Terpolymers As Precursors for CuO Nanoparticles Synthesis

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ABSTRACT: This work describes the synthesis of terpolymers of aniline, diphenylamine, and o-anthranilic acid (PANIDPAA) by 1 : 1 : 1 molar ratio of the respective monomers doped by different concentration of copper ions via *in situ* chemical terpolymerization. The results are justified by measuring spectral characteristics namely, UV-vis absorption spectra, FTIR, and TGA. Calcining these PANIDPAA terpolymers doped by copper at temperatures in the range of 700°C led to the formation of CuO nanoparticles in the nanoscale by thermal decomposition in air directly. The stages of decompositions and the calcination temperature of the precursors have been determined from thermal analysis data sheet. The obtained CuO nanoparticles have been characterized by X-ray diffraction and transmission electron microscope (TEM). TEM showed a particle size less than 40 nm. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41150.

INTRODUCTION

Polymers that exhibit high electrical conductivity have now been successfully synthesized and the past two decades have witnessed unabated interest in the synthesis and characterization of such conducting polymers, due to the potential technological applications of these materials.[1–3] In 1977, Heeger, MacDiarmid, and Shirakawa reported that conductivity of polyacetylene increased remarkably by doping with iodine.[4–6] The doping process enhances the conductivity of PANI by almost 8 orders of magnitude. The dopants range from inorganic acids to organic acids.[7] Self-doped PANI with substituents such as carboxylic,[8] sulfonic,[9] and phosphonic acid[10] groups and the copolymers of these substituted anilines with aniline have also been synthesized and characterized.[11,12]

Recently, a wide variety of p-conjugated polymers have been synthesized, and their physical and chemical properties have been investigated by many researchers.[13–16] These materials are prepared by polymerization of simple monomers that are able to form a network of highly delocalized electrons. Moreover, conjugated organic polymers have gained increasing interest in recent years as electrically conducting polymers [e.g., poly (p-phenylene), polypyrrole, polythiophene, and others.[17–20]]

Earlier, we investigated the binary copolymers of aniline and o-anthranilic acid with pyrogenic silica nanocomposites.[21] In contrast, studies on terpolymerization involving three aniline monomers are very scanty. It should be interesting to find out how the copolymerization of two aniline monomers is influenced by the introduction of a third aniline derivative. Li et al.[22] synthesized terpolymers of aniline, toluidine, and 2,3-xylidine, which were amorphous in the base (undoped) form and showed good solubility and high thermal stability. They also investigated terpolymers of pyridylamine, aniline, and xylidine as well as those of m-phenylenediamine, o-anisidine, and 2,3-xylidine, which were also reported to exhibit good solubility and higher thermal stability.[23,24] However, the conductivity of these terpolymers has not been investigated. Highly conductive soluble terpolymers of aniline with aniline derivatives having an electron-donating group as well as a self-doping group have been reported.[25] This was the first report, to the best of our knowledge, on terpolymers containing electron-donating and electron-accepting/self-doping units.

Different techniques were used to prepare copper oxide thin films such as activated reactive evaporation, thermal oxidation, spray pyrolysis,[26] chemical deposition,[27] sol-gel,[28] and electro-deposition.[29,30] Abdel Rafea et al.[31] have prepared CuO nanoparticles with average particle size 14–21 nm using SILAR technique. Xue and coworkers[32] have synthesized CuO with average particle size 26 nm by precipitation of $Cu(OH)_2$ from $Cu(NO_3)_2.6H_2O$ and annealing the hydroxide at 800°C. Hosny and Zoromba[33] have prepared CuO nanoparticles with particle size 8–20 nm from copper polymethacrylic acid precursors and annealing of the precursor was at 500°C. In this work, we prepared CuO nanoparticles with particle size less than 40 nm from doped copper poly(DPA : AA : AN) precursor.

A simple and environmentally benign solid state decomposition method was used. There are many advantages in this method

like, use of new precursor, relatively mild annealing temperature, saving time, energy, and free from volatile organic solvent. According to the reported results, some of the annealing temperatures were 500°C[33] and 800°C.[32] Other calcining temperatures were in the range of 900–1100°C.[34] In comparison with the literature work, the polymer under investigation was carried out under relatively mild annealing temperature 700°C.

