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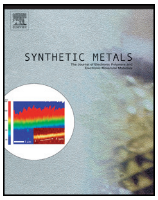

Synthesis of diphenylamine-*co*-aniline copolymers in emulsified systems using a reactive surfactant as the emulsifying agent and aniline monomer

Erasto Armando Zaragoza-Contreras[a,b,*], Claudia A. Hernández-Escobar[b], Anayansi Estrada-Monje[c], Takaomi Kobayashi[a]

[a] *Nagaoka University of Technology, Department of Materials Science, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan*
[b] *Centro de Investigación en Materiales Avanzados, S.C., Engineering and Materials Chemistry Department, Miguel de Cervantes No. 120, Chihuahua, Chih., Mexico*
[c] *Centro de Innovación Aplicada en Tecnologías Competitivas, Omega No. 201, Fraccionamiento Industrial Delta, León, Gto., Mexico*

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ABSTRACT

Poly(diphenylamine) (PDPA) and diphenylamine-*co*-aniline (DPA/aniline) copolymers were synthesized vía oxidative polymerization in oil in water (o/w) emulsified systems. To obtain emulsified systems, firstly, diphenylamine (DPA) was brought into liquid form by heating above its melting temperature and subsequently, emulsified by applying ultrasound. For DPA homopolymer synthesis, sodium dodecyl sulfate (SDS) was used as the emulsifying agent; however, for the synthesis of DPA/aniline copolymers anilinium dodecyl sulfate (P1), an amphiphile that has the property to perform the functions of surfactant and monomer of polyaniline (PAni) simultaneously, was used. Electron microscopy characterization showed that the products of copolymerization were spherical particles, as expected, considering the characteristics of the emulsified systems (micro-droplets of oil dispersed in an aqueous medium). The characterization by infrared spectroscopy (FTIR), UV–vis and X-ray diffraction (XRD) indicated that the copolymers more strongly preserve the characteristics of the PDPA. In addition, cyclic voltammetry (CV) indicated electro-activity in the products. The comparison between the copolymers and a physical mixture PAni/PDPA (1.0:1.0, w/w), characterized by FTIR and CV reported clear differences, which allowed us to conclude that the products are copolymers and not blends.

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1. Introduction

Polyaniline (PAni) and aniline based copolymers have been studied for many years; however, currently they remain the focus of intense study worldwide. PAni electro-physical properties make it extremely attractive for a number of applications in various technological fields like corrosion control [1–3], energy storage [4–8], microelectronics [9,10] or sensors [11–13]. Copolymers of aniline with other monomers of the aniline family; for example, *o*-anisidine [14],*o*-toluidine [15], 3-aminobenzoic acid [16], 2,5-dimethoxyaniline [17] or *p*-aminophenol [18] have been studied to modify some of the limiting characteristics of PAni, one of them, the poor solubility in solvents commonly used. These monomers are aryl-substituted anilines that do not alter the basic backbone of the PAni during copolymerization; however, the polymers obtained from *ortho*, *meta* or *para*-phenylenediamine are also considered as polyanilines with their own identity, as they exhibit similarities, but also significant differences regarding PAni [19–22]. Polydiphenylamine (PDPA) is obtained from the diphenylamine (DPA) monomer (an N-aryl substituted aniline) and is another member of the polyanilines' family to be taken into account because its homopolymer and copolymers also exhibit highly desirable properties. PDPA structure is analogous to that of polyaniline, except that, unlike polyaniline, the PDPA has in its backbone aromatic ring sequences of two instead of one and may exhibit v exhibit various oxidation states as PAni [23]. Due to the structural differences, PDPA and PAni properties (for instance, solubility, processability or electrochromism) are different as already pointed in literature [24–26]. Fig. S1 (see Supplementary

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* Corresponding author at: Nagaoka University of Technology, Department of Materials Science, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan.
E-mail address: armando.zaragoza@cimav.edu.mx (E.A. Zaragoza-Contreras).

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material) illustrates fragments of PAni, polyphenylenediamine and PDPA; the similarities in the arrangements are easy to see as well as the differences among them.

The synthesis of PDPA and diphenylamine (DPA) based copolymers has been performed through various routes (for instance, interfacial, organic solution or self-assembled systems) and by the electrochemical and oxidative mechanisms. Each route and each mechanism allow to obtain PDPA with particular properties; for instance, Athawale et al. [27] synthesized PDPA in organic solution via electrochemical pathway; they found that the polymer morphology and electroactivity were highly influenced by the concentration of the monomer during polymerization. Showkat et al. [28] synthesized PDPA within the porous structure of MCM-41; they induced DPA self-assembly, within the pores, by forming its salt with the addition of naphthalene sulfonic acid. With the addition of ammonium persulfate (oxidizing agent) tubular PDPA was obtained, which showed different properties regarding PDPA obtained conventionally. Orlok et al. [29,30] reported DPA oxidative polymerization in solution and interface. The products obtained in a homogeneous medium presented molar masses in the order of 10^3 g mol^{-1}, largely due to oxidative hydrolysis; however, polymers in the order of 10^4 g mol^{-1} were produced in toluene/water interfacial systems. They also found that the PDPA propagates through the formation of C—C bonds instead of C—N as for aniline. Massoumi et al. [31] synthesized DPA-aniline copolymers via oxidative polymerization in water/chloroform interfacial system. They found that the electrical conductivity depends on the content of aniline and dopant and that the morphology was dependent on acid strength. Permpool et al. [32] synthesized PDPA via oxidative polymerization in micellar systems provided by surfactants of various types in an aqueous phase. The micellar structures were used as templates. They found that the morphology of the polymer depended on the surfactant and the electrical conductivity depended on the concentration of the surfactant, which indicated that surfactants played the function of dopants. Santosh et al. [33] reported the electrochemical copolymerization between DPA and *o*-toluidine in sulfuric acid solution. By using cyclic voltammetry techniques and UV–vis absorption determined the formation of polymerization intermediate species; additionally, they determined the reactivities of the monomers and attributed to that difference the variations in the UV–vis absorption and electrochemical characterístics. Rajendran et al. [34] synthesized and compared aniline-DPA copolymers obtained via electrochemical pathway using a pulse potentiostatic method and via chemical using potassium persulfate as the oxidizing agent (both procedures in sulfuric acid solution). They developed an equation for copolymer growth based on the dependence of charge on variations in the experimental parameters employed during deposition of the films. The characterizations by UV–vis spectroscopy and cyclic voltammetry showed a great similarity between the PDPA and copolymers and further, that the synthesis route did not cause significant differences in the copolymers produced.

