A Water-Soluble Pyridine-Containing Polyacetylene: Poly(2-ethynylpyridinum bromide) Having Propargyl Side Chains

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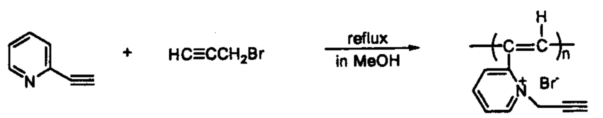
During the past four decades, extensive studies[1] on the polymerization of mono- and di-substituted acetylenes have been made to overcome some problems of polyacetylene such as its lack of processability and its thermal and environmental instabilities. The linear conjugated polymers from substituted acetylenes can be used as organic semiconductors, a membrane for gas separation and liquid-mixture separation, a side-chain liquid crystal, and nonlinear optical materials.[2] The polyelectrolytes having conjugated backbone were scarce and restricted to some cases as follows: the solid-state polymerization of propiolic salts by γ-irradiation,[3] water-soluble polyene polymers by quarterization of poly(6-bromo-1-hexyne),[4] and the synthesis of mono- and di- substituted ionic polyacetylene through the activation of the acetylene bond in ethynylpyridine by introduction of a strong electron withdrawing substituents in conjugation to it.[5]

Due to their extensive conjugation and ionic nature, these polymers have potential as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries and permselective membrane.[5a]

In recent years, we reported the synthesis and properties of various conjugated ionic polyelectrolytes by the polymerization of mono- and di-propargyl derivatives having bromide, tosylates, and tetraphenylborate as counter anions.[6] And also we reported the synthesis of water-soluble poly(2-ethynylpyridine) by the polymerization of 2-ethynylpyridine with W- and Mo-based catalysts.[7]

Now we report the synthesis of a novel water-soluble pyridine-containing conjugated ionic polymer, poly(2-ethynylpyridinum bromide) having a pendant propargyl moiety by the simple polymerization reaction of 2-ethynylpyridine and propargyl bromide in refluxing methanol as follow.



A typical polymerization prcedure was as follow: In a 100 mL flask, methanol (50 mL), 2-ethynylpyridine (1.00 g, 9.70 mmol), and propargyl bromide (1.16 g, 9.75 mmol) were introduced in the given order. And then the reaction mixture was refluxed in methanol for 24 hrs. As the reaction is proceeded, the color of reaction mixture was consecutively changed into dark-red the resulting solution was precipitated into a large amount of ethyl ether. The precipitated polymer was filtered and dried under vacuum at room temperature for 24 hrs. The obtained polymer was dark-red powders and the polymer yield was 95%.

The reaction of 2-ethynylpyridine alone in methanol reflux condition did not yield any tractable polymeric products besides somewhat color changes. This polymerization was assumed to be activated by the quarterization of 2-ethynylpyridine with propargyl bromide. Thus the polymerization mechanism was deduced to be similar to that for the spantaneous polymerization of 3- and 4-vinylpyidines on quarterization of the pyridine nitrogen by alkyl halides.[8]

The inherent viscosity of the polymer was 0.21 dL/g (in DMSO, 30 °C). This value was found to be relatively higher in comparison to those of the polymers from acetylenic salt monomers such as dihexyldipropargylammonium salts[5a] and propargyltriphenylphosphonium bromide[5b]

The bathochromic shifts were observed in the UV-visible spectrum of the polymer compared to that of the initial mixture of 2-ethynylpyridine and propargyl bromide. The broad absorption peak at 300-700 nm, which had been absent in the UV-visible spectrum of the initial mixture of 2-ethynylpyridine and propargyl bromide in methanol, were observed (λ_{max}: 524 nm), which is originated from the $\pi \rightarrow \pi^*$ transition of the conjugated polymer backbone. The elemental analysis data for polymer agreed well with the theoretical value: Calcd for $(C_{10}H_8NBr)_n$: C, 54.08%; H, 3.63%; N, 6.31%; Br, 35.97% Found: C, 54.01%; H, 3.54%; N, 6.30%; Br, 36.15%. ^1H NMR spectrum of the polymer (solvent: CD_3OD) showed a broad peak at 6.5-9.5 ppm, which is originated from the pendant aromatic protons of pyridyl substituent and the vinyl protons on the conjugated polymer backbone. The methylene protons of propargyl substituent was also observed in the range of 3.0-3.8 ppm, whereas the relatively sharp peak at 3.1 ppm, which is originated from the acetylenic proton of the resulting polymer, was also observed. The IR spectrum of polymer showed only one acetylenic C≡C stretching frequency of the pendant propargyl substituent. A new and relatively intense absorption band at 1590-1630 cm^{-1} is indicative of development of double bonds in polymer backbone, which is originated from the selective polymerization of ethynyl functional group.

The polymer was completely soluble in polar solvents such as water, methyl alcohol, DMSO, and DMF, but insoluble in nonpolar hydrocarbon solvents such as chlorobenzene, toluene, and chloroform.

The polymer properties of this polymer may be easily modified by the simple ion exchange reaction using ion exchange agents such as $NaBPh_4$, $NaClO_4$, and NaN_3. Further works on the modifications of polymer and the electrophysical properties of the polymers are now in progress.

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Synthesis and Characterization of $[Ho(hfa)_3(H_2O)_2]\cdot$triglyme; Molecular Assembly of the Potential Rare-Earth CVD Precursor

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Efficient, reproducible metalloorganic chemical vapor deposition (MOCVD) processes hinge critically upon the availability of high-purity metalloorganic precursors with high and stable vapor pressure. Minimizing molecular oligomerization by saturating the metal coordination sphere with sterically encumbered nonpolar and/or fluorinated anionic ligands is an attractive approach.[1] The β-diketonate ligand class provides an efficacious embodiment of these strategies as initially suggested by the existence of volatile β-diketonate complexes of nearly every metal ion.[2] Although the β-diketonates have been successfully utilized as MOCVD precursors, significant deficiencies still exist with respect to vapor pressure and vapor pressure stabilities. This is especially true for the rare-earth and alkaline earth complexes.[3] The general strategy associated with the synthesis of new stable water-free and volatile rare-earth metal precursors pointed toward the saturation of the metal coordination sphere using neutral polyether ligands.[4] These Lewis base effects appear to reflect saturation of the metal coordination spheres, thus maintaining monomeric character and thereby increasing precursor vapor pressure and stability.

The single-step reaction of lanthanide oxide with hexafluoroacetylacetone and polyether in benzene has been found to yield reproducible anhydrous, air-stable adducts.[5]

$$1/2Ln_2O_3 + 3Hhfa + L \rightarrow Ln(hfa)_3\cdot L + 3/2H_2O$$
$$Ln = La \text{ and } Eu;\ L = \text{diglyme and triglyme}$$

We have extended this synthetic method to the late rare-earth metal oxide for the preparation of MOCVD precursors. We herein describe the synthesis, structural characterization and sublimation properties of $[Ho(hfa)_3(H_2O)_2]\cdot$triglyme.[6,7]