Takakazu Seki

Highly ordered alignment of a vinyl polymer by host-guest cross-polymerization

Distefano, D.; Suzuki, H.; Tsujimoto, M.; Isoda, S.; Bracco, S.; Comotti, A.; Sozzani, P.; Uemura, T.; Kitagawa, S.* *Nat. Chem.* **2013**, *5*, 335–341.

1. Introduction

• Controlling of molecular orientation, especially macromolecules, has attracted much attention because the bulk properties and stability highly depend on the orientatin and anisotropy, e.g. electronically conductive polymer (Figure 1).[1]

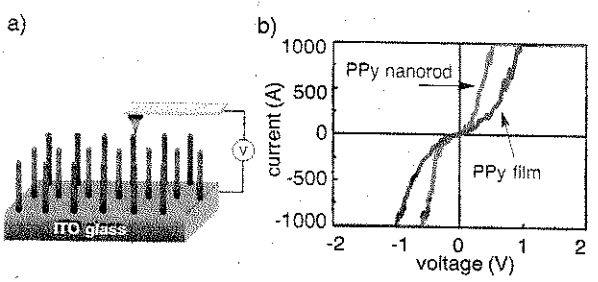


Figure 1. (a) Schematic of current-sensing AFM. (b) *I-V* curve of polypyrrole (PPy) nanorod and film. Reprinted from ref 1.

• Several strategies have been investigated to control chain packing of polymer, by mechanical rubbing, by using supramolecular aligner molecules etc (Figure 2).[2]

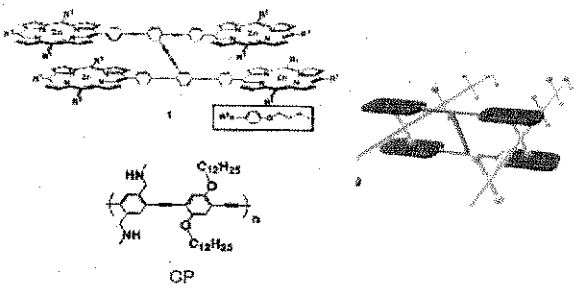


Figure 2. Chemical structure of molecular aligner and polymer (left). Schematic representation of molecular alignment of the polymer. Reprinted from ref 2

• However if the polymer aligned showed non-crystalline nature, external stimuli such as removal of template, heat and solvent easily induce collapse of the alignment.

➔ Highly stable polymer alignment of non-crystalline polymers is quite difficult and **there is no general methodology**.

• For that alignment, porous coordination polymers (PCP) is a one of the promising templates.[3] Various organic linkers can be used for ordered crosslink to suppress amouphous polymer.

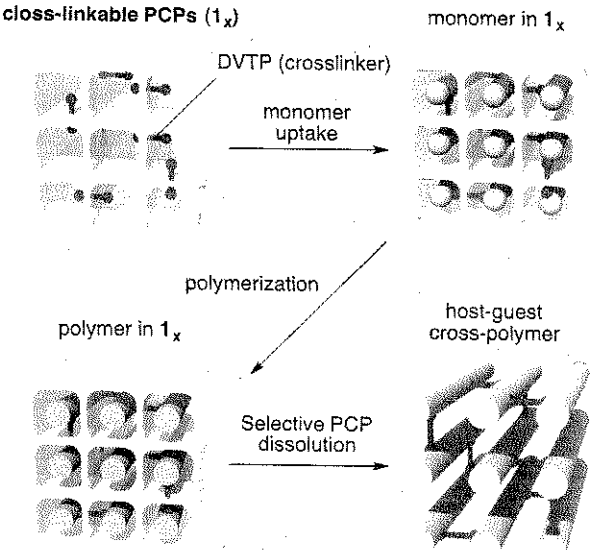


Figure 3. Concept of this work. Schematic image of host-guest cross-polymerization.

