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Effect of metal phthalocyanines on the synthesis and physicochemical properties of polyaniline

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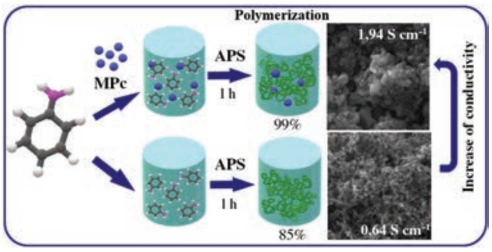
The polymerization of aniline in the presence of metal phthalocyanines was accomplished and the effect of the metal complexes on the physicochemical properties of polyaniline was examined based on UV-visible spectra, cyclic voltammograms, morphology and conductivity of the polymers. The formation of polyaniline in the presence of metal phthalocyanines led to an increase in polymer particle sizes and to a slightly higher conductivity of the samples, as compared to those of the initial polyaniline.



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Polyaniline is the most thoroughly studied electrically conductive polymer.[1] Interest in polyaniline arises from its unique properties, such as electrical conductivity, chemical and thermal stability, non-toxicity and availability.[1] A promising method for the production of polyaniline is its synthesis in the presence of organic metal complexes (in particular, a monoethanolamine cobalt complex, copper bisglycinate, photoadducts of potassium hexacyanoferrate(II) or poly-ligated cobalt(II) urea complex), metal oxides, carbon nanotubes, *etc*.[2–7]

Organic transition metal complexes are often used in the oxidative polymerization of aromatic compounds.[8,9] Metal phthalocyanines (MPc) are the most common and effective oxidation catalysts.[10] Since the discovery of phthalocyanines,[11] these compounds have been used in catalysis,[10] solar cells,[12] nonlinear optics,[13] photodynamic therapy[14] and molecular imaging.[15] Phthalocyanines and their derivatives have high chemical and thermal stability[16] and special optical and electrical properties.

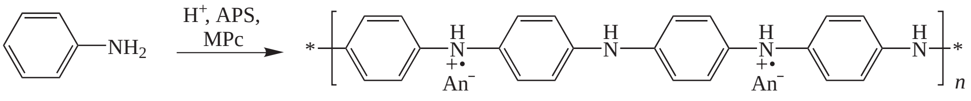
In this work, we developed an efficient method of the oxidative polymerization of aniline in the presence of transition metal phthalocyanines as catalysts. The oxidative polymerization was carried out in a hydrochloric acid solution and in the presence of ammonium peroxodisulfate (APS) (Scheme 1).[17–19] The catalysts (Table 1) were varied to determine the highest yield of polymer.

Note that the catalytic activity of metal complexes in the oxidative polymerization of aniline is observed only under heterogeneous catalysis conditions. The polymerization was carried out with Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Fe^{2+} phthalocyanines (Table 1) in order to study the effect of the metal on the yield of polymer. The highest product yields were obtained with cobalt and zinc phthalocyanines.

Table 1 Polymer yields depending on the catalyst ([MPc] = 0.01 g dm^{-3}; reaction time, 1 h).

Polymer sample	Catalyst	Yield (%)
1	-	81.0
2	CoPc	96.9
3	MnPc	90.1
4	ZnPc	96.4
5	NiPc	88.7
6	FePc	86.9

The catalytic effect of MPc was estimated by monitoring changes in the temperature and open-circuit potential (OCP) during aniline polymerization (Figure 1). The time dependence of reaction parameters is typical of aniline polymerization in an acidic medium.[19,20] A slight change in temperature in the initial period is associated with an induction period.[20] This period is significantly reduced upon the addition of a catalyst, as compared to the uncatalyzed process [Figure 1(*a*)]. After a slow initiation stage, a period of rapid chain growth begins. This stage is accompanied by a sharp increase in temperature and the solution turns blue. The color corresponds to the formation of a protonated pernigraniline form of polyaniline, which is an intermediate in this process.[19]



