Macromolecules

Article

pubs.acs.org/Macromolecules

Enhanced Thermal Stability of Polyaniline with Polymerizable Dopants

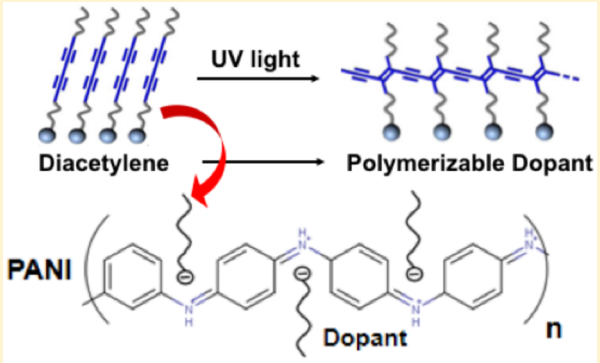
Yeol Kyo Choi,[†] Hyeong Jun Kim,[‡] Sung Ryul Kim,[‡] Young Min Cho,[†] and Dong June Ahn*[,†,‡]

[†]Department of Chemical and Biological Engineering, Korea University, Seoul 02841, Korea

[‡]KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 02841, Korea

Supporting Information

ABSTRACT: Diacetylene (DA) is an amphiphilic structure and has been studied as a variety of PDA-based chemosensors. However, the prospect of using diacetylene (DA) as dopant of polyaniline (PANI) is yet to be reported. In this study, new amphiphilic PCDA-taurine and PCDA-pBzS dopants were synthesized by changing the primary functional group to a sulfonic group. These polymerizable dopants are photopolymerized by UV irradiation in PANI solution. Thereby we expect to enhance the thermal stability and sustain the conductivity of PANI. The polymerizable dopants were characterized by FT-IR, NMR, and GC-MS. PANI with polymerizable dopants was analyzed by resonance Raman spectroscopy (RRS). The thermal stability and conductivity of PANI were characterized by thermogravimetric analysis (TGA). Comparing the TGA results of PANI doped with general dopants with PANI doped with polymerizable dopants, we found that PANI with polymerizable dopants showed enhanced thermal stability.



INTRODUCTION

Conjugated polymers are very unique polymers owing to a backbone with an extended π-conjugated system. The extended π-bonds contain delocalized electrons, which result in unique optical and electronic properties. Hence, electroactive polymers are used in a variety of applications, including light-emitting diodes,[1] batteries,[2] electromagnetic shielding,[3] antistatic agents,[4,5] gas sensors,[6−8] and activators.[9] Polydiacetylene (PDA) is one of the most attractive conjugated polymers for biosensor applications because it can be readily prepared by photopolymerization after self-assembly of diacetylene (DA) molecules.[10−16] In addition, PANI shows promising potential due to its ease of synthesis, environmental stability, and high electrical conductivity.[17] PANI is generally used as an antistatic agent in the plastics to prevent electrostatic discharge.[5,18−21] The molding temperature of plastics such as polyethylene (PE), polypropylene (PP), and polystyrene (PS) is approximately 300 °C. However, when PANI is doped with general dopants such as dodecylbenzenesulfonic acid (DBSA) and exposed to higher temperatures, especially above 250 °C, complete deprotonation and degradation of PANI were observed.[22] When PANI was dedoped, the conductivity decreased sharply.[22] Thus, there is the need to enhance the thermal stability of the doped PANI for use as antistatic agents. In this study, we developed diacetylenes as dopants by the changing carboxyl group to a sulfonic group and denoted polymerizable dopants as PCDA-taurine or PCDA-pBzS. Upon exposure to 254 nm UV, the polymerizable dopants underwent photopolymerization via a 1,4-addition reaction to form an ene−yne conjugated backbone.[23] By polymerization, we expect to enhance the thermal stability and sustain the conductivity of PANI with PCDA-taurine or PCDA-pBzS as the dopant.

EXPERIMENTAL SECTION

Materials and Instrumentation. 10,12-pentacosadiynoic acid (PCDA) was purchased from GFS Chemicals. *N*-Hydroxysuccinimde (NHS), *N*,*N*′-dicyclohexylcarbodimide (DCC), 2-aminoethanesulfonic acid, 4-aminobenzenesulfonic acid, triethylamine, and the necessary solvents were purchased from Aldrich, Korea. Aniline, ammonium persulfate (APS), and 4-dodecylbenzenesulfonic acid were also purchased from Aldrich, Korea. ^{1}H NMR spectra were recorded on a Varian Unitylnova (500 MHz) using DMSO-d_6 and $CDCl_3$ as the solvent. Fourier transform infrared (FT-IR) spectroscopy analysis was performed using a PerkinElmer Spectrum GX1 instrument. Morphological properties were observed by scanning electron microscopy (SEM). Gas chromatography−mass spectrometry data were recorded on a JMS-600W (ionization mode is fast atom bombardment). Thermal gravimetric analysis of PANI powders was carried out on a thermal gravimetric analysis Q 50 system. For conductivity measurements, the polymer samples were pressed into a 10 mm diameter disk and analyzed using four-probe conductivity instrument (FPP-RS 8 resistivity meter model).

Experimental Concept. Commercially available PCDA has an amphiphilic structure with a carboxyl functional group (−COOH) and

Received: November 30, 2016
Revised: March 14, 2017
Published: April 7, 2017

DOI: 10.1021/acs.macromol.6b02586
Macromolecules 2017, 50, 3164−3170