Bioinspired Modification of Polystyryl Matrix: Single-step Chemical Evolution to a Moderately Conducting Polymer

Ashutosh Saxena,[†] S. G. Srivatsan, Vishal Saxena,[†] and Sandeep Verma*
Department of Chemistry, Indian Institute of Technology-Kanpur, Kanpur-208016 (UP), India
[†]*Department of Electrical Engineering, Indian Institute of Technology-Kanpur, Kanpur-208016 (UP), India*

(Received January 26, 2004; CL-040094)

This report describes a simple, bioinspired approach for the conversion of an insulator, polystyrene, to a moderately conducting polymer by introducing adenine nucleobases.

Polystyrene (**PS**) is a rigid plastic possessing excellent electrical resistivity, low dissipation factor, and high arc resistance. These electrical parameters are responsible for its insulating nature and allow for its widespread use in the manufacture of capacitors. However, insulating properties of **PS** and other polymers can be modulated either by employing dopants or by blending with suitable conducting materials.[1–3]

Barton and co-workers provided the experimental proof of charge migration in DNA and since then, various laboratories have contributed to exciting developments in this area.[4–10] Electron transfer in DNA is primarily manifested by the overlap of the π-orbitals present in the stacked nucleobase pairs and it could be sustained over long molecular distances through a variety of mechanisms.[11–15] Recent observations by Giese et al. have indicated a crucial role of adenine residues in DNA charge transfer.[16,17]

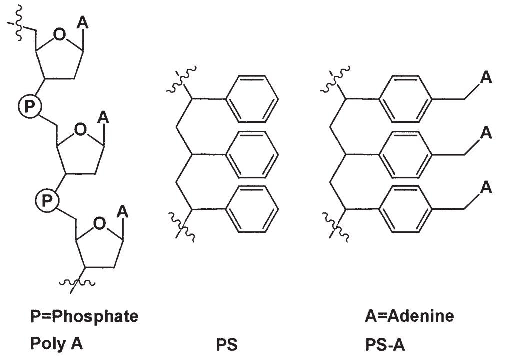

Figure 1. Molecular structures of polyadenylic acid (Poly A), polystyrene (PS), and adenylated polystyrene (PS-A).

In the present study, we have sought to modulate the electrical properties of **PS** by introducing adenine nucleobases in the polymer because nucleobases play a crucial role in DNA charge conduction. This bioinspired approach is expected to alter conduction properties of **PS** as a result of the introduction of repeated adenine units. Consequently, we have synthesized a non-ionic pendant homopolymer **PS-A** where adenine nucleobases are connected to the polystyryl chain via a methylene bridge, in contrast to **poly A** where negatively charged sugar phosphate backbone connects repetitive adenine units (Figure 1). This makes homopolymeric construct considerably more rugged and stable compared to DNA and moreover, moderate conduction observed in **PS-A** can be solely attributed to the sheer presence of adenine residues, as **PS** alone displays insulating character.

The monomer was synthesized from adenine and 4-vinylbenzyl chloride, under basic reaction conditions.[18] Free radical homopolymerization of 9-(4-vinylbenzyl)adenine (9VBA) resulted in the formation of **PS-A** as a white amorphous powder, which was thoroughly characterized by spectroscopic and GPC measurements ($M_w = 67.2$ kDa; $M_n = 34.8$ kDa; $M_w/M_n = 1.93$). The amount of copper impregnated in the polymer was estimated by atomic abosrption spectroscopy and it was found to be 20.8 mg/g polymer. **PS-A** and its metalated version also displayed high thermal stability as probed by thermogravimetric analysis (data not shown). Iodination of the polymer was accomplished according to a literature method.[19]

A customized U-glass-tube set-up was constructed for the electrical conductivity experiments. Unmodified and modified polymers were thoroughly ground in a mortar, sieved and filled in the glass capillary, which was followed by filling of mercury to provide proper connectivity to the copper electrodes leading to triaxial cables. DC conductivity measurements were performed at 30 °C using a source measure unit (SMU, Keithley 236). SMU supplies a controlled, fixed voltage between two terminals and measures the current flowing through the two terminals. As a cautionary measure, each reading was allowed to stabilize for at least 10 min, to minimize the effect of stray capacitance. Moreover, appropriate guarding techniques were used to keep leakage currents and noise ($\approx$1 pA) to a minimum level by employing tri-axial cables, with proper grounding.