Overview:

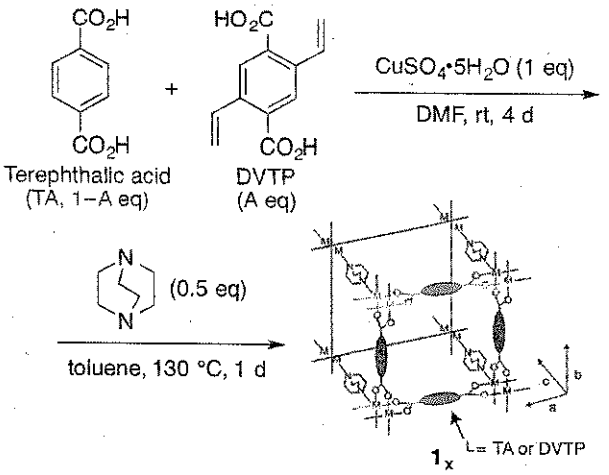
• By 'ordered crosslinks' in PCP, highly ordered polymer alignment was achieved. Because of the high microstructural regularity, PSt known as a non-crystalline polymer exhibited crystalline nature (Figure 3).

2. Results and Discussion

2.1. Preparation of a crosslinkable PCP

• Functionalized $[Cu(DVTP)_x(terephthalate)_{1-x}triethylamine_{0.5}]_n$ ($\mathbf{1}_x$) was synthesized in a two-step fashion (Scheme 1).

Scheme 1. Synthesis of crosslinkable PCP ($\mathbf{1}_x$)



• The crystal structure of mixed-ligand PCP was determined by X-ray powder diffraction (XRPD), which confirmed that it retained structure of pure **1** ($\mathbf{1}_0$) (up to $\mathbf{1}_{0.2}$, **1** retained high crystallinity.)

2.2. Host-guest cross-polymerization

• Polymerization in vinyl-functionalized PCP was conducted as follows (Figure 4).

1) Styrene (St) monomers and AIBN were incorporated in PCP framework.
2) After removal of excess St monomer, host-guest cross-polymerization was carried out at 70 °C for 48 h under N_2 atmosphere. Monomer conversion rate was estimated by thermogravimetric analysis (TGA).
3) Poly St (PSt) was obtained by selective PCP decomposition with Na_2-EDTA solution.

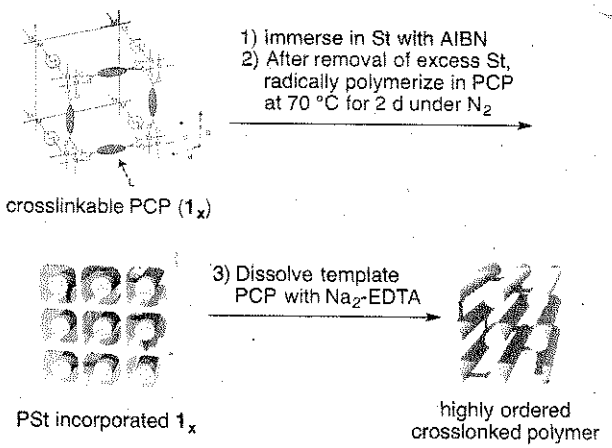


Figure 4. Schematic image of host-guest cross-polymerization.

• Also methylmetacrylate (MMA) can be polymerized following the above-mentioned method.

• Crosslinker coversion can be estimated by comparing the ^1H NMR spectra of the dissolved PCP matrix before and after polymerization. Based on monomer and crosslinker conversion, the final polymer composition was estimated.

2.3. Crystallinity of PSt

• Scanning electron microscopy (SEM) of the host-guest cross-polymers revealed that even after complete removal of the polymerization template, the resulting polymer retained the cubic morphology derived from PCP framework (Figure 5).

• XRPD measurement clearly revealed the highly ordered alignment of PSt chains obtained from the host-guest cross-polymerization method (Figure 6).

• The diffraction intensity ($2\theta = 18.0°$) increased, as the crosslink density increased. In case of PSt obtained from $\mathbf{1}_{0.06}$, highly sharp and intense peak was observed.

• The diffraction peak may correspond to an interplane distance of 4.9 Å. The value was well correlated to the steric encumbrance of the DVTP unit that acts as a molecular spacer and connects neighbouring chain.

