

Characterization of Polypyrrole/Azocalix[4]arene Salts: Electrical Properties and Thermal Stability

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ABSTRACT: Polypyrrole (PPy) was doped with the azocalix[4]arene [(5,11,17,23-tetrakis(*p*-carboxyphenyl)azo)25,26,27,28-tetrahydroxycalix[4]arene)] host species. PPy/azocalix[4]arene salts were characterized by FTIR, TGA, SEM, X-ray diffraction, and conductivity measurements. The properties of PPy were investigated in the presence of azocalix[4]arene host species. The conductivity of PPy increased in the presence of azocalix[4]arene. TGA results

indicated that the PPy/azocalix[4]arene salts have higher thermal stability than PPy. It was observed from SEM analysis that the particle diameter of PPy decreased with increasing content of azocalix[4]arene. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2697–2702, 2010

Key words: polypyrrole; azocalix[4]arene; electrical properties

INTRODUCTION

Polypyrrole (PPy) has drawn a lot of interests because of its high thermal and atmospheric stability in addition to its high conductivity.^{1,2} However, its inherently poor solubility in common solvents, which originates from the strong inter and intra-chain interactions, has limited PPy's practical applications in many areas.³ The noticeable advantages of PPys are the highly electrical conductivity and that ionic species can be reversibly trapped in and released from the polymer matrix by the electrochemical control. Electrochemical activities of PPys have been studied in view of the potential application to bio- and molecular- electronics.⁴ PPy is also an attractive conducting polymer for the application of biosensors because of the considerable flexibility in its chemical structure and redox characteristics.⁵

Calixarenes have, in particular, been at the origin of extensive studies for recognition and supramolecular chemistry.⁶ Calixarenes, which are known as cage compounds, recognize and immobilize ions and molecules with high selectivity. Azocalixarenes, which are generated by the insertion of nitrogen atoms into the *p*-position unit of the calixarene structure, have several isomers based on the position of the nitrogen atoms and the ring size.⁷

Recently, the inclusion of cage molecules into electroconducting polymers, ECPs, has opened new perspectives of application for the construction of ionic sensors. It is noted that sulfonated calixarenes can be immobilized in conducting polymers like PPy as dopants during electropolymerization.^{8,9} Dopant ions can be functional compounds as well as single atoms. Grafting of calixarene to PPy^{8,10} and polythiophene¹¹ has already been reported. Interactions between calixarene and polymer can involve several factors such as Van der Waals or dispersion forces, hydrophobic effect, dipolar and acid–base interactions, and electrostatic interactions.¹² Doping effect can be due to the conformational changes of polymeric chains and significant increase in the conductivity and processability.¹³

Host–guest chemistry has also been used to facilitate the preparation of conducting polymers in aqueous solution using nonpolar monomers. Reece et al.¹⁴ observed that solutions containing pyrrole and calix[6]arenehexasulfonic acid (C6S) contained a black precipitate after several days. They investigated the properties of PPy in the presence of a host/guest calixarene. Their conductivity measurements indicated the material to be insulating, whereas cyclic voltammetry studies demonstrated that it was electroactive. Bidan et al.⁸ obtained electrochemically modified PPy films including sulfonated calixarenes as dopants.

To the best of our knowledge, this work is the first report on the synthesis of PPy in the presence of water-soluble azocalix[4]arene [(5,11,17,23-tetrakis

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[(*p*-carboxyphenyl)azo]25,26,27,28-tetrahydroxycalix[4]arene)], which was obtained from diazo coupling reaction between calix[4]arene and diazonium salts. Azo groups provide calixarenes a chromogenic activity. The azocalix[4]arene was used as dopant anion in our work. The effect of the content of azocalix[4]arene on the properties of PPy was investigated. The materials have been characterized by infrared spectroscopy, scanning electron microscopy, thermogravimetric analysis, and conductivity measurements.

EXPERIMENTAL

Materials

Pyrrole was obtained from Aldrich (Taufkirchen, Germany), and it was distilled before use. $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (APS) and NaOH were purchased from Aldrich, and they were used without further purification. All solvents are commercially graded reagents, which are used without further purification. *p*-*tert*-Butylcalix[4]arene, calix[4]arene, azocalix[4]arene were synthesized as described in previously reported method.^{15–17} The obtained azo compound was purified by crystallization using DMF-H₂O. All of the other compounds were of analytical reagent grade. Deionized double-distilled water was used for the preparation of the solutions.