The current vs applied electrical field plot (V/I curves) clearly demonstrates the evidence of moderate DC conduction for **PS-A**, well above the measurable limit (Figure 2). The resistivity values calculated for **PS-A**, its metalated and iodinated derivatives were found to be 15e9, 11e9, and 21e9 ohm-cm, respectively, when compared to the value of 1e15–1e17 ohm-cm for unmodified polystyrene. These values reflect a significant modulation of resistivity ($\approx$1e6–1e8 fold) solely due to the introduction of adenine moieties at the *para* position in **PS**. Interestingly, the conduction behavior did not improve either by polymer metalation or by iodine-doping.

Lack of any dramatic change in conduction with the metalated derivative is curious. This observation is different from the results where metallic conduction was observed for zinc-metalated B-DNA.[20] In the latter case, imino protons of a base pair were completely substituted by zinc ions at elevated pH. We infer that random metalation of **PS-A** with copper ions cannot be translated to favorable overlap of the *p*-nitrogen and *d*-copper electronic states and that the "π-stack" in **PS-A** is also not favorably affected by the presence of metal ions. Furthermore, lack of effect of iodine doping confirms that the polymer is not easily oxidized thus obviating the possibility of hole generation within the poly-

Copyright © 2004 The Chemical Society of Japan

styryl matrix. It should be emphasized at this point that reproducible electrical measurements were obtained with repeated use of **PS-A** sample, suggesting that integrity of polymer structure and bulk conducting properties were unaltered by the passage of current.

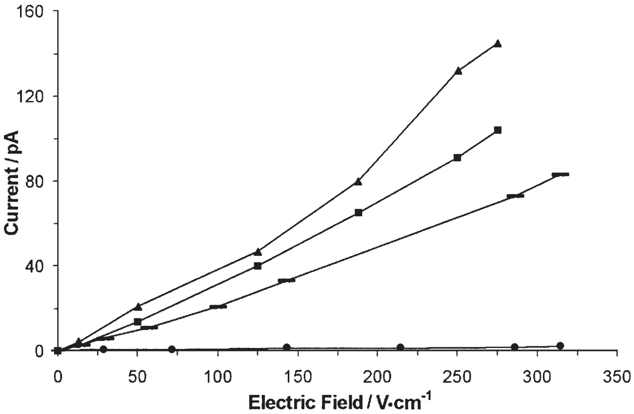

Figure 2. V/I profiles for polymeric copnstructs: (■) **PS-A**; (—) copper metalated-**PS-A**; (●) **PS** (measurable limit); (▲) iodized **PS-A**.

Control reactions were performed with **PS**, 9-(4-vinylbenzyl)adenine monomer and copper-metalated monomer. V/I curves for these entities were close to the measurable limit indicating lack of electrical conduction (Figure 3). UV spectral properties of the homopolymer remained unmodified before and after the passage of current, once again verifying the robust nature of the polymeric material (data not shown).

Continuing our efforts in developing adenine-containing polymers and their metalated derivatives for catalysis,[21–24] this report describes a simple, yet elegant, bioinspired conversion of an insulator to a moderately conducting polymer. Willner et al. have applied adenine redox cofactors for modulating the electrical properties of conducting polymer films and wires.[25,26]

Unlike DNA strand cleavage manifested through trapping reactions, **PS** polymeric backbone obviates any possibility of chemical modification. Importantly, the low level of bulk conductivity observed for **PS-A** is different from studies done with near semi-conducting profile of DNA, as the former studies are done in the solid state. However, it is surmised that future investigations in this area may result in the synthesis of other bioinspired electrical conductors with favorable V/I profiles. Investigations of electrical conductance with **PS-A** and related polymeric backbones, additionally containing varied guanine and adenine contents, as thin films are currently under progress.

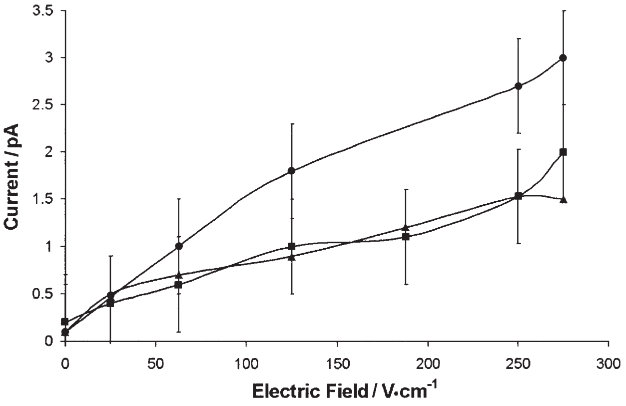

Figure 3. V/I profiles for control experiments: (■) **PS**; (●) 9VBA/Cu complex; (▲) 9VBA monomer.