In this article, we present a route for the synthesis and characterization of some new PANIDPAA terpolymers containing aniline, diphenylamine, and anthranilic acid moieties doped by different concentration of copper ions in the polymer main chain. The first major target of this work was to study the effect of copper moiety upon the properties of polyconjugated polymers, including their thermal stability and morphology. The second major target was to utilize PANIDPAA terpolymers as precursors for CuO nanoparticles synthesis by calcining of these PANIDPAA terpolymers doped by copper at temperatures in the range of 700°C.

EXPERIMENTAL

All the terpolymers were synthesized with equimolar quantities of the monomers. The names of the terpolymers are abbreviated on the basis of the monomers used. Thus, the terpolymer synthesized with the monomers aniline (ANI), diphenylamine (DPA), and o-anthranilic acid (AA) is denoted PANIDPAA.

Materials

The chemicals used were aniline, anthranilic acid, and diphenylamine (Aldrich), potassium dichromate (Merck), ammonia solution, hydrochloric acid (ADWIC), and Cu(II) acetate. All chemicals were used as received without any further purification.

Synthesis of Terpoly(aniline, diphenyl amine, and o-anthranilic acid)/Cu Composites.

The terpoly(aniline, diphenyl amine, and anthranilic acid)/copper composite was synthesized by an *in situ* chemical oxidative polymerization of aniline and anthranilic acid in presence of different percentages of copper ions. At first, aniline, o-anthranilic acid, and diphenyl amine monomers (1 : 1 : 1 in molar ratio) 1.69 g, 10 mmol DPA were dissolved in 20 mL ethanol under magnetic stirrer at room temperature. It was followed by addition of 1.37 g, 10 mmol AA, and 0.91 mL, 10 mmol of aniline into the reactor. The three monomers were left under magnetic stirrer at rpm 950 for 10 min. Then, 10 mL conc HCl (32%) were added into monomers mixture under above conditions. After that, the calculated amounts of Cu(II) acetate, 0.0, 0.1243, 0.2487, 0.4975, 0.995, 1.99, and 3.98 g to give the percentage of the copper in the composites as follows, (0.0% Cu, 5% Cu, 10% Cu, 20% Cu, 30% Cu, 40% Cu, and 50% Cu) were dispersed in 10–40 mL distilled water, respectively, under magnetic stirrer for 20 min at 600 rpm. Then, the obtained dispersed system was gradually added to the monomers solution with stirring at room temperature. At the same time, the slow addition of potassium dichromate (initiator) which was separately dissolved in distilled water 70 mL $K_2Cr_2O_7$ (8.8 g in 250 mL/distilled water) into the reactor. After the complete addition of the dichromate, the reactor was left under the stirrer for 2 h. Ammonia solution (30 mL of 33 % NH_4OH diluted by 30 mL distilled water) was added drop wisely during 20 min to the reactor mixture. The emeraldine base precipitates were filtrated using a Büchner funnel. The collected precipitates were washed several times with distilled water then washed by ethanol to remove monomer, oligomer, and excess oxidant until the filtrate became almost colorless and oven dried at 90°C for 24 h. The dried powder afforded terpoly(aniline, diphenyl amine, and o-anthranilic acid) emeraldine base (**T**) and terpoly(aniline, diphenyl amine and o-anthranilic acid) emeraldine base copper composites (**TCu-1**, **TCu-2**, **TCu-3**, **TCu-4**, **TCu-5** and **TCu-6**), respectively.

The terpolymer yield was calculated using the following relationship:

$$\text{Terpolymer yield} = \frac{100 \times \text{Amount of terpolymer (g)produced}}{\text{Amount of aniline, diphenyl amine, and anthranilic acid (g)charged}}$$

The terpolymer yields were 90.2%, 94.5%, 98.4%, 92.0%, 96.9%, 91.7%, and 95.8%, respectively.

Synthesis of CuO Nanoparticles.

The as-prepared terpolymer (diphenylamine : anthranilic acid : aniline)-Cu (1 : 1 : 1 : 2) (**TCu-6**) precursors was ignited in a muffle Furnace at 700°C. The heating rate was 15°C/min in air for 2 h after reaching to 700°C. PANIDPAA-Cu precursor 1.5 g was calcined under above conditions and it gave 0.4431 g of CuO nanoparticles. The calcination temperatures were >600°C because, in this temperature region, all organic materials are decomposed and the phases show high crystallinity, which avoids interference on mass-transport processes.[35]

$$\text{CuO Nanoparticles yield} = \frac{100 \times \text{Amount of CuO nanoparticles (g)produced}}{\text{Amount of terpolymer (g)charged}} = \frac{100 \times 0.4431\,\text{g}}{1.5\,\text{g}} = 29.54\%$$

