

A Self-Doped Ionic Conjugated Polymer: Poly(2-ethynylpyridinium-*N*-benzoysulfonate) by the Activated Polymerization of 2-Ethynylpyridine with Ring-Opening of 2-Sulfobenzoic Acid Cyclic Anhydride

Yeong-Soon Gal* and Sung-Ho Jin†

Polymer Chemistry Laboratory, College of General Education, Kyungil University, Kyungsan 712-701, Korea

†Department of Chemistry Education, Pusan National University, Pusan 609-735, Korea

Received October 24, 2003

Key Words : Self-dopable, Conjugated polymer, 2-Ethynylpyridine, 2-Sulfobenzoic acid cyclic anhydride, Polyelectrolyte

Polyelectrolytes are among the important classess of macromolecules. These polyelectrolytes are charged macromolecules containing a large number of ionizable or ionic groups and are mostly water-soluble. Polyelectrolytes have been actively studied for the past several decades.¹ For example, the natural polyelectrolytes have been used in water-cleaning processes for centuries. The building blocks of life, the nucleotides and proteins are polyelectrolytes.¹⁻⁴

For more than 30 years, electric conduction in organic solids has been one of the most fascinating topics for synthetic chemists and solid-state physics.⁵ Various polyacetylene-based conjugated polymers have been prepared by the simple linear polymerization of the corresponding acetylene monomers by various catalyst systems.⁶ Due to their extensive conjugation and ionic nature, these ionic polyacetylenes have potentials as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries, permselective membrane, and light-emitting devices.⁷

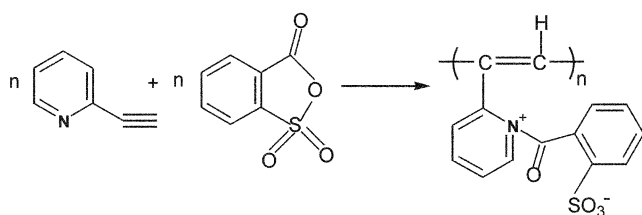
To date, the self-dopable π -conjugated polymers were also prepared to improve the rates of doping/undoping. Heeger and coworkers have prepared the self-dopable poly[n-(3'-thienyl)alkanesulfonic acid]s and their sodium salts with alkanes of carbon numbers 2 and 4, in which the dopants are covalently bonded to the side chains.⁸ Upon electrochemical doping of these polymers in electrolyte solutions, a charge transfer accompanied by a generation of polaron/bipolaron occurs by ejection of protons or metal ions from the bonded dopant and simultaneous ejection of π -electrons from the conjugated main chains, as reflected by an increase of the proton or metal ion concentration in the electrolyte solution

and the presence of free spins during the doping. Other examples of the heterocycle-based self-dopable polymers were also reported.⁹

Now, we report a very facile synthetic method of novel self-dopable ionic conjugated polymer, poly(2-ethynylpyridinium-*N*-benzoysulfonate) (PEPBS), by the activated polymerization of 2-ethynylpyridine with the ring-opening of 2-sulfobenzoic acid cyclic anhydride without any additional initiator or catalyst (Scheme 1).

2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and the consecutive dehydrobromination reaction.¹⁰ PEPBS was easily prepared by the activated polymerization of 2-ethynylpyridine with the ring-opening of 2-sulfobenzoic acid cyclic anhydride without any additional initiator or catalyst in DMF solvent as follows. The 1 : 1 mixture of 2-ethynylpyridine (1.0 g, 9.7 mmol) and 2-sulfobenzoic acid cyclic anhydride (1.78 g, 9.7 mmol) in DMF solvent was stirred for 24 hrs at 85 °C under nitrogen atmosphere. As the reaction proceeded, the color of reaction mixture changed from the light brown of the initial mixture into dark red. After the polymerization time, the resulting polymer solution was precipitated into a large excess of ethyl ether. The precipitated polymer was filtered and dried under vacuum at 40 °C for 24 hrs. The polymer yield according to the reaction time were calculated from the precipitation of the solution taken from the polymerization reactor. The polymer yield according to the polymerization time revealed that this polymerization proceeded gradually up to 24 hrs and the polymer yield after 24 hrs reaches 93% and then plateau. This polymerization also proceeded well in such organic solvents as DMF, DMSO, and NMP.