As seen, the strategy for the synthesis of PDPA has been widely varied. Each system has shown a great impact on the structure and electrical properties. The present study focused on the synthesis of diphenylamine-*co*-aniline (DPA/aniline) copolymers by oxidative polymerization using ammonium persulfate as the oxidizing agent. The synthesis of the copolymers was conducted in oil in water (o/w) systems emulsified by sonication at 60 °C. Anilinium dodecyl sulfate (P1) that performs the function of an emulsifying agent and a monomer precursor of polyaniline, was used to stabilize the emulsions. Structure, morphology, and electroactivity were characterized. It is worth mentioning that a study using DPA as the monomer in emulsified systems, meaning an emulsion as a dispersed system consisting of two immiscible or partially miscible "*liquids*", where one is the dispersed phase and the other the continuous phase, had not been published until now. In addition, it is worth mentioning that the use of P1 as a surfactant and as a polyaniline monomer for the synthesis of PAni based composites has already been reported by our group [35–37]. However, its use as an emulsifying agent and co-monomer for the synthesis of copolymers is reported here for the first time.

2. Experimental

2.1. Reagents

Diphenylamine (TCI Co., Ltd.) recrystallized from ethanol, ammonium persulfate (Nacalai Tesque) recrystallized from water, anilinium dodecyl sulfate (P1) synthesized as reported previously [35], sodium dodecyl sulfate (Nacalai Tesque), hydrochloric acid (WAKO), sodium hydroxide (Nacalai Tesque). Reagents were used as received unless other thing is indicated.

2.2. Synthesis of PDPA, PAni and copolymers

In this research, PDPA and DPA/aniline copolymers were synthesized in emulsified systems using the reactive surfactant called P1 as the emulsifying agent. For DPA homopolymerization, sodium dodecyl sulfate (SDS) was used as the emulsifying agent at a molar ratio 1.0:0.5 (DPA:SDS). A typical experiment was conducted as follows: a three-neck round-bottomed glass flask of 100 mL was used as the reactor. First, 40 mL of deionized water and the predetermined amounts of DPA were loaded into the reactor. Next, the reactor was warm to 60 °C to melt the DPA. Subsequently, the reactor was introduced to an ultrasonic bath preheated to 60 °C and P1 was loaded. To obtain the emulsion, the system was sonicated for 20 min, after which a white dispersion, aspect typical of an emulsion, was obtained. Then, the reactor was passed to a heating bath set at 60 °C; cooling and mechanical agitation systems (200 RPM) were adapted to the reactor. To launch polymerization 10 mL of ammonium persulfate (APS) acid solution (0.25 M HCl) was added in a 1.0:1.0 molar ratio relative to the total amount of monomer. The APS solution was added in a single shot. A few seconds after the addition of the APS the system acquired a light green hue, which became more pronounced throughout the polymerization. All polymerizations were left for 3 h. On the other hand, PAni was obtained in an aqueous micellar solution at 40 °C, as it is not possible to obtain an emulsion with P1, as a salt, when heated to 40 °C P1 is soluble in water. In the PAni synthesis, APS was also used as an oxidizing agent in a molar ratio of 1.0:1.0 regarding P1. At the end of the polymerizations, all products showed a green color. In all cases, after polymerization time, ethanol was poured to stop the polymerization. Subsequently, the products were purified by centrifugation, 4 times at 5000 RPM for 20 min, adding water/ethanol (80/20, v/v) mixture every time. All compositions are included in Table 1.

Table 1
Experimental composition for the synthesis of the copolymers, PAni, and PDPA.

Molar ratio (DPA:P1)	DPA ($\times10^{-3}$ mol)	P1 ($\times10^{-3}$ mol)	APS ($\times10^{-3}$ mol)
1.0:0.2	1.480	0.295	1.775
1.0:0.5	1.480	0.738	2.218
1.0:0.75	1.480	1.100	2.580
1.0:1.0	1.480	1.480	2.960
PAni[a]	–	1.48	1.48
PDPA[b]	1.48	–	1.48

[a] Polymerization at 40 °C in aqueous micellar system.

[b] Polymerization in emulsified system using sodium dodecyl sulfate as the emulsifying agent.

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