Characterization

The FTIR spectra of different powder were recorded using FTIR Spectrometer (Spectrum RX 1). The samples were prepared in the pellet form by mixing the Powder with KBr by the ratio 1 : 10 and pressing it in the Perkin Elmer hydraulic device using 15 tons pressure. UV-Vis spectra were recorded in dimethyl formamide (DMF) in the range 200–800 nm. All the UV-vis measurements were performed using a Shimadzu PC3101
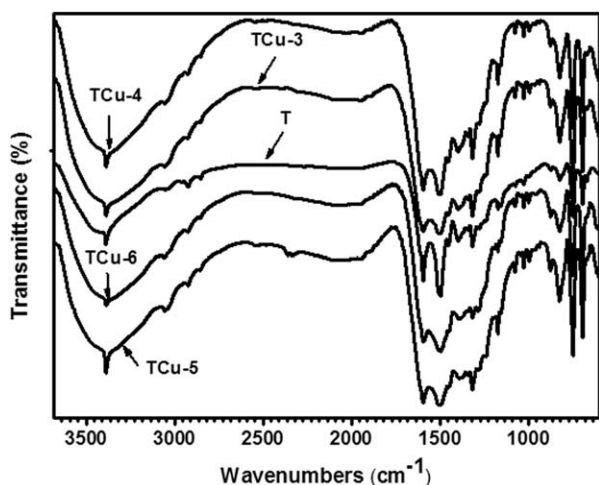
Figure 1. FTIR spectra of PANIDPAA and PANIDPAA-Cu (**T-TCu-6**).

spectrophotometer, under computer control. The thermal characteristic was studied by thermogravimetric analysis (TGA; Q50, TA Instruments). Experiment was carried out under N_2 atmosphere from 30°C to 500°C at a heating rate of 20°C/min. X-ray diffraction (XRD) analysis was performed using Philips diffractometer system (model X" Pert Pro) equipped with Cu target. A filtered CuKα radiation (k 1:5408 Å) was used. The X-ray tube voltage and current were 40 KV and 30 mA, respectively. The speed of the detector was 1 per min.The morphological study was carried out by transmission electron microscopy (TEM) technique using TEM Model: JEM-1230, Made in Japan (JEOL)energy 120 KV on steps, Line Resolution: 0.2 nm, Max. Magn.: 600 Kx.

RESULTS AND DISCUSSION

FTIR Spectral Studies

The FTIR spectra of the terpolymers PANID\PAA-Cu composites (**T-TCu-6**) are shown in Figure 1. The spectra of either PANIDPAA EB or PANIDPAA-Cu composites (**T-TCu-6**) have two major absorptions at 1593–1594 cm^{-1} and 1495–1505 cm^{-1} due to the C=C vibrations of benzenoid and quinoid units, respectively.[7] The number of quinoid units was almost higher than the number of benzenoid units in PANID-PAA and composites PANIDPAA-Cu emeraldine base composites (**T-TCu-6**) as there was apparent difference in the relative intensity of quinoid to benzenoid band which is a measure of the degree of the oxidation of the polymer chain.[35] The two bands appeared at 1317–1318 cm^{-1} and 1277–1284 cm^{-1} are due to C—N stretching vibrations of benzenoid-quinoid-benzenoid sequence.[35] The strong band at 1173–1174 cm^{-1} is the characteristic band of the charged defects.[36,37] The strong broad peak at 3387–3388 cm^{-1} may be due to the stretching vibration of N—H of secondary amines or O—H bond as was reported.[38] The occurrence of the band at 823–824 cm^{-1} in all the terpolymers indicates that the monomers were bonded head to tail.[39]

The appearance of additional bands around 669–670 cm^{-1} being in agreement with the reported band for polyanthranilic

acid metal nanocomposites around 675 cm^{-1}.[40] Literature shows that the anthranilic acid absorption is at 746 cm^{-1} in the structure of the rhodium/anthranilic acid complex.[41] For the terpolymer under investigation, the anthranilic acid 749 cm^{-1} band is clearly visible. In our previously published work, the C=O absorption band is at 1670–1676 cm^{-1} in the structure of aniline and o-anthranilic acid copolymer.[21] However, for the copolymer under investigation, the C=O stretching vibration band of the carboxyl group has almost disappeared. No clear statement concerning the absence of this vibration can be made. Another case of the absence of this vibration has been reported.[40]