The polymerization mechanism was assumed to include the initial ring-opening of 2-sulfobenzoic acid cyclic anhydride by the attack at carbonyl carbon with the non-bonding electron pair of 2-ethynylpyridine and the propagation step (linear polymerization) of the activated ethynylpyridines by the sulfonate anion of *N*-benzoysulfonate. In our previous works, the similar polymerization of 2-ethynylpyridine by using propargyl bromide¹¹ and propargyl tosylate¹² was also found to proceed well to give high yields of polymer, regardless of the counter anions (bromide, tosylate). Bromide and tosylate anions are known to initiate the activated acetylenic



Scheme 1

*Corresponding Author. e-mail: ysgal@kiu.ac.kr

functional groups of ethynylpyridinium compounds.

The ^1H -NMR spectrum of PEPBS in DMSO-d_6 showed the protons of pyridyl and *N*-benzoylsulfonate substituents at 6.4–9.5 ppm. The ^{13}C -NMR spectrum of PEPBS in DMSO-d_6 also showed the multiple peaks at the region of 110–154 ppm, which are originated from the aromatic carbons of pyridyl and *N*-benzoylsulfonate substituents and the vinyl carbons of conjugated polymer backbone. The carbonyl carbon peak of *N*-benzoylsulfonate substituents was also observed at 168.3 ppm. The FT-IR spectra of 2-ethynylpyridine, 2-sulfobenzoic acid cyclic anhydride, and PEPBS were measured in KBr pellets. The FT-IR spectrum of PEPBS did not show the acetylenic $\text{C}\equiv\text{C}$ bond stretching (2110 cm^{-1}) and acetylenic $\text{C}\equiv\text{C-H}$ bond stretching (3293 cm^{-1}) frequencies of 2-ethynylpyridine. Instead, the $\text{C}=\text{C}$ stretching frequency peak of conjugated polymer backbone at 1625 cm^{-1} became more intense than those of the $\text{C}=\text{C}$ and $\text{C}=\text{N}$ stretching frequencies of 2-ethynylpyridine itself. The strong peaks at 1187 and 1724 cm^{-1} are due to the $\text{S}=\text{O}$ and $\text{C}=\text{O}$ stretching frequencies of benzoyl sulfonate moieties, respectively. The hygroscopic nature of PEPBS is evidenced by the broad and intense peak at 3423 cm^{-1} . The UV-visible spectrum of PEPBS showed a characteristic peak at the visible region (300–750 nm), which is a characteristic peak of the conjugated polyene backbone system. From these spectral data, we concluded that PEPBS has a ionic conjugated polymer system bearing the *N*-benzoylpyridinium sulfonate moieties.

This zwitterionic polymer was found to be very hygroscopic, and soluble in such polar protic solvents as water, methanol, DMF, DMSO, *N,N*-dimethylacetamide, or organic acids capable of hydrogen bonding with the benzoyl sulfonate anion. The inherent viscosity of the PEPBS was 0.21 dL/g at 25°C in DMF. The electrical conductivity (σ) of undoped PEPBS was $5.7 \times 10^{-9}\text{ S/cm}$. This value is somewhat higher than those of similar pyridine-based conjugated polymers.¹² In this communication, we presented a facile synthetic method for self-dopable ionic conjugated polymer, PEPBS, by the activated polymerization of 2-ethynylpyridine with simultaneous ring-opening of 2-sulfobenzoic acid cyclic anhydride without any additional initiator or catalyst. This method may be applicable for the synthesis of conjugated polyelectrolytes by reaction of ethynylpyridines with ring-openable compounds such as 1,4-butanediol, ϵ -caprolactone, etc.

Acknowledgement. This work was supported by Korea Research Foundation Grant KRF-2002-015-CP0269. The authors thanks S. E. Chae of Korea Basic Science Institute-Taegu Branch for the measurement of the 500-MHz FT-NMR spectra of the polymers.