• In sharp contrast to PSt from $\mathbf{1}_{0.06}$, PSt from solutin-phase exhibited no significant peak because the PSt formed amorphous shape.

• However, an upper limit exists for the divinyl ligand content in the PCP. If the mole fraction of crosslinker unit x in **1** becomes equal to or higher than 0.10, the characteristic diffraction peak in the polymer dissapears probably because structure of inner pore and incorporation of St were sterically perturbed by crosslinkers embeded in the PCP.

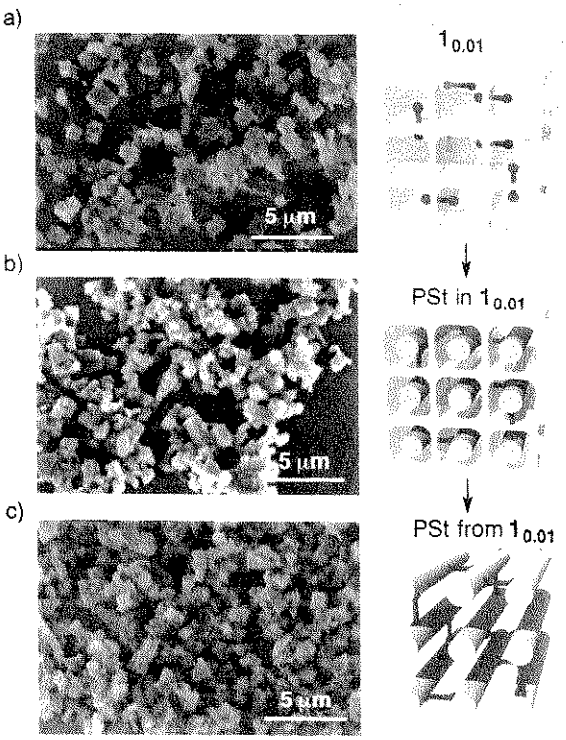


Figure 5. Shape replication process from PCP to polymer. SEM image of $\mathbf{1}_{0.01}$ (a), PSt in $\mathbf{1}_{0.01}$ (b) and host-guest cross-polymerized PSt from $\mathbf{1}_{0.01}$ (c)

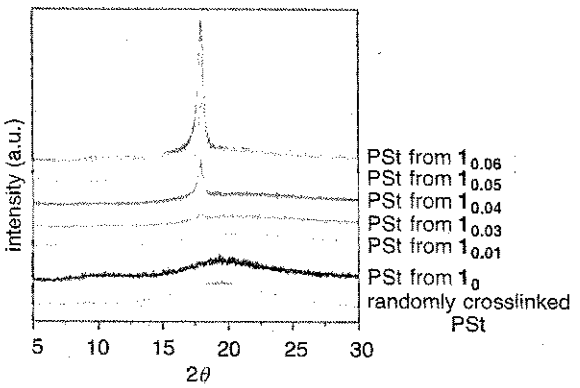


Figure 6. Crystalline arrangement of PSt. X-ray powder diffract grams of host-guest cross-polymerized PSt from $\mathbf{1}_x$ (x = 0.01, 0.03, 0.04, 0.05 and 0.06), PSt obtained in non-functionalized PCP ($\mathbf{1}_0$) and randomly cross-linked St_{90}-$DVTP_{10}$ prepared in solution.

• The retention of molecular alignment of polymers after removal of PCP was confirmed by N_2 adsorption. Compared to amorphous PSt, well-aligned PSt showed higher adsorption (Figure 7).

• To visuallize the molecular alignment of the polymer chains, high-resolution transmission electron microscopy (HR-TEM) was utilized and it revealed that the presence of parallel lattice fringes with a period of 4.9 Å, in agreement with the lateral distance of PSt chains observed in XRPD (Figure 8).

• Because of high crystallinity of PSt, electron diffraction pattern could be obtained. Fast Fourier transform (FFT) analysis on the HR-TEM image shows additional lattice spacings of 3.6 and 2.4 Å, indicating that the square arrangement of PSt chains is derived from the tetragonal symmetry of the host PCP.

