acsapm.8b00025](https://doi.org/10.1021/acsapm.8b00025).
- [15] He, M.; Liu, C.; Luo, G.; Wang, C. Synthesis and Characterization of Lewis Acid Doped Polyaniline and Its Application as Catalysts for Acetalization of Carbonyl Compounds. *Polym. Plast. Eng.* **2007**, *46*(2), 145–149. DOI: [10.1080/03602550601152952](https://doi.org/10.1080/03602550601152952).
- [16] Kweon, H.; Lin, C.-W.; Hasan, M. M. F.; Kaner, R.; Sant, G. N. Highly Permeable Polyaniline–Graphene Oxide Nanocomposite Membranes for CO₂ Separations. *ACS Appl. Polym. Mater.* **2019**, *1*(12), 3233–3241. DOI: [10.1021/acsapm.9b00426](https://doi.org/10.1021/acsapm.9b00426).
- [17] Mondal, S.; Rana, U.; Das, P.; Malik, S. Network of Polyaniline Nanotubes for Wastewater Treatment and Oil/Water Separation. *ACS Appl. Polym. Mater.* **2019**, *1*(7), 1624–1633. DOI: [10.1021/acsapm.9b00199](https://doi.org/10.1021/acsapm.9b00199).
- [18] Wang, Y.; Zheng, H.; Jia, L.; Li, H.; Li, T.; Chen, K.; Gu, Y. Optimizing the Polymerization Conditions of Soluble Polyaniline Doped with Itaconic Acid. *J. Macromol. Sci., Part A. Pure Apply. Chem.* **2014**, *51*(7), 577–581. DOI: [10.1080/10601325.2014.916179](https://doi.org/10.1080/10601325.2014.916179).
- [19] Almtiri, M.; Dowell, T. J.; Chu, I.; Wipf, D. O.; Scott, C. N. Phenoxazine-Containing Polyaniline Derivatives with Improved Electrochemical Stability and Processability. *ACS Appl. Polym. Mater.* **2021**, *3*(6), 2988–2997. DOI: [10.1021/acsapm.1c00152](https://doi.org/10.1021/acsapm.1c00152).
- [20] Deb, K.; Sarkar, K.; Bera, A.; Debnath, A.; Saha, B. Coupled Polaron-Electron Charge Transport in Graphite Functionalized Polyaniline on Cellulose: Metal Free Flexible p-Type Semiconductor. *Synth. Met.* **2018**, *245*, 96–101. DOI: [10.1016/j.synthmet.2018.08.011](https://doi.org/10.1016/j.synthmet.2018.08.011).
- [21] Firda, P. B. D.; Malik, Y. T.; Oh, J. K.; Wujcik, E. K.; Jeon, J.-W. Enhanced Chemical and Electrochemical Stability of Polyaniline-Based Layer-by-Layer Films. *Polymers*. **2021**, *13*(17), 2992. DOI: [10.3390/polym13172992](https://doi.org/10.3390/polym13172992).
- [22] MacDiarmid, A. G.; Epstein, A. J. Secondary Doping: A New Concept in Conducting Polymers. *Macromol. Symp.* **1995**, *98*(1), 835–842. DOI: [10.1002/masy.19950980170](https://doi.org/10.1002/masy.19950980170).
- [23] Kim, Y.-G.; Nguyen, H.-L.; Kinlen, P. Secondary Dopants of Electrically Conducting Polyanilines. *Polymers*. **2021**, *13*(17), 2904. DOI: [10.3390/polym13172904](https://doi.org/10.3390/polym13172904).
- [24] Su, S.-J.; Kuramoto, N. Optically Active Polyaniline Derivatives Prepared by Electron Acceptor in Organic System: Chiroptical Properties. *Macromolecules*. **2001**, *34*(21), 7249–7256. DOI: [10.1021/ma010747p](https://doi.org/10.1021/ma010747p).
- [25] Soares, B. G.; Nascimento, M. R. S.; Sena, A. S.; Indrusiak, T.; Souto, L. F. C.; Pontes, K. Polyaniline Co-Doped with Dodecyl Benzene Sulfonic Acid and Zwitterionic-Based Ionic Liquids Prepared by Inverse Emulsion Polymerization. *Synth. Met.* **2020**, *266*, 116435. DOI: [10.1016/j.synthmet.2020.116435](https://doi.org/10.1016/j.synthmet.2020.116435).
- [26] Yamabe, K.; Nakajima, K.; Goto, H. Polaron Radical Polymerization. *J. Polym. Sci. Part A-Poly. Chem.* **2018**, *56*(7), 805–811. DOI: [10.1002/pola.28956](https://doi.org/10.1002/pola.28956).
- [27] Majidi, M. R.; Kane-Maguire, L. A. P.; Wallace, G. G. Facile Synthesis of Optically Active Polyaniline and Polytoluidine. *Polymer*. **1996**, *37*(2), 359–362. DOI: [10.1016/0032-3861\(96\)81111-6](https://doi.org/10.1016/0032-3861(96)81111-6).
- [28] Geniès, E. M.; Boyle, A.; Lapkowski, M.; Tsintavis, C. Polyaniline: A Historical Survey. *Synth. Met.* **1990**, *36*(2), 139–182. DOI: [10.1016/0379-6779\(90\)90050-U](https://doi.org/10.1016/0379-6779(90)90050-U).
- [29] MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Somasiri, N. L. D.; Epstein, A. J. Polyaniline: Synthesis and Characterization of the Emeraldine Oxidation State by Elemental Analysis, In *Conducting polymers; special applications: proceedings of the workshop held at Sintra, Portugal*, p. 105–120, July 28–31, 1986. Edited by Luis Alcacer, D. Reidel Publishing Company, Holland, **1987**.