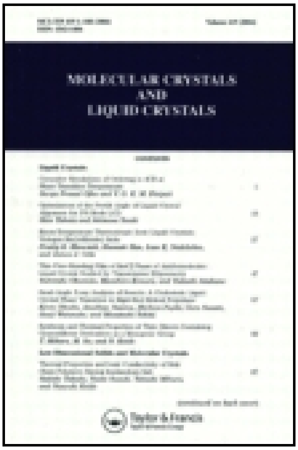

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Synthesis of Poly(2-ethynylpyridinum bromide) Containing Propargyl Side Chain and Its Photoluminescence Properties

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Synthesis of Poly(2-ethynylpyridinum bromide) Containing Propargyl Side Chain and Its Photoluminescence Properties

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Water-soluble conjugated ionic polymer was prepared by the polymerization of 2-ethynylpyridine with propargyl bromide in refluxing methanol. The polymerization proceeded well in homogeneous manner to give a high polymer yield (95%). The resulting poly(2-ethynylpyridinium bromide) having propargyl side chain was mostly brown powder and soluble in the polar solvents such as methanol, water, DMF, and DMSO. The inherent viscosities of the polymer were in the range of 0.10-0.21dL/g. This polymer exhibited good film surface by microscope, and characteristic UV-visible absorption band at 2.3 eV and red PL spectrum at 760nm corresponding to the photon energy of 1.63 eV.

Keywords conjugated polymer; propargyl side chain; photoluminescence; poly(2-ethynylpyridinum bromide)

INTRODUCTION

Conjugated polymers from acetylene derivatives have potentials as organic semiconductor, membranes for gas separation and for liquid-mixture separation, as materials for enantioseparation of racemates by HPLC, as side-chain liquid crystal, as materials for chemical sensors, and as materials for nonlinear optical property and for photoluminescence and electroluminescence properties [1-5]. The ionic conjugated polymers also have potentials as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries and permselective membrane [6,7]. Now we report the synthesis of water-soluble ionic conjugated polymer by the reaction of 2-ethynylpyridine and propargyl bromide in methanol reflux condition and the photoluminescence properties of resulting ionic conjugated polymer

EXPERIMENTAL

The synthesis of poly(2-ethynylpyridinum bromide) having propargyl side chain was performed under mild reaction condition by the simple mixing of 2-ethynylpyridine and propargyl bromide without any initiator or catalysts. As the reaction proceeded, the color of reaction mixture was gradually changed into dark-red. The resulting homogeneous polymer solution was precipitated into a large excess amount of ethyl ether. The photoluminescence spectra were obtained by a 488 nm Ar laser as an excitation or Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube). The emission signal was collected by using the conventional photoluminescence arrangement of a laser, samples, a cryostat (Air Products 1R02-A displex), a monochromator (Spex750M), and a photomultiplier (Hamamatsu R943-02). The signal from the photomultiplier was amplified by an EG&G 5101 lock-in amplifier with the chopping frequency of 170Hz, and converted to the digital signal in the autoscan system.

RESULTS AND DISCUSSION

The activated polymerization of 2-ethynylpyridine by propargyl bromide proceed well to give a high yield of polymer (95%). This polymerization was assumed to be activated by the quarternarization of 2-ethynylpyridine with propargyl bromide. The bathochromic shifts were observed in the UV-visible spectrum of the polymer compared to the initial mixture of 2-ethynylpyridine and propargyl bromide. The broad absorption peak at 300-700nm, 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 ^{1}H-NMR spectrum of the polymer 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 polymer was completely soluble in polar solvents such as methanol, water, DMSO, and DMF.

This polymer exhibits good film surface by microscope, and characteristic UV-Visible absorption band at 2.3 eV and red PL spectrum at 760nm corresponding to the photon energy of 1.63 eV. The band gap energy of this polymer was estimated to be 2.01 eV from the analysis of the absorption edge with a plot of (hν) vs. $(\alpha h\nu)^2$, where α, h, and ν are the absorbance, Plank's constant, and the frequency of light, respectively. A characteristic absorption band at 2.3 eV, which is originated from the $\pi \rightarrow \pi^*$ transition of conjugated double bond, was newly observed. The temperature-dependent photoluminescence spectra of polymer film were also measured. As the temperature was increased, the photoluminescence intensity decreased. This is because the non-radiative decay channels are increased as the temperature increased. But there were no changes in the location of the peak and the line shape of the spectrum as the temperature was varied. Thus the temperature does not affect exciton states of the present polymer.

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