UV-Vis Absorption Spectra Measurements

The UV-visible absorption spectra were recorded for terpolymers PANIDPAA EB and PANIDPAA-Cu composites (T-TCu-6) using solutions of the terpolymers in DMF [Figure 2(a,b)]. It could be seen that, the terpolymers showed the first major absorption band at about 375–392 nm, which is attributed to π→π* transition at higher energy side. Therefore, it is a measure of the extent of conjugation between the adjacent phenyl rings and benzenoid to quinoid exciton transitions at lower energy side.[42,43] The second major absorption broad band appeared at about 585 nm, which is attributed to polaronic excitation of benzenoid to quinonoid ring.
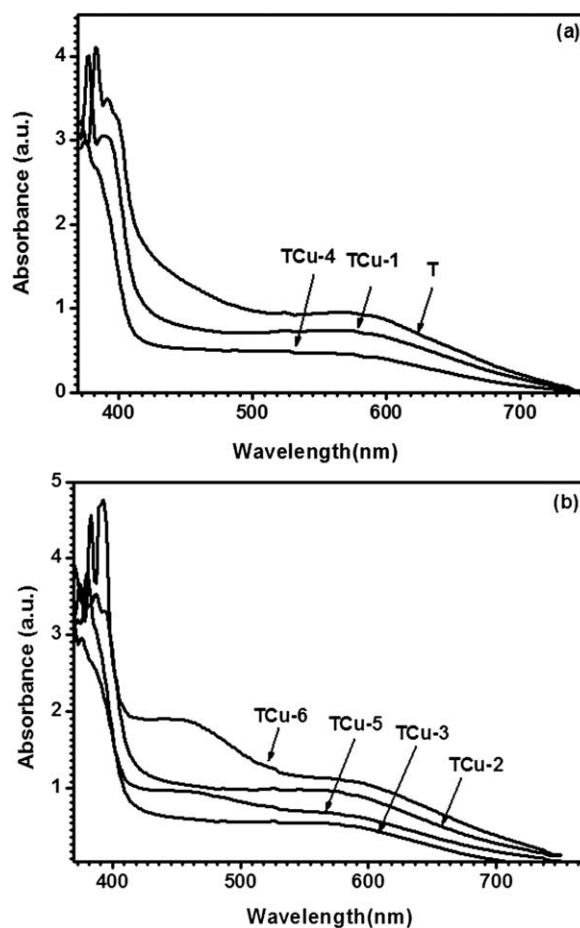

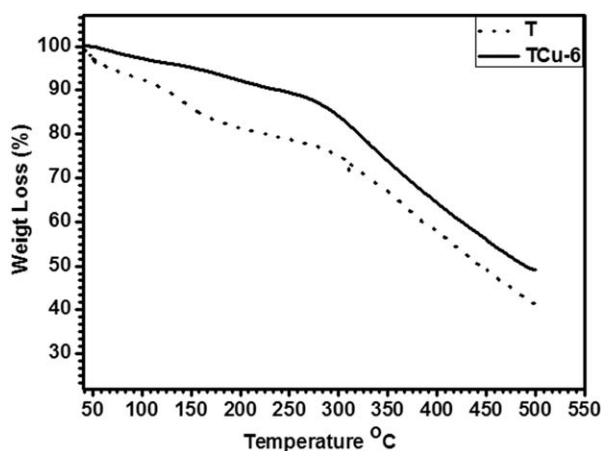**Figure 2.** UV-VIS spectra of PANIDPAA and PANIDPAA-Cu (T-TCu-6) in DMF.

Figure 3. TGA curves of curves of **T** (PANIDPAA EB) and **TCu-6** (PAN-IDPAA EB-Cu) composite; under nitrogen flow (at a heating rate of 20°C min^{-1}).