References

- (a) Oosawa, F. *Polyelectrolytes*; Marcel-Dekker: New York, 1971. (b) Dai, L.; Winkler, B.; Dong, L.; Tong, L.; Mau, A. W. H. *Adv. Mater.* **2001**, *13*, 915. (c) Lowe, A. B.; McCormick, C. L. *Chem. Rev.* **2002**, *102*, 4177. (d) Tripathy, S. K.; Kumar, J.; Nalwa, H. S. *Handbook of Polyelectrolytes and Their Applications*; American Scientific Publishers: California, 2002. (e) Ji, E. K.; Ahn, D. J.; Kim, J. M. *Bull. Korean Chem. Soc.* **2003**, *24*, 667.
- Nguyen, M. T.; Kasai, P.; Miller, J. L.; Diaz, A. F. *Macromolecules* **1994**, *27*, 3625.
- Buchhammer, H. M.; Petzold, G.; Lunkwitz, K. *Langmuir* **1999**, *15*, 5306.
- Liu, R. C. W.; Morishima, Y.; Winnik, F. M. *Macromolecules* **2001**, *34*, 9117.
- (a) Chien, J. C. W. *Polyacetylene*; Academic Press: New York, 1984. (b) Toshima, N.; Hara, S. *Prog. Polym. Sci.* **1995**, *20*, 155. (c) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537. (d) Ferraris, J. P.; Cowan, D. O.; Walatka, V. J.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948. (e) Chiang, C. K.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098. (f) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci.: Part A: Polym. Chem.* **1974**, *12*, 11. (g) Shirakawa, H. *Angew. Chem. Int. Ed.* **2001**, *40*, 2574. (h) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2003**, *103*, 4175. (i) Kim, E. J.; Park, J. W.; Kim, Y. R.; Park, Y. *Bull. Korean Chem. Soc.* **2003**, *24*, 484.
- (a) Chausser, M. G.; Rodinov, Yu. M.; Mishin, V. M.; Cherkashin, M. I. *Russ. Chem. Rev.* **1974**, *45*, 348. (b) Masuda, T.; Higashimura, T. *Acc. Chem. Res.* **1981**, *17*, 51. (c) Gal, Y. S. *J. Chem. Soc. Chem. Commun.* **1994**, 327. (d) Choi, S. K.; Lee, J. H.; Kang, S. J.; Jin, S. H. *Prog. Polym. Sci.* **1997**, *22*, 693. (e) Choi, S. K.; Gal, Y. S.; Jin, S. H.; Kim, H. K. *Chem. Rev.* **2000**, *100*, 1645. (f) Gal, Y. S.; Jin, S. H.; Lee, H. J.; Kim, S. H.; Lee, W. C.; Choi, S. K. *Macromol. Res.* **2003**, *11*, 80. (g) Jin, S. H.; Jin, J. Y.; Kim, Y. I.; Park, D. K.; Gal, Y. S. *Macromol. Res.* **2003**, *11*, 501. (h) Anders, U.; Nuyken, O.; Buchmeiser, M. R. *J. Mol. Cat. A: Chem.* **2004**, *213*, 89. (i) Gal, Y. S.; Jin, S. H.; Choi, S. K. *J. Mol. Cat. A: Chem.* **2004**, *213*, 115.
- (a) Blumstein, A.; Subramanyam, S. *US patent* 5,037,916 (Aug. 6, 1991). (b) Blumstein, A.; Samuelson, L. *Adv. Mater.* **1998**, *10*, 173. (c) Bhowmik, R. K.; Burchett, R. A.; Han, H.; Cebe, J. J. *J. Polym. Sci.: Part A: Polym. Chem.* **2001**, *39*, 2710. (d) Gui, T. L.; Jin, S. H.; Park, J. W.; Ahn, W. S.; Koh, K. N.; Kim, S. H.; Gal, Y. S. *Opt. Mater.* **2002**, *21*, 637. (e) Gal, Y. S.; Gui, T. L.; Jin, S. H.; Park, J. W.; Koh, K. N.; Lee, W. C.; Kim, S. H.; Kim, S. Y. *Syn. Met.* **2003**, *135-136*, 353. (f) Gui, T. L.; Jin, S. H.; Park, J. W.; Lim, K. T.; Kim, S. Y.; Gal, Y. S. *Mater. Sci. & Eng. C* **2004**, *24*, 217.
- (a) Patil, A. O.; Ikenoue, Y.; Basescu, N.; Colameri, N.; Chen, F.; Wudl, F.; Heeger, A. J. *Syn. Met.* **1987**, *20*, 151. (b) Ikenoue, Y.; Votani, N.; Patil, A. O.; Wudl, F.; Heeger, A. J. *Syn. Met.* **1989**, *30*, 305.
- (a) Chen, S. A.; Hua, M. Y. *Macromolecules* **1993**, *26*, 7108. (b) Child, A. D.; Reynolds, J. R. *Macromolecules* **1994**, *27*, 1975. (c) Lin, H. K.; Chen, S. A. *Macromolecules* **2000**, *33*, 811.
- Gal, Y. S.; Cho, H. N.; Kwon, S. K.; Choi, S. K. *Polymer (Korea)* **1988**, *12*, 30.
- Gal, Y. S.; Lee, W. C.; Lee, S. J.; Park, J. W.; Ko, J. M.; Chun, J. H. *J. Macromol. Sci.-Pure and Appl. Chem.* **1999**, *A36*, 1503.
- Gal, Y. S.; Lee, W. C.; Kim, S. Y.; Park, J. W.; Jin, S. H.; Koh, K. N.; Kim, S. H. *J. Polym. Sci.: Part A: Polym. Chem.* **2001**, *39*, 3151.