

Dual conductivity of ionic polyacetylene by the metathesis cyclopolymerization of dendronized triazolium-functionalized 1,6-heptadiyne

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ABSTRACT

Ionic polyacetylenes (iPAs) with the *trans* configuration and a five-membered ring structure were synthesized by the metathesis cyclopolymerization of dendronized triazolium-functionalized 1,6-heptadiyne. The iPAs bearing flexible pendants had a low glass transition temperature of $-37\text{ }^{\circ}\text{C}$, a high decomposition temperature of $349\text{ }^{\circ}\text{C}$, and a relatively high intrinsic ionic conductivity of $7.3 \times 10^{-5}\text{ S}\cdot\text{cm}^{-1}$ at room temperature, which further increased to $1.4 \times 10^{-4}\text{ S}\cdot\text{cm}^{-1}$ by doping with lithium bis(trifluoromethanesulfonyl)imide. Moreover, the iodine-doped iPAs exhibited dual conductivity, i.e., ionic and electronic conductivities of 7.1×10^{-5} and $5.0 \times 10^{-5}\text{ S}\cdot\text{cm}^{-1}$, respectively. Therefore, the conjugated iPAs with a good film-forming property provide a potential for making dual-conductive flexible electronics.

1. Introduction

Conducting polymers can be divided into electronic conducting polymers and ionic conducting polymers. Polyacetylene (PA) [1], polypyrrole [2], polythiophene [3], polyaniline [4], and poly(phenylene ethynylene) [5] are typically electronic conducting polymers, and their conjugated structure of alternating single and double bonds makes charge transfer in the main chain when they are chemically doped. Polyelectrolytes are the representatives of ionic conducting polymers, and their ionic conductivity is caused by the migration of ions in a solution or solid [6–8]. These two types of materials have been independently used for a long time. However, materials with dual ionic-electronic conductivity have been required in applications such as electrochemical energy conversion and in the production of storage devices and bioelectronic materials. Recently, more and more dual-conductivity materials have been synthesized. For example, poly(3-hexylthiophene)-*block*-poly(ethylene oxide) (P3HT-PEO), a dual-conductivity material, compounded with LiFePO_4 was used to assemble the cathode of lithium batteries [9]. P3HT-PEO served as the binder and transporter of electronic charge and lithium ions, which greatly simplified the structure of lithium batteries compared with that of traditional lithium batteries, whose cathode part is usually made of an inert polymer to bind the cathode particles, including carbon additives for

electronic conduction and a liquid electrolyte for lithium ion conduction. The electronic and ionic conductivities of P3HT-PEO- LiFePO_4 were $(6.73 \pm 2.05) \times 10^{-6}$ and $(1.09 \pm 0.47) \times 10^{-4}\text{ S}\cdot\text{cm}^{-1}$, respectively, and the battery performance testing indicated that P3HT-PEO- LiFePO_4 was suitable for preparing responsive electrodes. Another kind of composite material consisting of PA-type conjugated polymer and 1-propyl-3-methylimidazolium ionic liquid (IL) was also prepared [10]. PA is a brittle polymer with poor mechanical properties, extremely low solubility, and poor stability, which greatly limit its utility [11,12]. The addition of IL to the polyene film not only imparted ionic conductivity, showing the electronic and ionic conductivities of 1.1×10^{-5} and $2.1 \times 10^{-6}\text{ mS}\cdot\text{cm}^{-1}$, respectively, but also improved the mechanical properties, including an increase of 1500% in the elongation of break with 33 wt% IL. In addition, for bioelectronic materials, the introduction of an anion or cation group to conjugated polymers not only enhanced the electrical conductivity of conjugated polyelectrolytes but also facilitated the communication between electronic conductors and biological systems by providing an ideal interface for signal transduction between electron- and ion-mediated systems [12,13]. Polymerization of an IL-type monomer 1-dodecyl-3-propargylimidazolium bromide was reported to yield a nanostructured ionic PA with a conductivity of $7.02 \times 10^{-5}\text{ S}\cdot\text{cm}^{-1}$, and the amphiphilic imidazolium pendants promoted the formation of nanostructured

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ionic PA and improved solubility [14].