Synthesis of polypyrrole/azocalix[4]arene salts

Pyrrole (2.88×10^{-3} mol; 0.2 mL) was dispersed in 50 mL of water at 25°C. Azocalix[4]arene dissolved in 0.01M NaOH was added dropwise into 0.05M pyrrole solution. $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (72 mL; 0.1 M) solution was added to the mixture of pyrrole and azocalix[4]arene. Polymerization time was 24 h (pH of medium is 2.1), and the precipitates were filtered and washed with distilled water and finally dried at 50°C under vacuum for 24 h. The PPy/azocalix[4]arene salts including different contents of azocalix[4]arene were prepared by dissolving azocalix[4]arene (0.029, 0.057, and 0.059 g) in 7, 10, and 12 mL of 0.01M NaOH, respectively. PPy homopolymer was synthesized in the same experimental conditions without azocalix[4]arene. The chemical structure of PPy/azocalix[4]arene salt is shown in Figure 1.

Instrumentation

FTIR spectra were recorded between 400 and 4000 cm^{-1} with a 4 cm^{-1} resolution from KBr pellets on a Perkin Elmer Spectrum BX FTIR system (Beaconsfield, Buckinghamshire, HP91QA, England). Thermograms of the polymers were recorded by using a Perkin Elmer thermogravimetric analyzer in the

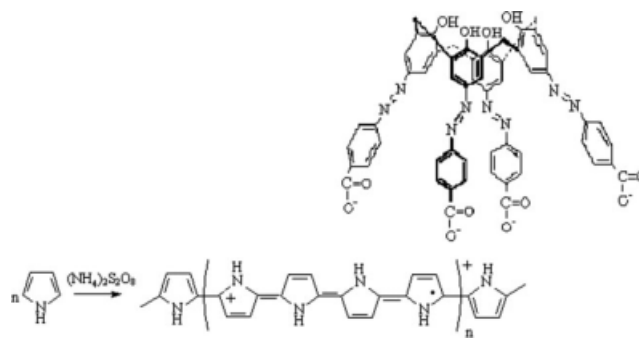


Figure 1 Chemical structure of polypyrrole/azocalix[4]arene salt.

presence of N₂ atmosphere from 50 to 900°C with a heating rate of 10°C/min. The direct current electrical conductivity of the PPy/azocalix[4]arene salts was measured by standard four-probe method using PCI-DAS6014 for a current source, voltmeter, and temperature controller. Dry powders were made into pellets using a steel die having 13-mm diameter in a hydraulic press under a pressure of 700 MPa. Temperature-dependent electrical conductivity of the polymer samples was measured by computerized four-probe system, and the temperature of pellets was recorded using a thermocouple. The isothermal stability measurement of electrical conductivity of the PPy/azocalix[4]arene salts was carried out at 100°C. The loss of conductivity of the PPy/azocalix[4]arene salts were measured for 60 min at selected temperature. The temperature dependence of the electrical conductivity of polymers was measured over a temperature range from 25 to 100°C. For SEM analysis, samples were sputter-coated with gold layers, and photographs were taken on a scanning electron microscope model Philips XL-30S FEG. XRD signals were recorded using a Rigaku D/MAX-Ultima+/PC X-ray diffraction equipment.

RESULTS AND DISCUSSION

FTIR results

The infrared spectra of PPy and PPy/azocalix[4]arene salts are shown in Figure 2. Several research groups^{18,19} have made the assignments of vibration modes of PPy. The bands at 1558–1557 cm^{-1} in the spectra of PPy and PPy/azocalix[4]arene salts correspond to the C–C stretching vibrations of pyrrole ring. The band at 1476 cm^{-1} in the spectrum of PPy and the bands at 1474–1471 cm^{-1} in the spectra of PPy/azocalix[4]arene salts indicate C–N stretching vibration in the ring. The broad band from 1400 to 1250 cm^{-1} is attributed to C–H or C–N in-plane deformation modes and it has a maximum at 1304 cm^{-1} for PPy. The band of C–H and N–H in-plane deformation vibration is situated at 1098 cm^{-1} , and