SGS thanks CSIR, India, for a Senior Research Fellowship. Prof. Anil Kumar, IIT-Bombay, India, is thanked for GPC measurements. Part of this work was supported by a grant from MHRD, India, to one of us (SV).

References

1 P. C. P. Watts, W. K. Hsu, G. Z. Chen, D. J. Fray, H. W. Kroto, and D. R. M. Walton, *J. Mater. Chem.*, **11**, 2482 (2001).
2 T. Hamieh, Y. Baalbaki, M. Zoaeter, and J. Schultz, *Macromol. Symp.*, **181**, 435 (2002).
3 M. A. Valente, L. C. Costa, S. K. Mendiratta, F. Henry, and L. Ramanitra, *Solid State Commun.*, **112**, 67 (1999).
4 C. J. Murphy, M. R. Arkin, Y. Jenkins, N. D. Ghatlia, S. H. Bossmann, N. J. Turro, and J. K. Barton, *Science*, **262**, 1025 (1993).
5 H. W. Fink and C. Schonenberger, *Nature*, **398**, 407 (1999).
6 D. Porath, A. Bezryadin, S. de Vries, and C. Dekker, *Nature*, **403**, 635 (2000).
7 A. Yu. Kasumov, M. Kociak, S. Guéron, B. Reulet, V. T. Volkov, D. V. Klinov, and H. Bouchiat, *Science*, **291**, 280 (2001).
8 Y. A. Berlin, A. L. Burin, and M. A. Ratner, *Chem. Phys.*, **275**, 61 (2002).
9 U. Santhosh and G. B. Schuster, *J. Am. Chem. Soc.*, **124**, 10986 (2002).
10 J. Jortner, M. Bixon, A. A. Voityuk, and N. Rosch, *J. Phys. Chem.*, **106**, 7599 (2002).
11 G. B. Schuster, *Acc. Chem. Res.*, **33**, 253 (2000).
12 C. Z. Wan, T. Fiebig, O. Schiemann, J. K. Barton, and A. H. Zewail, *Proc. Natl. Acad. Sci. U.S.A.*, **97**, 14052 (2000).
13 F. D. Lewis, R. L. Letsinger, and M. R. Waiselewski, *Acc. Chem. Res.*, **34**, 159 (2001).
14 R. N. Barnett, C. L. Cleveland, A. Joy, U. Landman, and G. B. Schuster, *Science*, **294**, 567 (2001).
15 B. Giese, *Annu. Rev. Biochem.*, **71**, 51 (2002).
16 B. Giese, J. Amaudrut, A. K. Kohler, M. Spormann, and S. Wessely, *Nature*, **412**, 318 (2001).
17 T. Kendrick and B. Giese, *Chem. Commun.*, **2002**, 2016.
18 S. G. Srivatsan, S. Verma, and M. Parvez, *Acta Crystallogr.*, **C58**, o378 (2002).
19 M. Özyalçin and Z. Küçükyavuz, *Synth. Met.*, **87**, 123 (1997).
20 A. Rakitin, P. Aich, C. Papadopoulos, Y. Kobzar, A. S. Vedeneev, J. S. Lee, and J. M. Xu, *Phys. Rev. Lett.*, **86**, 3670 (2001).
21 C. Madhavaiah and S. Verma, *Chem. Commun.*, **2003**, 800.
22 S. G. Srivatsan, M. Parvez, and S. Verma, *Chem.—Eur. J.*, **8**, 5184 (2002).
23 S. G. Srivatsan and S. Verma, *Chem.—Eur. J.*, **7**, 828 (2001).
24 S. G. Srivatsan and S. Verma, *Chem. Commun.*, **2000**, 515.
25 E. Katz and I. Willner, *J. Am. Chem. Soc.*, **125**, 6803 (2003).
26 Y. Xiao, F. Patolsky, E. Katz, J. F. Hainfield, and I. Willner, *Science*, **299**, 1877 (2003).

Published on the web (Advance View) May 24, 2004; DOI 10.1246/cl.2004.740