

## Self-organized supramolecules of poly(2,5-pyridinediyl)

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### Abstract

Polypyridines are remarkably stable and good charge transport materials having high photoluminescence quantum yield. They form supramolecules that form lamellar self-organized structures due to bonding between pyridine and sulphonic acid unit and polar nonpolar effects combined. Some examples are demonstrated here using synchrotron radiation and small angle X-ray scattering (SAXS) method.

**Keywords:** Self-organization in macromolecules, Other conjugated and conducting polymers, X-ray scattering, Liquid crystalline phase transitions

### 1. Introduction

Self-organization [1] and supramolecule formation concepts [2] are nonlithographic tools to form nanoscale structures. Also the electronic properties of conjugated polymeric material can be tailored due to self-organization [3], supramolecular self-organization [4], or supramolecular network formation [5]. The construction of such structures is not always straightforward because of the rigid conformation of the backbone and therefore much can be learnt from simple model systems.

Polypyridines [6–9] have good electronic properties and they allow preparation of efficient light-emitting devices [10, 11]. Poly(2,5-pyridinediyl) (PPY) is structurally among the simplest  $\pi$ -conjugated rigid polymers that contain specific sites needed to construct supramolecules. In addition, polypyridines are remarkably stable and they can be dissolved in selected solvents. These properties make PPY feasible to study general aspects of the supramolecules and their self-organization based on  $\pi$ -conjugated rigid polymers.

Supramolecular structures of pyridine oligomers [12] or their polymeric modifications [13], have typically been based on coordination. Covalent bonding [14] has been used to produce polypyridine-based hairy rods and internal hydrogen bonding [15] to planarize such architectures. In this work, supramolecules are based on the acid-pyridine interaction and further hydrogen bonding to amphiphiles. Their self-organization arises from the bonding, and polarity differences combined.

### 2. Experimental

PPY was synthesized by dehalogenation polycondensation of 2,5-dibromopyridine with tetrakis(triphenylphosphine)nickel(0) prepared *in situ* from reduction of  $\text{NiCl}_2$  by Zn in the presence of  $\text{PPh}_3$  in *N,N*-dimethylformamide. The molecular weight was  $M_n=6000$  g/mol and PPY consisted of random mixture of head-to-head and head-to-tail units. Complexation of PPY and dodecylbenzenesulfonic acid (DBSA) to form  $\text{PPY}(\text{DBSA})_x$  was performed in dilute solution of formic

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acid that was removed by vacuum drying and heating. Stoichiometric complex of PPY and methanesulfonic acid,  $\text{PPY}(\text{MSA})_{1.0}$  was prepared dissolving equal number of moles of MSA and repeat units of PPY in formic acid as a 1 wt-% solution at room temperature. After mixing, the solvent was evaporated at room temperature. The complexes were dried at 60 °C for 2 days. Complexes with octyl gallate (OG) were prepared similarly in dilute solutions of formic acid, followed by rapid evaporation and vacuum drying. To ensure the formation of homogeneous complexes the samples were annealed at 195 °C for 10 minutes. In another set of materials, camphorsulfonic acid (CSA) was used instead of MSA and hexylresorcinol (HRES) instead of OG.

Small angle X-ray scattering experiments (SAXS) were carried out using synchrotron radiation at the Dutch-Belgian beamline at ESRF [16]. The sagittally focusing double crystal monochromator (Si(111)), the meridionally focusing coated mirror and the energy of 10 or 16 keV ( $\lambda=0.124$  or 0.078 nm) were used. The bending radius of the crystal mirror was adjusted to focus the beam at the two-dimensional wire chamber detector. The distance between the sample and the detector was 1.28 or 1.7 m.

### 3. Results and Discussion

PPY can be complexed with sulfonic acids [17]. When acid molecule is amphiphilic, such as DBSA [18], the supramolecules consist of polymer backbone complexed with the DBSA molecules and they form lamellar self-organized structures with alternating polar and nonpolar layers. Because of the strong ionic attraction and strong repulsion, the structure exhibits no phase transitions until it is destroyed at ca. 300 °C. When the acid is not amphiphilic, in the simplest case MSA, and if an additional specific amphiphile, such as OG, is hydrogen bonded to it, the mixture with PPY is a disordered (or isotropic) fluid at high temperatures. A self-organized, (or smectic-like) fluid phase appears upon cooling past disorder-order transition temperature, 180 °C. Another transition to an organized co-crystalline solid is observed after further cooling [19]. If the acid is selected to be CSA and the amphiphile is HRES, the material is fluid-like down to lower temperature. The components of the supramolecules and SAXS data indicating their self-organization are illustrated below. The results demonstrate self-organized supramolecules of PPY. The concept can be applied for related polymers as well.