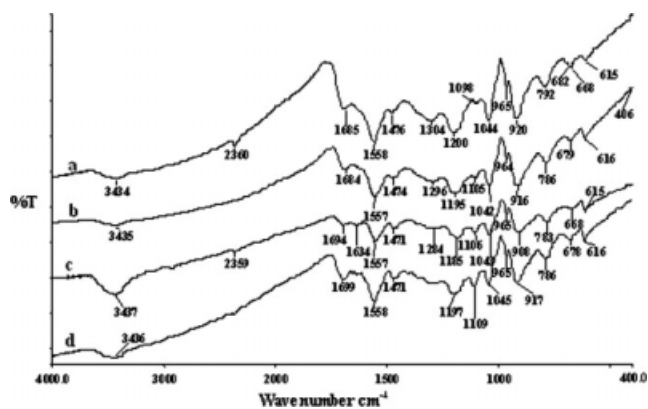


Figure 2 FTIR spectra of PPy and PPy/azocalix[4]arene salts: (a) PPy, (b) PPy/azocalix[4]arene (8%), (c) PPy/azocalix[4]arene (18%), and (d) PPy/azocalix[4]arene (28%).

the band of the C—C out-of-plane ring deformation vibration is situated at 1044 cm^{-1} for PPy. These bands are also observed in the spectra of PPy/azocalix[4]arene salts. A broad band at 3436 cm^{-1} indicates the presence of azocalix[4]arene due to —OH groups. It is observed from FTIR spectra of PPy/azocalix[4]arene salts that the intensity of C—N band at 1304 cm^{-1} decreases with increasing content of azocalix[4]arene. These shifts indicate the interaction between PPy and azocalix[4]arene.

TGA results

Figure 3 shows the TGA curves of the PPy/azocalix[4]arene salt (18%), PPy, and azocalix[4]arene. It is clear that azocalix[4]arene [Fig. 3(e)] begins to lose its weight around 154°C , whereas PPy [Fig. 3(a)] undergoes degradation at a temperature of 191°C ,

implying that PPy is more stable than azocalix[4]arene when being heated. Decomposition of azocalix[4]arene has occurred in three steps. The first weight loss at 154°C exhibits to volatile DMF (synthesis solvent) released from the lattice compound.⁷ The last two steps at 303 and 503°C attributes to decomposed azo groups in azocalix[4]arene structure.

PPy and PPy/azocalix[4]arene salts [the curve of PPy/azocalix[4]arene salt (18%) is only given in Fig. 3] have small weight loss (5–10 wt %) at low temperatures (under 100°C). PPy is a hygroscopic polymer, and this weight loss indicates the expulsion of water molecules/moisture adsorbed in materials. The main degradations have started at 191 , 206 , and 214°C with increasing azocalix[4]arene amount for PPy/azocalix[4]arene salts. PPy/azocalix[4]arene salt (18%) [Fig. 3(b)] has higher degradation temperatures than those of both PPy and azocalix[4]arene. The thermal stability of PPy has increased with the doping effect of azocalix[4]arene. Moreover, the effect of surfactant dopants on the thermal stability of PPy was investigated by Omastova et al.²⁰ They exhibited that thermal stability of PPy improved with doping in the presence of anionic surfactant. Thus, the azocalix[4]arene has also played a dopant anion role in the PPy/azocalix[4]arene salts in our work. PPy/azocalix[4]arene salts have indicated higher thermal decompositions than aliphatic and aromatic sulfonate-doped polymers given in the literature.⁵ Additionally, the thermal stabilities of PPy/azocalix[4]arene salts were compared with that of mechanical mixture of PPy and azocalix[4]arene [Fig. 3(c)], and the different thermal degradation behaviors were obtained for two systems. This shows that PPy/azocalix[4]arene salts prepared