Copper-catalyzed azide-alkyne cycloaddition click chemistry toward triazole has attracted great attention in the past decades, and the derived triazolium-based PILs have been used to prepare ionic conducting materials [15,16]. Herein, ionic polyacetylenes (iPAs) with the *trans* configuration and a five-membered ring structure were synthesized by the metathesis cyclopolymerization (MCP) of dendronized triazolium-functionalized 1,6-heptadiynes, and the introduction of flexible dendronized triazolium pendants to the rigid PA backbone is envisioned to modify the solubility, improve the stability and flexibility, and enhance the conductivity of iPAs. In addition, the conjugated iPAs doped with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) or iodine (I_2) were expected to further promote the ionic and electronic conductivities, and the relationship between ionic density and conductivity was investigated.

2. Results and discussion

2.1. Synthesis and characterization of dendronized ionic monomers

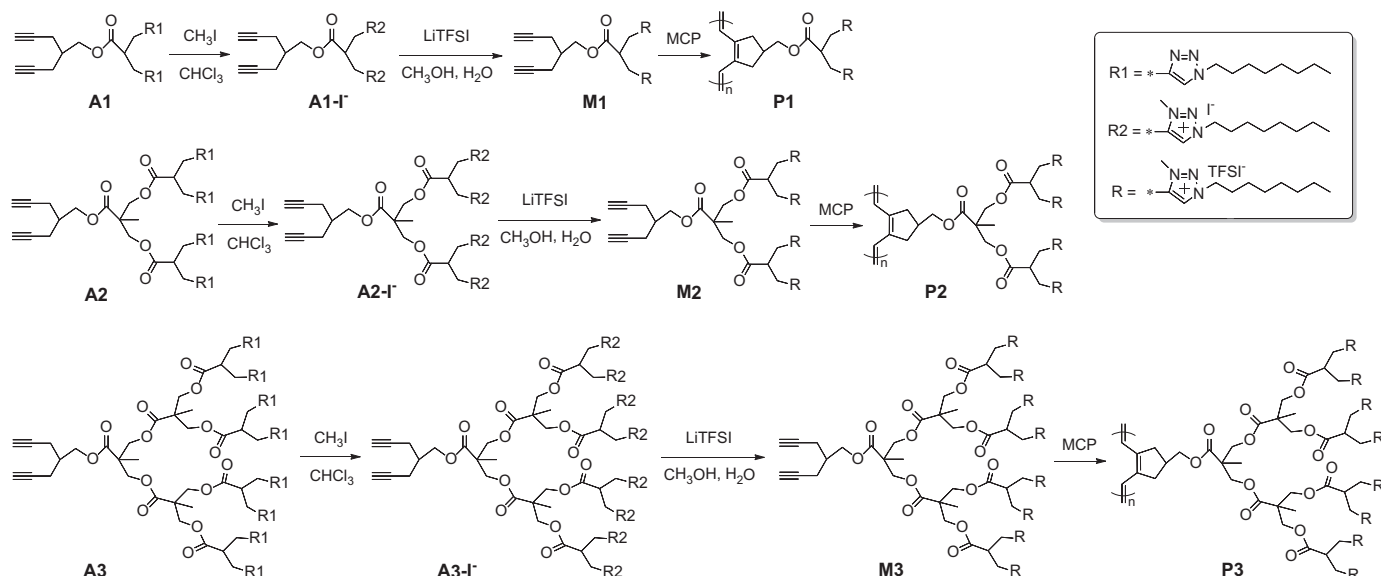
First, neutral 1,6-heptadiyne monomers (**A1–A3**) prepared according to a previous procedure [17] were reacted with CH_3I to obtain N-alkylation intermediates (**A1-I⁻**–**A3-I⁻**), which were then reacted with LiTFSI by the anion exchange of I^- with $TFSI^-$ to obtain the final ionic 1,6-heptadiyne monomers **M1**, **M2**, and **M3**. The synthetic protocol is shown in Scheme 1.