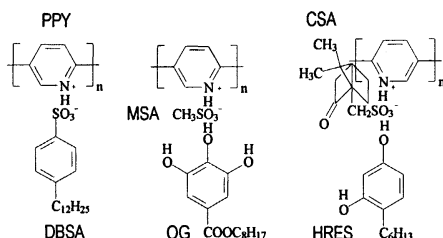


Fig. 1. Examples of supramolecules that form self-organized structures. OG = octyl gallate, HRES = hexylresorcinol.

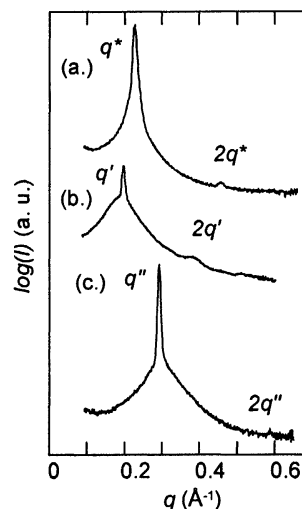


Fig. 2. (a) SAXS patterns of  $\text{PPY}(\text{DBSA})_{1.0}$  at room temperature, (b) the mixture of  $\text{PPY}(\text{MSA})_{1.0}$  and OG in the molar ratio 1.0:2.0 at 130 °C, and (c) the mixture of  $\text{PPY}(\text{CSA})_{0.5}$  and HRES in the molar ratio 1.0:0.5 at 85 °C, indicating fluid-like lamellar structures with the long periods of 27 Å, 32 Å and 21 Å, respectively.

### References

- [1] M. Muthukumar, C.K. Ober, E.L. Thomas, *Science*, 277 (1997) 1225.
- [2] M.C.T. Fyfe, J.F. Stoddart, *Acc. Chem. Res.*, 30 (1997) 393.
- [3] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, D. M. de Leeuw, *Nature*, 401 (1999) 685.
- [4] S. Ghosh, J. Rasmussen, O. Inganäs, *Adv. Mater.*, 10 (1998) 1097.
- [5] Reghu M., C. O. Yoon, C. Y. Yang, D. Moses, P. Smith, A. J. Heeger, Y. Cao, *Phys. Rev. B*, 50 (1994) 13931.
- [6] T. Yamamoto, T. Maruyama, Z-h Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda, K. Kubota, *J. Am. Chem. Soc.*, 116 (1994) 4832.
- [7] J.W. Blatchford, S. W. Jessen, L. B. Lin, J. J. Lih, T. L. Gustafson, A. J. Epstein, D. K. Fu, M. J. Marsella, T. M. Swager, A. G. MacDiarmid, S. Yamaguchi, H. Hamaguchi, *Phys. Rev. Lett.*, 76 (1996) 1513.
- [8] H. Yun, T.K. Kwei, Y. Okamoto, *Macromolecules*, 30 (1997) 4633.
- [9] Y. Eichen, G. Nakhmanovich, V. Gorelik, O. Epshtein J. M. Poplawski, E. Ehrenfreund, *J. Am. Chem. Soc.*, 120 (1998) 10463.
- [10] S. Dailey, M. Halim, E. Rebourt, L. E. Horsburgh, I. D. W. Samuel, A. P. Monkman, *J. Phys.: Condens. Matter*, 10 (1998) 5171.
- [11] Y.Z. Wang, A.J. Epstein, *Acc. Chem. Res.*, 32 (1999) 217.
- [12] P. Baxter, J.-M. Lehn, A. DeCian, J. Fischer, *Angew. Chem. Int. Ed. Engl.*, 32 (1993) 69.
- [13] S.S. Zhu, P.J. Carroll, T.M. Swager, *J. Am. Chem. Soc.*, 118 (1996) 8713.
- [14] C. Wang, M. Kilitziraki, J. A. H. MacBride, M. R. Bryce, L. E. Horsburgh, A. K. Sheridan, A. P. Monkman, I. D. W. Samuel, *Adv. Mater.*, 12 (2000) 217.
- [15] D.A.P. Delnoye, R.P. Sijbesma, J.A.J.M. Vekemans, E.W. Meijer, *J. Am. Chem. Soc.*, 118 (1996) 8717.
- [16] M. Borsboom, W. Bras, I. Cerjak, D. Detollenaere, D. G. van Loon, P. Goedtkindt, M. Konijnenburg, P. Lassing, Y. K. Levine, B. Munneke, M. Oversluizen, R. van Tol, E. Vlieg, *J. Synchrotron Rad.*, 5 (1998) 518.
- [17] A.P. Monkman, M. Halim, I.D.W. Samuel, L.E. Horsburgh, *J. Chem. Phys.*, 109 (1998) 10372.
- [18] M. Jonforsen, S. Grigalevicius, M.R. Andersson, T. Hjertberg, *Synth. Met.*, 102 (1999) 1200.
- [19] O. Ikkala, M. Knaapila, J. Ruokolainen, M. Torkkeli, R. Serimaa, K. Jokela, L. Horsburgh, A. Monkman, G. ten Brinke, *Adv. Mater.*, 11 (1999) 1206.