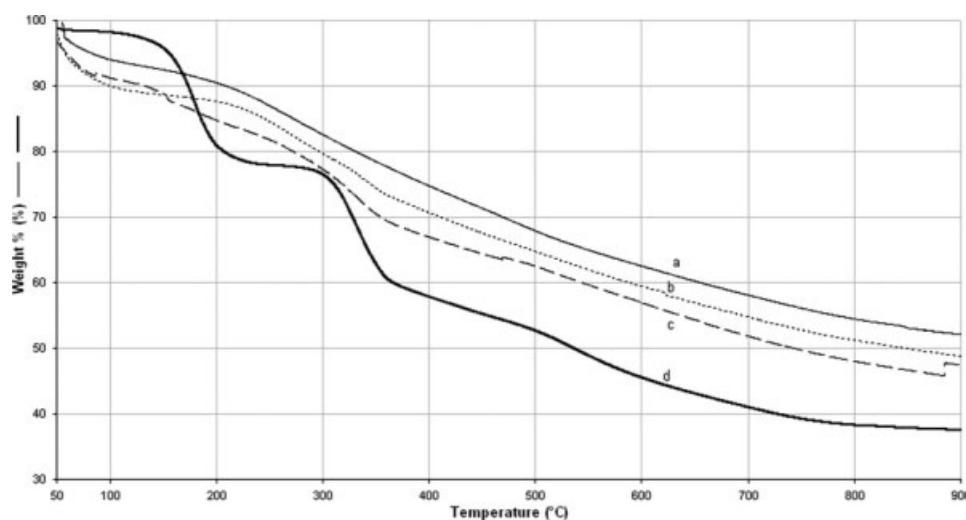


Figure 3 TGA curves of samples: (a) PPy, (b) PPy/azocalix[4]arene (18%), (c) PPy/azocalix[4]arene mechanical mixture, and (d) azocalix[4]arene.

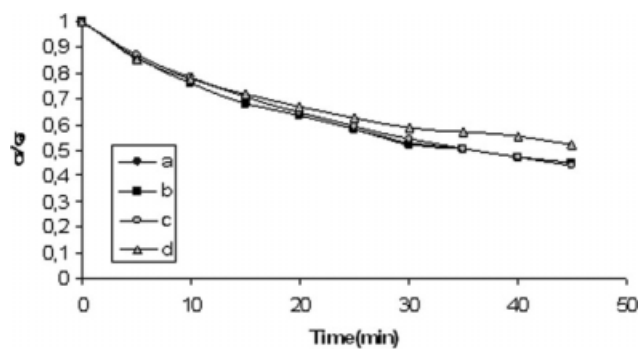


Figure 4 Isothermal stability of (a) PPy, (b) PPy/azocalix[4]arene (8%), (c) Py/azocalix[4]arene (18%), and (d) PPy/azocalix[4]arene (28%) in terms of retention of σ with respect to time at 100°C.

in situ are not a simple mixture, and azocalix[4]arene has played a dopant anion role for PPy.

Conductivity and thermal stability of conductivity

Conductivity of PPy homopolymer is 2.13×10^{-4} S/cm. The conductivity of bulk PPy synthesized using APS is lower than that obtained when using milder oxidants such as FeCl_3 .²¹ This difference is probably due to over oxidation of conducting polymer.²² Also, the presence of 1685 cm^{-1} band in Figure 2(a) indicates carbonyl groups formed due to over oxidation. Moreover, the conductivities of PPy-surfactant systems are approximately in the order of magnitude lower than that of bulk-PPy.²³ This effect has been explained depending on inhomogeneously distributed surfactant onto polymer. However, in this work, conductivity of the PPy/azocalix[4]arene salt has increased in the presence of azocalix[4]arene. Similarly, a significant enhancement of the conductivity up to 90 S/cm was obtained by using poly(ethylene glycol) as additive.²⁴

PPy/azocalix[4]arene including 18 wt % of azocalix[4]arene indicates the highest conductivity to be 2.80×10^{-1} S/cm. Moreover, it has the lowest intensity of band of carbonyl group as seen in Figure 2(c). This increase can be explained with lower over oxidation and lower particle size of PPy in the presence of azocalix[4]arene dopant. Decreasing (1.50×10^{-2} S/cm) of the conductivity with further increase of azocalix[4]arene (28%) may be concluded as the formation of agglomerates and inhomogeneous dispersion of azocalix[4]arene in the PPy structure.

The temperature dependence of conductivity of PPy/azocalix[4]arene salts was measured *in situ* during thermal aging (Figs. 4 and 5). The samples were placed in the temperature-controlled chamber and characterized during heating. The thermal treatments were done at 100°C. The conductivity of PPy indicated 55% loss at 100°C (Fig. 4). A loss in conductivity was also observed with increasing temper-

atures for PPy/azocalix[4]arene salts (Fig. 4). Among all samples, PPy/azocalix[4]arene salt (28%) has the least conductivity loss at 100°C. It can be seen from Figure 5 that the samples have followed the Arrhenius equation for temperature dependence of electrical conductivity and they have a positive temperature coefficient of conductivity. These indicate the semiconducting nature of the samples. Temperature-dependent conductivity measurements show the characteristic "thermal activation behavior."²⁵ This observation may be due to the mobility of charge on polymer chain or the hopping process between the polymer chains. This is a characteristic behavior of semiconductors.²⁶ However, there can also be thermal curing. It affects the chain alignment of the polymer and leads to the increase of the conjugation length, which brings about the increase of conductivity. Also, there had to be molecular rearrangement during heating process, which made the molecular conformation favorable for electron delocalization.²⁷