The structures of ionic 1,6-heptadiyne monomers were characterized by 1H NMR, ^{13}C NMR, ^{19}F NMR, and FT-IR spectroscopy. In the 1H NMR spectra of ionic monomers (Fig. 1), the signal at 8.56–8.75 ppm could be assigned to the triazolium proton of M-TFSI, while no signal was observed at about 9.63 ppm for the triazolium proton of A-I⁻ residue (Fig. S1), which confirmed that the anion exchange from I^- to $TFSI^-$ occurred completely; the signal at 4.33 ppm was considered to be the methyl protons connected to the triazolium ring group, and the signal at 2.01 ppm was the characteristic peak of the terminal acetylenic proton. In the ^{13}C NMR spectra of ionic monomers (Figs. S2–S4), the signal at 171.11 ppm was considered to be the ester carbon atom, the signal at 70.61 ppm denoted the characteristic peak of the acetylenic carbon, the peaks at 141.60 and 128.86 ppm represented the carbon atoms in the triazolium group, and the new peaks that appeared at 123.43–115.78 ppm corresponded to the carbon atoms of the $TFSI^-$ group.

In ^{19}F NMR spectra (Fig. S5), the single signal at -78.80 ppm was the characteristic peak of F atom in $TFSI^-$ for each monomer, which demonstrated the occurrence of anion exchange reaction. In FT-IR spectra (Fig. S6), the peaks at 3296 and 2128 cm^{-1} were indicative of the existence of $-C\equiv CH$, the triazolium absorption peak appeared at 3119 cm^{-1} , and the peak at 1737 cm^{-1} corresponded to the ester group. All these observations demonstrate that the anion exchange was completed and proved the successful synthesis of ionic monomers.

2.2. Polymerization of ionic 1,6-heptadiyne monomers

The MCP of 1,6-heptadiyne derivatives might generate PA with five- or six-membered rings in the backbone, and the five-membered ring structure-based PA possessed higher conductivity because of the better packing, improved coplanarity, and thus induced higher effective conjugation length [18,19]. Third-generation Grubbs catalyst (**Ru-III**) [20] has been proved to be an effective catalyst for the MCP of neutral 1,6-heptadiyne derivatives for the selective preparation of conjugated polymers with five-membered ring backbone, controlled molecular weight (M_n), and a low polydispersity index (PDI) [21]. However, the MCP of ionic 1,6-heptadiyne derivatives has rarely been reported [22]. In general, there are two ways to prepare ionic polymers: one is the ionization of neutral polymers having acidic or basic groups [23,24] and the other is the polymerization of ionic monomers [25–27]. In this article, the latter was adopted to directly synthesize iPAs, rather than the N-alkylation of triazole groups on neutral PAs, ensuring that the neutral triazole groups transformed into triazolium groups completely. Three types of iPAs (**P1–P3**) were obtained by the MCP of ionic monomers **M1–M3** under various reaction conditions, and the results are listed in Table 1. Considering **M1** with two triazolium pendants as an example, the MCP of **M1** using dichloromethane as solvent and 3,5-dichloropyridine as additive was performed with a good control over M_n (23.5 kDa) and PDI (1.14) (run 1). As the $[M]/[Cat]$ ratio increased to 50 and 100 (runs 2 and 3, respectively), M_n values of **P1** increased to 30.0 and 49.8 kDa, respectively, with low PDIs around 1.20 and high yields above 80%, indicating that a fine polymerization occurred. However, the MCP was hampered by the increased pendant size. The MCP of **M2** with four triazolium pendants was worse than that of **M1** as $[M]/[Cat]$ ratios increased from 25 to 50 and 100 (runs 4–6), although the as-synthesized **P2** still had narrow PDIs and high yields, M_n values of **P2** were 27.8, 36.3, and 38.2 kDa, respectively, it seems that M_n of **P2** was limited by the increased steric hindrance of pendants. With



Scheme 1. Syntheses of ionic 1,6-heptadiynes (**M1–M3**) and ionic polyacetylenes (**P1–P3**).

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