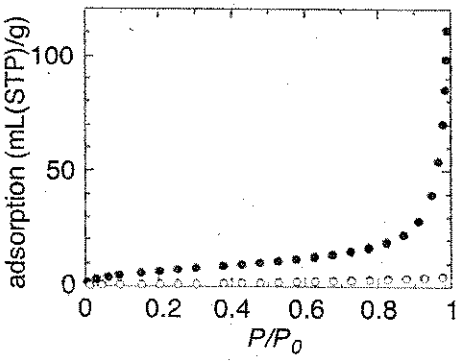


Figure 7. N_2 adsorption isotherms on PSt obtained from $\mathbf{1}_{0.01}$ (filled circles) and solution polymerized PSt (open circles) at 77 K. STP means standard temperature and pressure.

2.4. Thermal property of crosslinked PSt

• Unconventional degradation behavior was observed. For ordinary PSt, themal decomposition occurred at 420 °C.

• After treated at 500 °C, host-guest polymerized PSt from $\mathbf{1}_{0.06}$ (7% of DVTP) exhibited the persistence of a diffraction peak. It indicated that even under extreme thermal condition the alignment was retained though slight shift of the peak was observed.

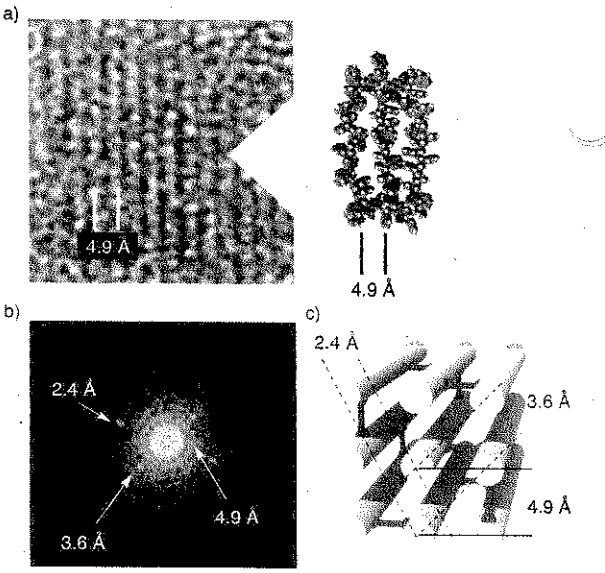


Figure 8. Controlled uniaxial alignment of PSt chains. (a) HR-TEM image of PSt from $\mathbf{1}_{0.06}$. A fast Fourier transform (FFT) of HR-TEM image reveals spots with d-spacings of 4.9 Å, 3.6 Å and 2.4 Å, in agreement with a two-dimensional square latt with a lattice constant of a = 4.9 Å. (c) Square arrangement of PSt chains derived from $\mathbf{1}_x$.

3. Conclusion

• Highly ordered crystalline packing of polymer chains were obtained by 'ordered crosslinks', even though PSt was known as a non-crystalline polymer.

• Unlike solution chemistry, present method generates crosslinking among aligned polymer chains at specific locations. The precise order of the PCP host is transferred into a polymeric material at both the molecular and morphological hierarchical levels. This method can be general procedure to obtained well-aligned polymer architectures.

< References>

[1] Lee, J. I.; Cho, S. H.; Park, S.-M.; Kim, J. K.; Kim, J. K.;: Yu, J. W.; Kim,Y. C.; Russell, T. P. *Nano Lett.***2008**, *8*, 2315–2320.

[2] Kubo, Y.;Kitada, Y.; Wakabayashi, R.; Kishida, T.; Ayabe, M.; Kaneko, K.; Takeuchi, M.; Shinkai, S. *Angew. Chem. Int. Ed.* **2006**, *45*, 1548–1553.

[3] Uemura, T.;,Ono, Y.; Hijikata, Y.; Kitagawa, S. *J. Am. Chem. Soc.* **2010**, *132*, 4917–4924.