Scheme 1

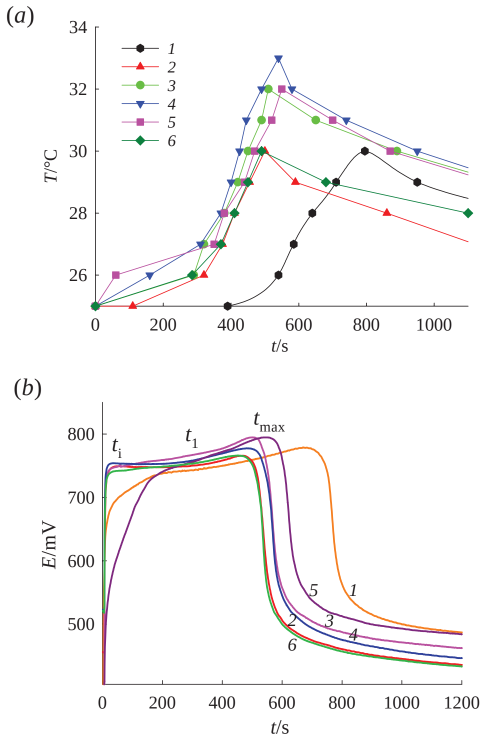


Figure 1 (*a*) Temperature and (*b*) OCP profiles in the oxidation of 0.1 M aniline with 0.125 M APS in a 0.2 M HCl solution using MPc (*1*)–(*6*) 1–6, respectively (0.01 g dm^{-3}).

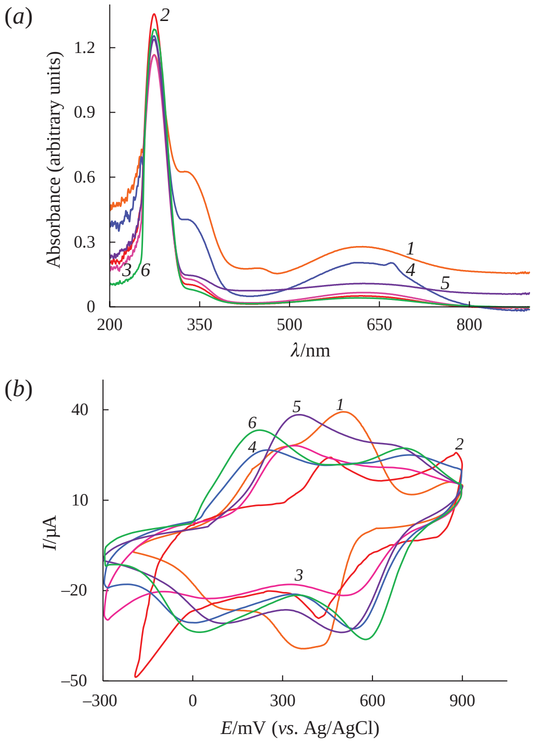


Figure 2 (*a*) UV-VIS spectra of polymers (*1*)–(*6*) 1–6 (10^{-2} g dm^{-3}) in DMSO and (*b*) cyclic voltammograms of polymers (*1*)–(*6*) 1–6, respectively, in 1 M H_2SO_4 at a scan rate of 100 mV s^{-1}.

A comparison of the temperature dependences of aniline polymerization in the presence of MPc did not reveal significant differences. The catalysts equally accelerated the process, however the reaction temperature slightly increased with samples 3, 4, and 6, probably, due to the metal in MPc. Several consecutive stages can be distinguished in the OCP–time profiles of aniline polymerization: an induction period (t_i); appearance of an insoluble pernigraniline phase (t_1), acceleration of the reaction and complete consumption of APS (t_{max}); and formation of emeraldine salt by reduction of pernigraniline (after t_{max}).[21] A catalyst reduces the time required to reach t_{max}, which indicates that the formation of pernigraniline and APS consumption are accelerated [Figure 1(*b*)]. All the catalysts show the same effect on the OCP profile, except for NiPc. In this case, t_{max} is shorter than that with the other catalysts. The OCP– and temperature–time profiles (see Figure 1) reveal that MPc catalyze the process to shorten the induction period.

Figure 2 shows the electronic spectra of the test samples in DMSO. Polyaniline sample 1 in the UV-visible region is characterized by absorption maxima at 300, 350 and 620 nm.[22] The maximum observed at 330–350 nm corresponds to the π–π* electron transition between adjacent aromatic rings in the conjugated polymer system. At 450 nm, a polaron peak characteristic of the emeraldine polyaniline salt is observed. The absorption maximum at 603 nm corresponds to the n–π* electron transition between the nonbonding isolated electron pair of a nitrogen bonded to a benzenoid ring and the π* of the quinonoid ring. The spectra of samples 2–6 exhibit a decrease in the maximum in the visible spectral region [Figure 2(*a*), curves *2, 4, 6*] caused by the catalysts used, which affect the electronic structure of the polymer. The differences in the UV spectra are due to the presence of the metal complex catalysts in the materials.