SEM results

Figure 6(a–c) shows the SEM micrographs of azocalixarene, PPy, and PPy/azo[4]calixarene salts. Azocalix[4]arene has a uniform surface with the layer [Fig. 6(a)]. SEM image of PPy powder indicates a globular structure with uniform particle size under $1 \mu\text{m}$ in diameter [Fig. 6(b)]. It was clearly observed that the morphology of resulting PPy/azocalix[4]arene salts was considerably different from PPy and azocalix[4]arene. As seen from Figure 6(c), PPy/azocalix[4]arene salt containing (18%) azocalix[4]arene indicates a morphology with smaller globules (quite submicrometer-sized) than that of PPy. The morphological properties of the PPy/azocalix[4]arene salts can be explained depending on the doping effect. Omastova et al. revealed the effect of dopant anion on the morphology of PPy. They have synthesized

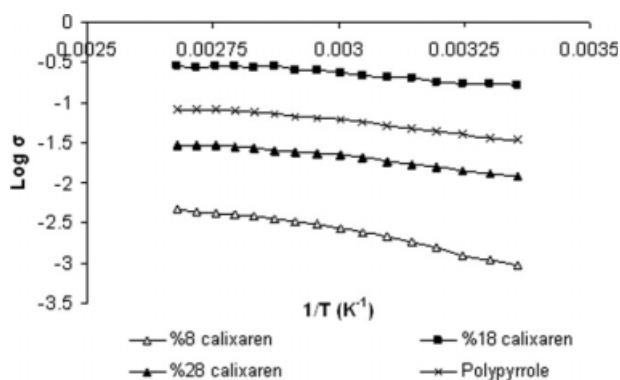


Figure 5 Arrhenius equation of (a) PPy, (b) PPy/azocalix[4]arene (8%), (c) PPy/azocalix[4]arene (18%), and (d) PPy/azocalix[4]arene (28%) in terms of retention of σ with respect to time.

PPy by chemical polymerization in aqueous solution containing an oxidant FeCl_3 or $\text{Fe}_2(\text{SO}_4)_3$, an anionic surfactant, sodium dodecylbenzenesulphonate (DBSNa). PPy- SO_4 revealed the globular structure of the PPy.²⁸ In our study, PPy showed the similar morphology because of SO_4^{2-} anions, which came from oxidant $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The SO_4^{2-} anions played the role of dopant anion in the synthesis medium. The structure of PPy/azocalix[4]arene looks more compact, and the particle size of PPy/azocalix[4]arene is much smaller than that of PPy. It is known that there is a relation between morphology and conductivity.²⁹ PPy/azocalix[4]arene salts exhibit

