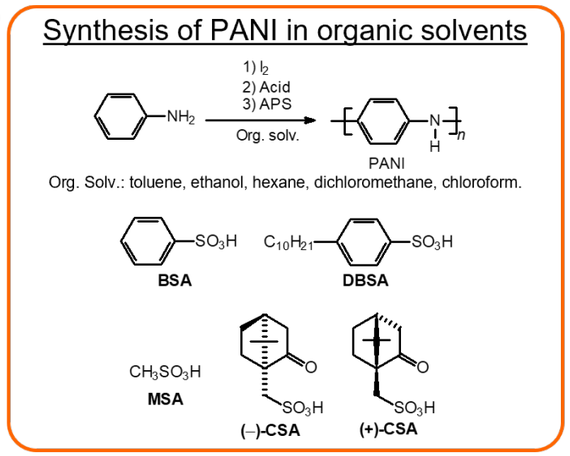
Polyaniline and Polymer Alloys Prepared in Organic Media

Polyaniline (PANI) was successfully synthesized in common organic solvents, such as ethanol, toluene, chloroform, dichloromethane, and hexane with an aid of a small amount of iodine [1]. We also synthesized PANI-based polymer alloys with nonconductive polymers to synthesize PANI in the noncoductive polymer solution in the presence of iodine. The chemical structure of the PANI and PANI-based alloy thus obtained was confirmed with infrared absorption spectroscopy measurements and synchrotron XRD measurements. The conductivity of the PANI and PANI-based conductive alloy was examined using 4-point probe method.

Polyaniline (PANI) is a promising conductive polymer. PANI can be synthesized in water medium under ambient air with ammonium persulfate (APS) as an initiator. PANI has been applied to batteries, gas sensors, electromagnetic shielding materials, catalysts, and separation materials.

In this research, we succeed to synthesize PANI in organic solvents with a small amount of iodine. Iodine supports APS as an oxidant for the polymerization in the organic solvents. Ethanol, dichloromethane, chloroform, hexane, and toluene are used as a solvent for synthesis of PANI. Further, conductive alloys (PANI/plastic composites) are synthesized in organic solvents. Molecular structure was evaluated by infrared (IR) spectroscopy and synchrotron XRD measurements. Conductive of PANI and the polymer alloys thus prepared was estimated by 4-probe method.

(a)

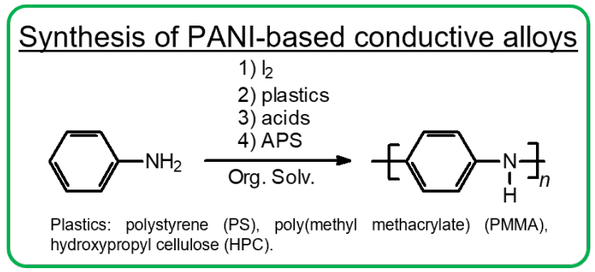


(b)

Org. Solv.	Organic acid	Conductivity (S/cm)
Toluene	(–)-CSA	0.92
Hexane	(–)-CSA	2.79
Ethanol	(–)-CSA	0.13
DCM	(–)-CSA	0.28
	(–)-CSA	0.03
CHL	(+)-CSA	0.15
	BSA	1.95
	MSA	0.90
	DBSA	0.82

Figure 1: (a) Synthesis of polyaniline in organic solvents, **(b)** conductivity.

(a)



(b)

Sample	Org. Solv.	Organic acid	Plastic	Conductivity (S/cm)
PS/PANI	Toluene	-	PS	5.3×10^{-2}
PMMA/PANI	DCM	(-)-CSA	PMMA	1.5×10^{-5}
HPC/PANI	CHL	(-)-CSA	HPC	$<10^{-9}$

Figure 2: (a) Synthesis of polyaniline-based conductive alloys in organic solvents, **(b)** conductivity.

Polymerization of aniline was conducted according to **Fig. 1**. Aniline, an organic acid and a small amount of iodine were dissolved in an organic solvent. After cooled down to 0 ºC, APS were added and stirred overnight. The solution was filtrated and washed with water, acetone and methanol. The precipitates were dried under vacuum. Camphor sulfonic acid (CSA), benzene sulfonic acid (BSA), methane sulfonic acid (MSA), and dodecylbenzene sulfonic acid (DBSA) were used as an acid catalyst. Hexane, toluene, chloroform and ethanol were used as organic solvents. Sulfuric acid cannot be used for synthesis of PANI in organic solvents as an acid catalyst.

Preparation of the alloys was conducted according to **Fig. 2**. Polystyrene (PS), hydroxypropyl cellulose (HPC) and poly(methyl methacrylate) (PMMA) resin were combined with PANI. Polymerization of aniline with a small amount of iodine was performed in the plastic polymer solutions in chloroform for obtaining polymer alloys.

Molecular structure was evaluated with infrared (IR) spectroscopy measurements. PANI synthesized in organic solvents had both benzenoid and quinonoid structures. The IR signals from PANI were no detected for the alloys due to overlap of intense IR absorption signals from the plastics components.

Synchrotron XRD measurements were conducted to investigate crystal structure of the PANI and conductive alloys thus obtained. PANI synthesized with CSA and dodecyl benzene sulfonic acid (DBSA) was named $PANI_{CSA}$ and $PANI_{DBSA}$, respectively. Both $PANI_{CSA}$ and $PANI_{DBSA}$ showed 4 signals. PANI synthesized general method also showed the diffraction signals.

The electrical conductivity measurements of the alloys were carried out. The conductivity comes from the PANI component in the alloys. Electrical conductivity measurements with the 4-probe method revealed that PS/PANI, PMMA/PANI and HPC/PANI were 5.3×10^{-2}, 1.5×10^{-5} and $< 10^{-9}$ S/cm, respectively. PS/PANI and PMMA/PANI showed moderate conductivity.

Addition of a trace amount of iodine in the polymerization reaction, PANI was successfully synthesized in organic solvents. This is a first example of production of PANI in organic solvents with an aid of iodine. This method allows us to produce conductivepolymer/nonconductive polymer alloys in synthesis of PANI, which greatly expanded the possibilities of conductive polymers for progress in plastic electronics.

REFERENCE

[1] H, Goto, K. Komaba, T. Yonehara, R. Miyashita and R. Kumai, *Polym-Plast. Tech. Mat.* **61**, 1593 (2022).

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K. Komaba[1], R. Miyashita[1], T. Yonehara[1], R. Kumai[2] and H. Goto[1] ([1]Univ. of Tsukuba, [2]KEK-IMSS)