The electrochemical properties of samples 1–6 were studied using cyclic voltammetry (CV) [Figure 2(*b*)]. Sample 1 exhibited two pairs of redox peaks at 0.29 and 0.62 V on scanning at a rate of 100 mV s^{-1} in a potential range from –0.3 to 1.0 V.[23] Sample 2 exhibited a redox pair at 0.46 V, which is shifted relative to that of sample 1. This is due to the fact that CoPc has its own redox activity associated with a transition from Co^{II} to Co^{III}.[24] Samples 3–6, similarly to sample 1, had two redox pairs. The shift of maxima is associated with the presence of a small catalyst amount in the polymer, which is consistent with the evidence for other metal phthalocyanine containing conductive materials.[25] A shift in the oxidation potential and a change in the profile of the CV curves confirm that the catalysts are incorporated in the polymer structure.

It is well known that the polymerization of aniline occurs on the surface rather than in the bulk.[26] Hence, monomer adsorption on the surface is of paramount importance in heterogeneous catalysis. The subsequent growth of a polymer chain occurs at the polymerization center with the catalyst as a base. The SEM images show that the catalyst has an insignificant effect on the formation of the polymer supramolecular structure (Figure 3). The test samples have the same globular morphology as sample 1. The metal in the phthalocyanine structure did not significantly affect the supramolecular structure and particle size of the polymers. The globular morphology of the samples is clearly

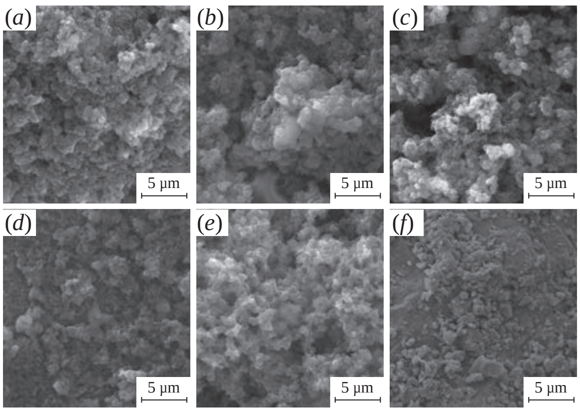


Figure 3 SEM images of polymer samples (*a*) 2, (*b*) 4, (*c*) 5, (*d*) 6, (*e*) 1, and (*f*) CoPc.

Table 2 Electrical conductivity of polymer samples.

Polymer sample	σ/S cm^{-1}	Polymer sample	σ/S cm^{-1}
1	0.64	4	0.69
2	1.04	5	1.41
3	1.94	6	0.33

visible, which is characteristic of the entire range of polymers.[27] The average particle size was 281.5 nm for polyaniline synthesized without catalysts. Samples obtained in the presence of MPc had an average size of >350 nm due to the use of metal complexes in the polymerization.[19]

Table 2 summarizes the electrical conductivity of the test compounds. A significant factor affecting the electrical conductivity of polyaniline is its morphology.[26,27] The electrical conductivity of samples 2, 3 and 5 is slightly higher than that of sample 1 due to their larger particle sizes because the diffusion of electrons occurs inside polymer agglomerates rather than between polymer particles. Cobalt, manganese and nickel phthalocyanines led to a slight increase in electrical conductivity.

Thus, we developed an efficient method for the synthesis of polyaniline in the presence of metal phthalocyanines as catalysts. The use of cobalt and zinc phthalocyanines in the aniline polymerization enabled us to achieve the highest yield per 1 h, as compared to other catalysts. The catalytic effect of metal phthalocyanines was confirmed by changes in the temperature and open-circuit potential during the polymerization. The UV-visible spectra and cyclic voltammograms of catalytically synthesized polymers showed that they are similar to classical polyaniline and changes in the spectra indicated a slight effect of the metal complexes on electronic transitions within the polymer chain. The electrical conductivity (0.64–1.94 S cm^{-1}) and morphology of the polymers were determined. Thus, the use of transition metal phthalocyanines in the oxidative polymerization of aniline leads to an increase in electrical conductivity and average particle size in the fibrillar structure of polymers.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.09.024.

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