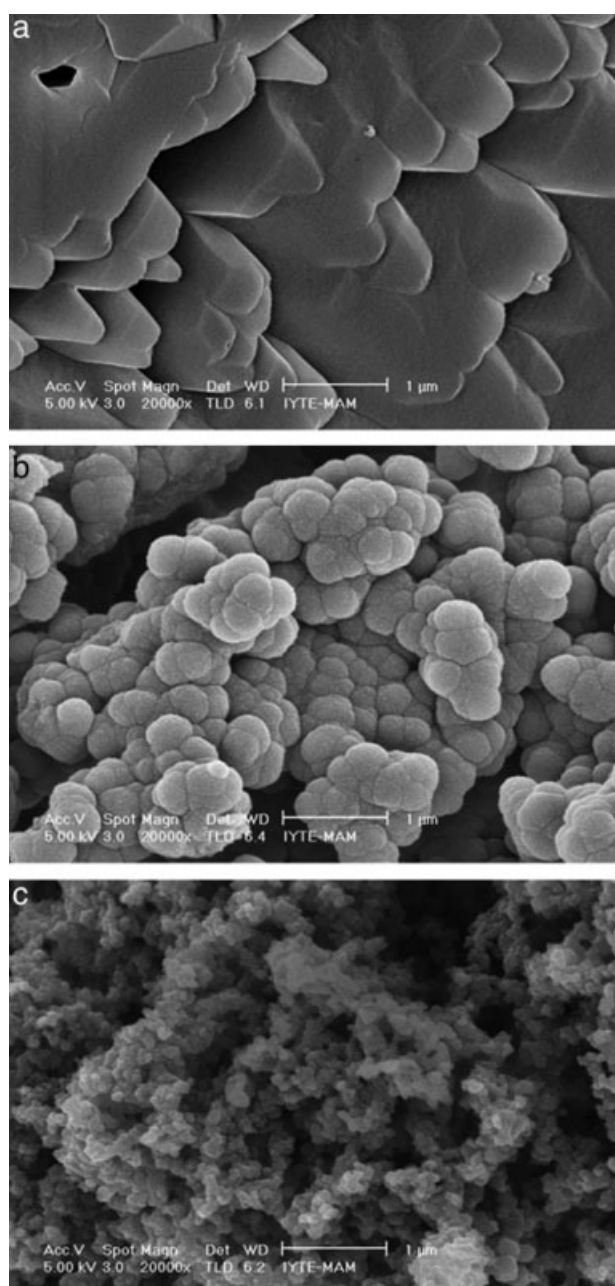


Figure 6 SEM images of (a) azocalix[4]arene, (b) PPy, and (c) PPy/azocalix[4]arene (18%).

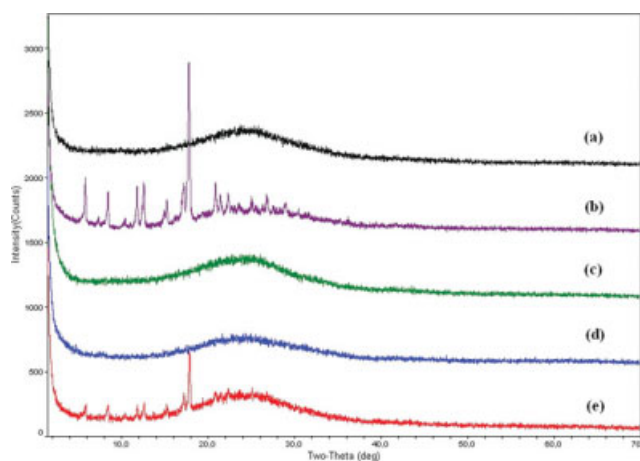


Figure 7 X-ray scattering patterns of samples: (a) PPy, (b) azocalix[4]arene (c) PPy/azocalix[4]arene (18%), (d) PPy/azocalix[4]arene (28%), and (e) PPy/azocalix[4]arene (18%) mechanical mixture. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

more ordered and dense structures (smaller sizes with high density of granules per unit area) when compared with PPy. It may show that the improvement in the conductivity of the PPy/azocalix[4]arene salts could be attributed to more ordered and dense structure enhancing interchain electron hopping. By comparing the conductivity values of samples, it can be seen that the conductivity value of PPy/azocalix[4]arene (2.8×10^{-1} S/cm) is higher than that of PPy (2.13×10^{-4} S/cm) because of the smooth surface of PPy/azocalix[4]arene.

X-ray results

Figure 7(a) indicates X-ray diffraction pattern of PPy homopolymer, which has a broad peak at about $2\theta = 25^\circ$, a characteristic peak of amorphous PPy.³⁰ Pure azocalix[4]arene [Fig. 7(b)] has higher crystallinity than PPy homopolymer. X-ray diffraction patterns of PPy/azocalix[4]arene salts and PPy: azocalix[4]arene mechanical mixture are shown in Figure 7(c–e). PPy/azocalix[4]arene salt and mechanical mixture have quite different diffraction patterns from each other. The salts have amorphous nature such as PPy, whereas mechanical mixture indicates properties of both PPy and azocalix[4]arene, showing their heterogeneous system. PPy/azocalix[4]arene salts are homogeneous PPy salts, such as characteristic-doped PPy.

CONCLUSIONS

In this study, PPy/azocalix[4]arene salts were chemically synthesized and the doping effect of azocalix[4]arene on the properties of PPy were investigated.

Existence of the dopant in PPy powders, including azocalix[4]arene, was confirmed by FTIR spectroscopy, SEM analysis, conductivity measurements, and thermal analysis. Both conductivity and thermal properties of PPy were enhanced in the presence of azocalix[4]arene. It was detected that the PPy/azocalix[4]arene salts have higher degradation temperatures than those of both PPy and azocalix[4]arene. SEM results confirmed that the morphology of PPy/azocalix[4]arene was more compact and the particle sizes were very small according to PPy. It can be concluded that these changes on the morphology of polymers lead to an increase in the conductivity.

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