TGA

Thermal studies of terpolymers PANIDPAA EB and PANIDPAA EB-Cu composites (**T** and **TCu-6**) had been analyzed and compared with that of pure polymer under non-oxidative (inert gases) conditions. The weight loss patterns are shown in Figure 3 and the thermal degradation data of PANIDPAA EB and PANIDPAA EB-Cu composites are listed in Table I. The thermograms of the polymer samples taken between the room temperature and 500°C were measured (Figure 3). In case of absence of copper particles, the first weight loss (~9.491%) at ~120°C of PANIDPAA EB (**T**), is attributed to the loss of water molecules. The second stage within the temperature range of 120–300°C is related to removal of CO_2 molecules from the PANIDPAA EB terpolymer. Similar results were reported.[44] However, in case of presence of copper particles in **TCu-6**, it is obvious that the weight loss due to the loss of water molecules (~6.17%) respectively, occurred at ~175°C. The weight loss observed in **T** and **TCu-6** between 300 and 500°C corresponds to the thermo-oxidative degradation of the polymer chain. Similar results were reported.[45] The present results suggest that the use of PANIDPAA EB-Cu (**TCu-6**) offers some advantages in terms of thermal stability over PANIDPAA EB (**T**) at temperature > 300°C, under this experimental concentration and conditions.

Table I. Thermal Degradation Data of the PANIDPAA EB and PANIDPAA EB-Cu Composites (**T** and **TCu-6**), Based on the TGA Results Under Nitrogen Flow

Polymer code	T_{15}[a]	T_{50}[b]	W_{500}[c]	Char yield at 500°C[d]
T	157	413	59	41
TCu-6	295	490	51	49

[a] T_{15}: Temperature of 15% weight loss.
[b] T_{50}: Temperature of 50% weight loss.
[c] W_{500}: Weight loss at 500°C, determined from TGA curve.
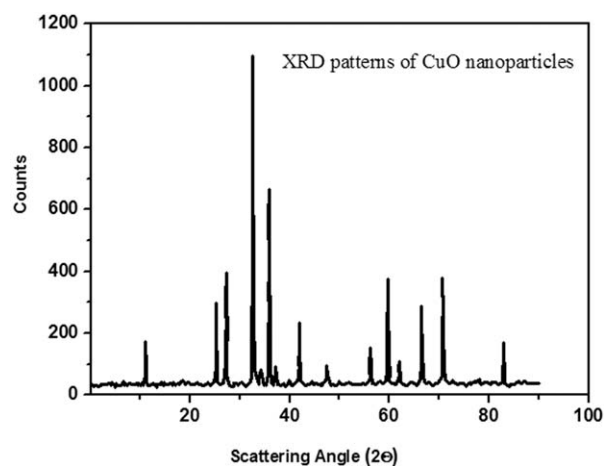[d] The remaining of the terpolymer at 500°C.

Figure 4. XRD patterns of CuO obtained by the thermal treatment of the precursor **TCu-6** at 700°C.

When the temperature was increased to 500°C, both of the samples **T** and **TCu-6** were not fully degraded and still residual or remnant, where the PANIDPAA EB-Cu composite (**TCu-6**) possessed ~49% residual. Therefore, the mass content of copper in the composite cannot be confirmed at 500°C. This result is not in accordance with that of the mass of used copper during the synthesis of **TCu-6** (~50% Cu). It may be caused by existing aromatic polymer back bone.

The temperature of 15% weight loss of pure PANIDPAA EB (**T**) was 157°C, but that of the PANIDPAA EB-Cu composite (**TCu-6**) was 295°C. This is indicating 138°C improvement with 50 wt % of the copper loadings.

The 50% degradation temperature of bare PANIDPAA EB (**T**) was 413°C, but that of the PANIDPAA EB-Cu composite (**TCu-6**) was 490°C. This is indicating 77°C improvement with 50 wt % of the copper loadings. Char yield is an easy and important measurement which correlates to the ability to sustain combustion.[46] The maximum char yield at 500°C was obtained for **TCu-6** (49%) and the minimum was obtained for **T** (41%) in nitrogen. The TGA data are summarized in Table I.

Results showed that the incorporation of copper composite has better thermal stability than the bare terpolymer PANIDPAA EB with no significant unwanted effect on the thermal degradation.

X-ray Powder Diffraction

The XRD pattern of as prepared CuO nanoparticles is shown in Figure 4. The intensities and positions of peaks are in good agreement with the reported values (JCPDS file No. 05–661). No peaks of impurities are found in XRD pattern. The peaks are sharp due to the nano-size effect. The average crystallite size of CuO nanoparticles is found to be less than 40 nm using TEM.

Morphology Analyses by TEM

The TEM analyses of PANIDPAA-Cu precursors (**TCu-6**) and CuO nanoparticles are shown in Figure 5(a,b). Based on the TEM analyses, the particle size of CuO nanoparticles is lying in the range from 35 to 39 nm. Figure 5(a) TEM of copper doped
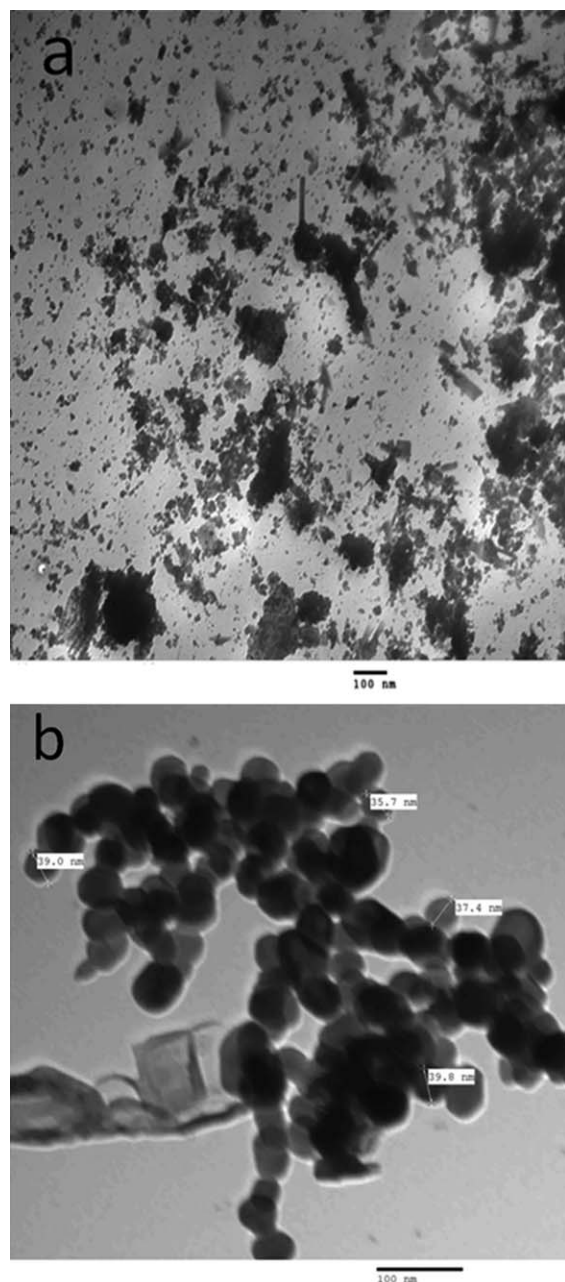
Figure 5. TEM images of a) copper doped poly(DPA : AA : AN) before calcination and b) copper oxide nanoparticles after calcinations process.

poly(DPA : AA : AN) shows amorphous phase for doped polymer while Figure 5(b) shows micrograph for the crystal phase of CuO nanoparticles. The actual size of nano particles is estimated from TEM micrograph. Most of the nanoparticles have the same size less than 40 nm and which is in correlation with the particle size analyzer data. The TEM graph also showed that the copper oxide nanoparticles are spherical in shape and nearly uniform. It could be noted that Pearl-necklace-like aggregation intertwined with the nanowires.

The agglomeration between the copper oxide particles which produced from PANIDPAA-Cu precursors (**TCu-6**) is less than polymethacrylic acid copper (PMAA-Cu) doped by copper

according to the reported results.[33] It might be attributed to the thermal resistance produced from the chemical stability of PANIDPAA-Cu due to its aromatic backbone with copper metal than PMAA backbone with aliphatic backbone.

CONCLUSIONS

A route for the synthesis and characterization of new PANID-PAA terpolymers containing aniline, diphenylamine, and anthranilic acid moieties doped by different concentration of copper ions in the polymer main chain was utilized. The effect of copper moiety on the properties of polyconjugated polymers, including their spectral characteristics namely, UV-vis absorption spectra, FTIR, thermal stability, and morphology was recorded. Moreover, PANIDPAA terpolymers utilized as precursors for CuO nanoparticles synthesis by calcining of these PANIDPAA terpolymers doped by copper at temperatures of 700°C.

Spherical CuO nanoparticles have been successfully prepared by a thermal decomposition method with mean diameter of 35 ± 5 nm. This method does not require organic solvents, expensive raw materials, and complicated equipment. So, it is concluded that the presented method is superior to the other methods for the synthesis of CuO nanoparticles from copper doped terpolymer.

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